borane. Protonolysis using a mixture of AcOH, THF, and MeOH, followed by oxidation, afforded the desired (*Z*)-7-tetradecen-1-ol (**12a**) in 85% yield. The usual PCC oxidation[16] (using sodium acetate) of (*Z*)-7-tetradecen-1-ol (**12a**) furnished (*Z*)-7-tetradecenal (1) in 80% yield: bp 87–89 °C/0.05 mm; $n^{20}_D$ 1.4499; GC analysis, >98% isomeric purity; IR (neat) $\nu$ 1720 $cm^{-1}$ (CHO); $^1H$ NMR ($CDCl_3/Me_4Si$) $\delta$ 0.7–1.84 (m, 17 H), 1.88–2.75 (m, 6 H), 5.34 (m, 2 H) 9.92 ppm (closed t, 1 H); $^{13}C$ NMR (neat) $\delta$ 199.64 (*C*HO), 129.59, 129.02 (C=C), 43.33, 31.55, 29.47, 29.23, 28.69, 28.51, 26.88, 26.67, 22.34, 21.67, 13.55 (alkyl *C*).

**(*Z*)-7-Hexadecenal (2).** Following the above procedure, (*Z*)-7-hexadecenal was prepared in 81% yield: bp 110–112 °C/0.05 mm; $n^{20}_D$ 1.4525; GC analysis >98% isomeric purity; IR (neat) $\nu$ 1725 $cm^{-1}$ (CHO); $^1H$ NMR ($CDCl_3/Me_4Si$) $\delta$ 0.7–1.79 (m, 21 H), 1.85–2.70 (m, 6 H), 5.35 (m, 2 H), 9.96 (closed t, 1 H); $^{13}C$ NMR (neat) $\delta$ 199.58 (*C*HO), 129.66, 129.04 (C=C), 43.39, 31.74, 29.55, 29.33, 29.14, 28.58, 26.96, 26.74, 22.45, 21.73, 13.65 (alkyl *C*).

**7-Tetradecyne (13).** A dry, 100-mL flask equipped with a magnetic stirring bar and septum inlet was flushed with nitrogen.[8] The flask was charged under nitrogen with ($n$-Hex)$_2$BOMe[17] (2.70 mL, 10 mmol) and 10 mL of dry tetrahydrofuran and then cooled to 0 °C. In another dry nitrogen-flushed flask equipped with a magnetic stirring bar and septum inlet were added 10 mL of tetrahydrofuran and 1-octyne (1.46 mL, 10 mmol). The flask was then cooled in an ice bath and 4.60 mL (10 mmol) of a 2.17 M solution of $n$-butyllithium in hexane was added. The reaction mixture was stirred at 0 °C for 0.5 h. The resulting 1-octynyllithium was then transferred into the flask containing ($n$-Hex)$_2$BOMe at 0 °C. The reaction mixture was cooled to −78 °C and a solution of 2.54 g (10 mmol) of iodine in 10 mL of tetrahydrofuran was added with efficient stirring. The stirring was continued at −78 °C for 3 h. It was then allowed to warm to room temperature. The solution was then washed with 10 mL of 3 M NaOH (containing 1 mL of saturated $Na_2S_2O_3$ to remove residual iodine). The aqueous phase was then extracted with 25 mL of ether. $n$-Hexadecane (2.92 mL, 10 mmol) was then added as an internal standard. The combined organic phase was then treated with 10 mL of 3 M NaOH, followed by the dropwise addition of 3 mL of 30% $H_2O_2$ to oxidize the boronic acid byproduct. Saturation of the aqueous phase with $K_2CO_3$ yielded an organic phase which was then subjected to GC analysis. The reaction was repeated with various dialkylalkoxyboranes with 1-octynyllithium and in each case percentage yields of 1-iodo-1-octyne and 7-tetradecyne were established (please see Table III). The same procedure was employed to prepare unsymmetrical alkyne from di-$n$-alkymethylborane ($R_2BCH_3$) and 1-octynyllithium. The percentage yields of the products were established by GC analyses using $n$-hexadecane as an internal standard (eq 9).

