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# Vinylic Organoboranes. 4. A General, One-Pot Synthesis of 6- and 7-Alkyn-1-ols via Boracyclanes. Influence of Steric Effects in the Iodination of Lithium Alkynyl "Ate" Complexes of Dialkylborinates

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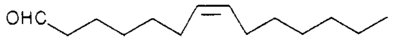
The iodination of the "ate" complexes derived from various *B*-alkoxyborinane derivatives and 1-alkynyllithium has been investigated. The results indicate the ate complex from *B*-methoxyborinane is converted into the desired 6-alkyn-1-ol in a yield of only 22%, with much larger amounts, 65%, of the undesired 1-iodo-1-alkyne. Increases in the steric bulk of the alkoxy group on boron increase the yield of the required 6-alkyn-1-ol with the best results realized with *B*-(triphenylmethoxy)borinane. Treatment of *B*-(triphenylmethoxy)borinane with 1-alkynyllithium affords the corresponding "ate" complex. Subsequent iodination induces the migration of one end of the cycloalkyl chain from boron to the adjacent carbon, resulting in