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# Vinylic Organoboranes. 5. An Improved, Convenient Synthesis of Unsymmetrical Alkynes via Iodination of Lithium Alkynyl "Ate" Complexes of Thexylalkylborinates†

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The transfer reaction induced by iodination of lithium alkynyl "ate" complexes of organoboranes represents a novel route to unsymmetrical alkynes. Several potential "blocking" groups were examined in order to achieve the selective migration of one primary alkyl group and thereby increase the efficiency of this process. Best results were obtained with the combined use of the thexyl and methoxy moieties as "blocking" groups in this reaction. The required thexylalkylborinate intermediates were conveniently prepared in high yield from thexylchloroborane via hydroboration and methanolysis. Subsequent complexation with an appropriate lithium alkyne, followed by iodination, produced the desired unsymmetrical alkyne in high yield. Minimum amounts of the product resulting from competitive migration of the thexyl group were observed. Under these conditions, an efficient utilization of a primary alkyl group in this transfer reaction is achieved. Furthermore, the high tolerance of thexylchloroborane toward many functional groups and its high regioselectivity in terminal alkene hydroboration produces intermediates that are particularly useful for the synthesis of insect pheromones and not readily accessible via conventional organometallic procedures.

## Introduction

Many insect pheromones have straight-chain (*Z*)-monoolefinic structures with functional groups at the terminal position.[2] The classical approach, which has often been used to synthesize this type of compound, utilizes the semihydrogenation of the corresponding alkyne. Organoboranes have been shown to be useful intermediates for the preparation of unsymmetrical alkynes.[3] Recently, this procedure has been specifically adapted to the synthesis of *Z*-monoolefinic insect pheromones[4a] (eq 1). The overall yield based on $BH_3$·THF for this essentially one-pot synthesis is generally high. None of the corresponding *E*

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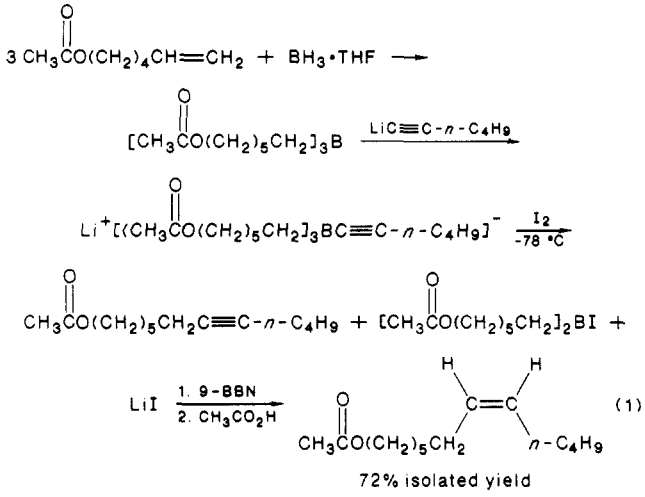
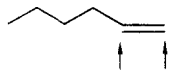



(1)

isomer was detected by $^{13}C$ NMR spectroscopy.

However, there is one major disadvantage to this approach. Since only one of the three alkyl residues on boron participates in the desired transfer reaction, the conversion of alkyl groups to the desired product is a maximum of only 33%. This problem is frequently encountered in many reactions of organoboranes and is particularly troublesome in those cases in which one wishes to use a valuable intermediate.[5]

Fortunately, there is a simple solution which has been very effective in circumventing this problem in other types of transfer reactions. If one replaces two of the alkyl groups on boron with carbon ligands which exhibit relatively low migratory aptitudes, then one is able to make more efficient use of a valuable substrate during the desired transfer reaction.[5] Several dialkylboranes, such as 9-borabicyclo[3.3.1]nonane (9-BBN), dicyclohexylborane ($Chx_2BH$), and disiamylborane ($Sia_2BH$), are readily available and have been used effectively as "blocking" groups in many $\alpha$-transfer reactions.[5] These dialkylboranes offer another advantage over $BH_3$·THF in that their high regioselectivity in the hydroboration reaction virtually eliminates any undesired side product arising from the hydroboration of the internal position of a terminal double bond.



| | | |
|---|---|---|
| $BH_3$·THF | 6 | 94 |
| $Sia_2BH$ | 1 | 99 |
| 9-BBN | <0.5 | >99.5 |

Recently the high regiochemical hydroboration of 9-BBN has been employed in the tri-*n*-butyltin chloride induced migration, followed by elimination with iodine, to yield internal acetylenes.[4b]

The replacement of one of the three groups in trialkylboranes by alkoxy groups of large steric requirements or by a methyl group achieved partial success.[6] However, this solution still involved in most cases a loss of one of the two alkyl groups on boron.

We therefore undertook a systematic study to develop suitable boron-bound carbon ligands with relatively low migratory aptitudes that could serve as synthetically useful blocking groups in the transfer reaction induced by iodination of lithium alkynyl "ate" complexes, permitting the complete utilization of the alkyl group undergoing transfer. Because of our interest in developing efficient syntheses of straight-chain insect pheromones via organoborane intermediates, we focused our attention on achieving the selective migration of a primary alkyl group in the presence of the blocking agent.

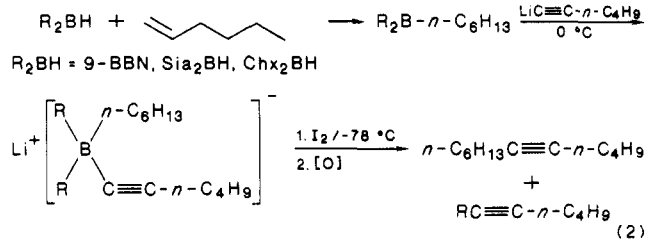
**Table I. Observed Alkyl Group Migration in *B*-*n*-Hexyldialkylboranes after Iodination of the Corresponding Lithium (1-Hexynyl)trialkylborate**

| $R_2B$-*n*-$C_6H_{13}$, $R_2B$ = | alkyne products, % RC≡C-*n*-$C_4H_9$ | alkyne products, % *n*-$C_6H_{13}$C≡C-*n*-$C_4H_9$ | % migration[a] |
|---|---|---|---|
| 9-BBN | 75[b] | 25 | 84 |
| $Chx_2B$ | 50[c] | 50 | 92 |
| $Sia_2B$ | 30[d] | 70 | 90 |

[a] Based on mmol of $R_3B$. [b] R = 5-hydroxycyclooctyl. [c] R = cyclohexyl. [d] R = 3-methyl-2-butyl.

## Results and Discussion

Several readily available dialkylboranes, such as 9-BBN, $Sia_2BH$, and $Chx_2BH$, were examined first to determine their utility as effective "blocking" groups. Each was treated with 1-hexene to produce the corresponding trialkylborane containing the *n*-hexyl group as a representative primary substituent. These trialkylboranes were then treated with 1-lithio-1-hexyne to form the corresponding "ate" complexes. Iodine was added to induce the migration. After oxidation, the products were analyzed by GC to determine the relative amount of *n*-hexyl migration vs. blocking group migration (eq 2). The results are summarized in Table I.




(2)

As shown in Table I, with 9-BBN the undesired product arising from the competitive migration of the bicyclooctyl moiety was the major product of the reaction. This is consistent with previous observations.[4a,7] With $Chx_2BH$, the undesired product resulting from the competitive migration of the cyclohexyl group comprised about 50% of the migration product. A smaller but still significant amount (~30%) of undesired product was observed with $Sia_2BH$. Although a completely selective migration was not achieved with $Sia_2BH$, the side product arising from the migration of the 3-methyl-2-butyl group can often be removed from the desired product by simple distillation. Several other dialkylboranes, such as borinane[8] and dilongifolylborane,[9] were also examined, but these gave even less favorable results.

These results led us to conclude that the selective migration of a primary alkyl group in the presence of a secondary alkyl blocking group would be difficult to achieve in this reaction. We therefore sought to improve these results by introducing an appropriate tertiary blocking group. It has been previously observed that the bicyclooctyl ring of 9-BBN can be transformed into the 1-bicyclo[3.3.0]nonanyl structure by treating lithium tetra-

(5) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Syntheses via Boranes*; Wiley-Interscience: New York, 1975.
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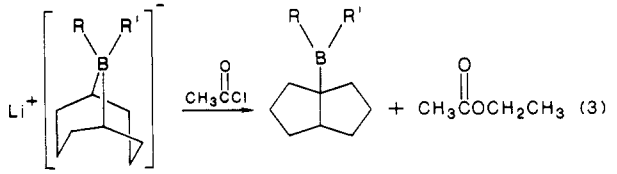
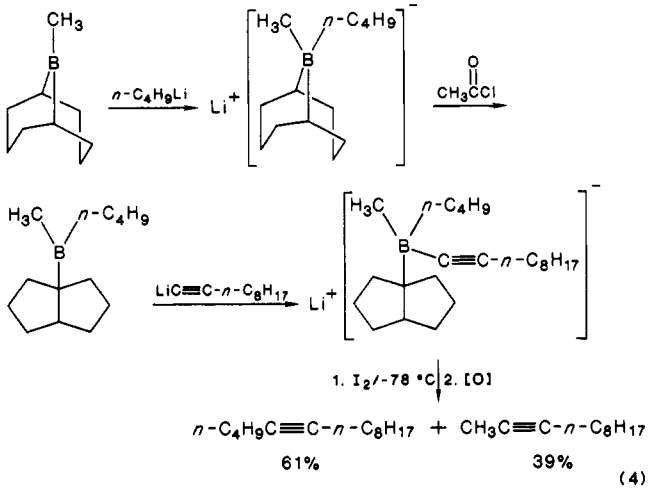
alkylborate derivatives of 9-BBN with acetyl chloride[10] (eq 3). The 1-bicyclo[3.3.0]nonanyl moiety is a tertiary alkyl



(3)

group. Therefore, like the thexyl group,[7] it might also show a relatively low migratory aptitude. In certain reactions, the methyl group also displays some resistance to migration.[11] Consequently, we sought to combine these effects by examining the iodination of an alkynyl "ate" complex containing both the 1-bicyclo[3.3.0]nonanyl residue and a methyl substituent (eq 4). Indeed, there was a minimum

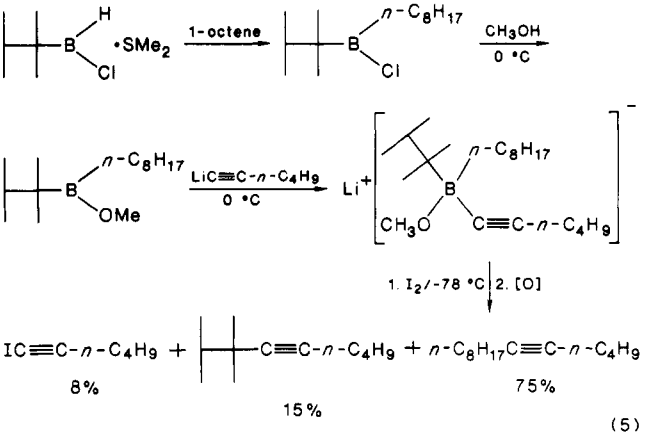


(4)

amount of migration from the 1-bicyclo[3.3.0]nonanyl group. Unfortunately, GC analysis revealed a high percentage of competitive migration from the methyl group.

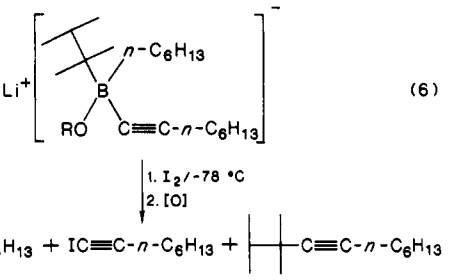
These results led us to believe that the selective migration of a primary alkyl group could be achieved in the presence of a tertiary blocking group. However, two tertiary substituents would undoubtedly hinder the formation of the intermediate alkynyl "ate" complex. Recently, thexylchloroborane–methyl sulfide was demonstrated to be a very stable monohydroborating agent with exceptional regioselectivity.[12] The resulting thexylalkylchloroboranes can be easily methanolyzed to the corresponding borinic esters. The possible low migratory aptitude of the thexyl group, combined with the nonmigratory character of the methoxy group, made these intermediates likely candidates for achieving the desired selective migration (eq 5).

Indeed, this approach solved the problem. Good yields of the desired 5-tetradecyne were observed after oxidation. Two other side products were observed by GCMS in the crude reaction mixture. The minor component (8%) was identified as 1-iodohexyne. The other component (10–15%) was identified as 2,3,3-trimethyl-4-nonyne, i.e., the product resulting from the undesired competitive migration of the thexyl group. The relatively high volatility of these byproducts allowed them to be easily separated from the desired product by vacuum distillation.



(5)

Other alkoxy groups were introduced in the borinate intermediate in an attempt to reduce these side products. A comparison of the relative yields of each product obtained from these intermediates is summarized below (eq 6). It is apparent from these results that the amount of



(6)

| | | % yields | |
|---|---|---|---|
| R = $CH_3$ | 75 | 8 | 14 |
| $C_2H_5$ | 68 | 15 | 12 |
| $i$-$C_3H_7$ | 75 | 20 | 5 |
| $t$-$C_4H_9$ | 15 | 68 | 3 |

the competitive thexyl group migration product can be reduced, but only at the expense of increasing the amount of iodoalkyne in the reaction. Presumably, increasing the steric bulk of the borinate intermediate retards "ate" complex formation. Thus, more free lithium alkyne is available in solution to react with iodine and produce iodoalkyne. Since the methylborinate intermediates were the most convenient to prepare, we proceeded to examine the synthetic utility of this method (eq 5).

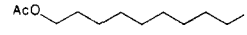
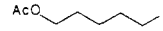
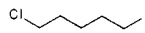
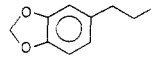
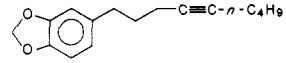
Several unsymmetrical alkynes were prepared via this procedure. The results are summarized in Table II. Moderate to good yields of isolated products were obtained after distillation. This approach represents a practical solution to the problem of achieving the selective migration of a primary alkyl group in the transfer reaction induced by iodination of lithium alkynyl "ate" complexes of organoboranes. This method was demonstrated to be compatible with several common functional groups. Thus, this procedure should allow one to efficiently use a valuable substrate in this transfer reaction. Indeed, the essentially one-pot synthesis of 1-chloro-7-dodecyne (I) dramatically

$$Cl(CH_2)_6C{\equiv}C(CH_2)_3CH_3$$
I

illustrates the advantage of this procedure over many of the other common organometallic-based routes to unsymmetrical alkynes. In addition, since a previous study has demonstrated the direct conversion of these unsymmetrical alkynes to the corresponding (*Z*)-olefins[4a] (eq 1), this approach therefore also provides intermediates that are particularly valuable for the synthesis of insect pheromones.

(10) Kramer, G. W.; Brown, H. C. *J. Am. Chem. Soc.* **1976**, *98*, 1964–1965.
(11) (a) Zweifel, G.; Horng, A. *Synthesis* **1973**, 672–674. (b) Zweifel, G.; Fisher, R. P. *Ibid.* **1974**, 339–340.
(12) (a) Zweifel, G.; Pearson, N. R. *J. Am. Chem. Soc.* **1980**, *102*, 5919–5920. (b) Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D. *J. Org. Chem.* **1980**, *45*, 4540–4542; (c) **1982**, *47*, 863–872.
(13) Evans, D. A.; Crawford, T. C.; Thomas, R. C.; Walker, J. A. *J. Org. Chem.* **1976**, *41*, 3947–3953.

**Table II. Synthesis of Unsymmetrical Alkynes via Iodination of Lithium Alkynyl "Ate" Complexes of Methyl Thexylalkylborinates**

| acetylene | thexylalkylborinates[a] ThxBROCH)3, R = | product[16] | isolated yield,[b] % |
|---|---|---|---|
| 1-hexyne | $n$-$C_8H_{17}$ | 5-tetradecyne[15] | 74 |
| 1-hexyne |  | 11-hexadecyn-1-ol[19,c] | 67 |
| 1-hexyne |  | 7-dodecyn-1-ol[20,c] | 49 |
| 1-decyne | $n$-$C_{13}H_{27}$ | 9-tricosyne[21] | 55 |
| 1-hexyne | $n$-$C_{10}H_{21}$ | 5-hexadecyne[22] | 55 |
| 1-hexyne |  | 1-chloro-7-dodecyne[18] | 53 |
| 1-hexyne |  |  | 53 |

[a] 30 mmol reaction. [b] Based on thexylalkylborinate. [c] Hydrolyzed product.

## Conclusion

A reaction sequence has been developed which utilizes thexylalkylborinic esters as intermediates for the preparation of unsymmetrical alkynes. The objective to achieve the selective migration of a primary alkyl group in the presence of an appropriate blocking group was largely accomplished. The combined use of the thexyl and methoxy moieties as blocking groups in the transfer reaction results in the efficient utilization of the starting alkene in the reaction. Furthermore, the high tolerance of ThxBHCl·$SMe_2$ toward many functional groups and its high regioselectivity in alkene hydroborations produce intermediates which are particularly valuable for the synthesis of insect pheromones.

## Experimental Section

The reaction flasks and other glassware required for the experiments were predried at 140 °C for several hours, assembled hot, and cooled under a stream of prepurified nitrogen (Airco). Syringes were assembled and fitted with needles while hot and then cooled. All reactions were carried out under a static pressure of nitrogen in flasks fitted with septum-covered side arms using standard techniques for handling air-sensitive materials.[5]

**Materials.** Commercial grade THF was distilled from excess lithium aluminum hydride and stored under nitrogen prior to use. The starting olefins and alkynes were purchased either from the Chemical Samples Division of Albany International or Aldrich Chemical Company. The alkenes were distilled from excess lithium aluminum hydride and stored under nitrogen. The alkynes were distilled from sodium borohydride and stored under nitrogen prior to use. Spectro-quality, anhydrous methanol was degassed and stored under nitrogen over 3 Å molecular sieves. The hydrocarbons employed as internal standards for GLC analyses were obtained from Phillips Petroleum Company and were labeled >99% pure. Hexane solutions of $n$-butyllithium were obtained from the Ventron Corporation and were standardized by using literature procedures.[14] Reagent grade iodine (Mallinckrodt) was used as received. THF solutions of 9-BBN, $Sia_2BH$, and $Chx_2BH$, and $Chx_2BH$ were prepared and standardized according to literature procedures.[5] $CH_2Cl_2$ solutions of ThxBHCl·$SMe_2$ were prepared as described previously.[11b]

**GC Analyses.** GC analyses were carried out on a Varian Model 1200 FID chromatograph equipped with a 12 ft × 0.125 in. column of 10% SP-2100 on 100/120-mesh Supelcoport. All GC yields were determined by a suitable internal standard and authentic synthetic mixtures.

**Spectra.** When necessary, spectra were obtained under an inert atmosphere by using apparatus and techiques described elsewhere.[5] $^{11}B$ and $^{13}C$ NMR spectra were recorded on a Varian FT-80A spectrometer equipped with a broadband probe and a Hewlett-Packard 3335A frequency synthesizer. All $^{11}B$ NMR chemical shifts are reported relative to $BF_3$·$OEt_2$ ($\delta$ 0) with the chemical shifts downfield from $BF_3$·$OEt_2$ assigned as positive. $^1H$ NMR spectra were obtained with a Varian T-60 (60 MHz) spectrometer. All $^1H$ and $^{13}C$ NMR chemical shifts are reported relative to tetramethylsilane ($\delta$ 0). Infrared spectra were obtained on a Perkin-Elmer Model 1420 spectrometer equipped with Data Station. Mass spectral data were obtained on a Finnegan GC-MS Model 4000.

**General Procedure for Examining Alkyl Group Migration in *B*-*n*-Hexyldialkylboranes.** The following procedure using *B*-*n*-hexyldisiamylborane is representative. Five millimoles of $Sia_2BH$ were prepared at 0 °C in a 100-mL round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet by combining 1.06 mL of 2-methyl-2-butene (0.70 g, 10.0 mmol) with 2.6 mL of 1.93 M $BH_3$·THF (5.0 mmol). Then 0.63 mL of 1-hexene (0.42 g, 5.0 mmol) was added and the resulting solution was stirred at 0 °C for 30 min. Meanwhile, a solution of 1-lithio-1-hexyne (5 mmol) was prepared under nitrogen at 0 °C by adding 2.10 mL of 2.38 M $n$-butyllithium (5.0 mmol) in hexane dropwise via syringe into a solution of 0.57 mL of 1-hexyne (0.41 g, 5.0 mmol) in 5 mL of THF. The cold lithium acetylide solution was then transferred dropwise via a double-ended needle into the cold trialkylborane solution. The resulting clear solution was then cooled to −78 °C and a solution of iodine (1.27 g, 5.0 mmol) in 5 mL of THF was added dropwise through a Teflon tube. After 45 min at −78 °C, the reaction mixture was allowed to warm to room temperature. Then 2 mL of 3.0 N aqueous sodium hydroxide was added. The mixture was cooled to 0 °C and 2 mL of 30% aqueous hydrogen peroxide was added dropwise. The mixture was allowed to warm to room temperature. GC analysis of the organic layer revealed the presence of 3.2 mmol of 5-dodecyne and 1.3 mmol of 2,3-dimethyl-4-nonyne. A summary of the other experimental results is shown in Table I.

**Iodination of the Alkynyl "Ate" Complex of Methyl-*n*-hexyl(1-bicyclo[3.3.0]nonanyl)borane.** A dry, 100-mL, round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet was charged at 0 °C with 10 mL of prepurified hexane and 0.79 mL of *B*-methyl-9-BBN[5] (0.68 g, 5.0 mmol). Then 2.03 mL of 2.47 M $n$-butyllithium (5.0 mmol) in hexane was added dropwise via syringe. An $^{11}B$ NMR spectrum of the resulting solution indicated the clean formation of the desired tetraalkyl "ate" complex ($\delta$ −19.7). Then 0.36 mL of acetyl chloride (5.0 mmol) was added and the reaction mixture was stirred at 0 °C for 1 h. The $^{11}B$ NMR spectrum of this solution indicated clean conversion to the desired trialkylborane ($\delta$ 82.9). A solution of 1-lithio-1-decyne (10 mmol) in THF/hexane was then added via the double-ended needle. The $^{11}B$ NMR spectrum again indicated the clean formation of the desired alkynyl "ate" complex ($\delta$ −17.1). After 15 min at 0 °C, the flask was cooled to −78 °C and a solution of iodine (1.27 g, 5.0 mmol) in 5 mL of THF was added dropwise through a Teflon tube. After 45 min at −78 °C, the reaction mixture was allowed to warm to room temperature. At this point, a $^{11}B$ NMR spectrum showed the complete disappearance of the signal due to the alkynyl "ate" complex. Then 2.0 mL of the 3 N aqueous sodium hydroxide was added. The reaction was cooled to 0 °C and then 2.0 mL of 30% aqueous hydrogen peroxide was added dropwise. After warming to room temperature, GC analysis of the organic layer revealed the presence of 2.65 mmol of 5-tetradecyne along with 1.71 mmol of 2-undecyne.

(14) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155–158.

**General Procedure for Preparing Unsymmetrical Alkynes by Iodination of Lithium Alkynyl "Ate" Complexes of Thexylalkylborinates.** The following procedure for the preparation of 5-tetradecyne is representative. A dry, 100-mL, round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet was charged at 0 °C with 1.57 mL of 1-octene (1.12 g, 10.0 mmol) and 4.8 mL of 2.1 M cold ThxBHCl·$SMe_2$ (10.0 mmol) in $CH_2Cl_2$. After 5 min at 0 °C, the ice bath was replaced with a tapwater bath and the resulting clear solution was stirred at room temperature for 1 h. The solution was then cooled to 0 °C and 1.0 mL of absolute methanol (25 mmol) was slowly added. The solution was stirred at room temperature for 1 h and then was concentrated in vacuo to a constant weight by using a water aspirator and then a vacuum pump (0.1 torr). The resulting clear oil was dissolved in 20 mL of THF at 0 °C. the $^{11}B$ NMR spectrum of this THF solution showed only the desired methyl thexylalkylborinate ($\delta$ 53.8). A solution of 1-lithio-1-hexyne (10 mmol) in THF/hexane was added dropwise at 0 °C. A $^{11}B$ NMR spectrum of the resulting clear solution showed the clean formation of the desired "ate" complex ($\delta$ −0.3). After 15 min at 0 °C, the flask was cooled to −78 °C and a solution of iodine (2.54 g, 10.0 mmol) in 10 mL of THF was added dropwise through a Teflon tube. After 1 h at −78 °C, the orange heterogeneous mixture was allowed to warm to room temperature and was then stirred an additional 2 h. The $^{11}B$ NMR spectrum showed the complete disappearance of the signal due to the "ate" complex. The reaction was then treated with 4.0 mL of 3 N aqueous sodium hydroxide. The $^{11}B$ NMR spectrum of the resulting mixture showed the clean formation of a thexylboronate species ($\delta$ 33.0). The mixture was then cooled to 0 °C and 4.0 mL of 30% aqueous hydrogen peroxide was added dropwise. After warming to room temperature, *n*-hexadecane was added as an internal standard. GCMS analysis showed the formation of 7.5 mmol of 5-tetradecyne, 1.5 mmol of 2,3,3-trimethyl-4-nonyne, and 0.8 mmol of 1-iodohexyne.

The reaction was then repeated on a 30-mmol scale. After the oxidation step, the organic phase was separated, dried, and concentrated in vacuo to remove the solvent, alcohol by products, 1-iodohexyne, and the 2,3,3-trimethyl-4-nonyne. A pentane solution of the resulting yellow liquid was then passed through a short plug of silica gel 60 (E. Merck, 40–63 $\mu$m); 4.3 g (74%) of 5-tetradecyne[15] was obtained as a clear liquid, 97% pure by GC: $^1H$-decoupled $^{13}C$ NMR ($CDCl_3$) $\delta$ 80.1, 32.1, 31.6, 29.5, 29.1, 22.9, 22.2, 19.0, 18.7, 14.2, 13.7.

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The following alkynes[16] were prepared by using a similar procedure.

**5-Hexadecyne:**[17] 3.7 g (55%) of a clear liquid isolated after distillation, bp 71–73 °C (0.04 mm); $n^{20}_D$ 1.4470; $^1H$ NMR ($CDCl_3$) $\delta$ 1.9–2.25 (br, 4 H), 1.3 (br, 18 H), 0.95 (br, 6 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 80.2, 80.1, 32.0, 31.4, 29.7, 29.6, 29.5, 29.4, 29.3, 29.0, 22.8, 22.0, 18.9, 18.6, 14.1, 13.6; MS, *m/e* 222. Anal. Calcd for $C_{16}H_{30}$: C, 86.41; H, 13.59. Found: C, 86.03; H, 13.61.

**1-Chloro-7-dodecyne:**[18] 3.4 g (53%) of a clear liquid isolated after distillation, bp 92–93 °C (0.5 mm); $n^{20}_D$ 1.4625 [lit. $n^{21}_D$ 1.4619]; $^{13}C$ NMR ($CDCl_3$) $\delta$ 80.4, 79.8, 44.9, 32.7, 31.4, 29.0, 28.1, 26.5, 22.0, 18.7, 18.5, 13.6. Anal. Calcd for $C_{12}H_{21}Cl$: C, 71.80; H, 10.54; Cl, 17.66. Found: C, 72.08; H, 10.54; Cl, 17.30.

**5-(4-Nonynyl)-1,3-benzodioxole:** 3.8 g (53%) of a clear liquid isolated after distillation, bp 110–111 °C (0.04 mm); $n^{20}_D$ 1.5199; $^1H$ NMR ($CDCl_3$) $\delta$ 6.65 (s, 3 H), 5.85 (s, 2 H), 2.65 (t, 2 H), 2.18 (t, 4 H), 1.8 (dd, 2 H), 1.5 (m, 4 H), 0.90 (t, 3 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 148.0, 146.0, 136.1, 121.5, 109.3, 108.4, 101.0, 81.1, 79.9, 34.9, 31.6, 31.2, 22.3, 18.8, 18.4, 13.6; MS, *m/e* 244. Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.54; H, 8.54.

**Isolation and Characterization of 2,3,3-Trimethyl-4-nonyne.** In all of the acetylene preparations that utilized a thexylalkylborinate intermediate with 1-lithio-1-hexyne, a common species was observed by GC. GCMS analysis showed a weak molecular ion at 166; (166, 0.4), (151, 0.5), (123, 34.5), 122 (19.3), (109, 13.6), (108, 1.4), (107, 5.7), (95, 15.5), (82, 23.0), (81, 100), (80, 6.3), (79, 25.0). Preparative GC using a 6 ft × 0.5 in. column of 20% SP-2100 at 115 °C produced a clear liquid. $^1H$ NMR ($CDCl_3$): $\delta$ 2.18 (t, 2 H), 1.5 (m, 1 H), 1.4 (br, 4 H), 1.1 (s, 6 H), 0.95 (d, 6 H), 0.95 (t, 3 H). $^{13}C$ NMR ($CDCl_3$): $\delta$ 87.1, 80.6, 38.2, 35.2, 31.8, 27.7, 27.7, 22.2, 18.3, 18.2, 13.7. IR (neat): 1390, 1378, 1146 $cm^{-1}$ High resolution MS: exact mass *m/e* 166.1706, calcd for $C_{12}H_{22}$ *m/e* 166.3080.

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(16) The physical constants and spectral characteristics for all known characterized compounds were consistent with those reported in the literature.

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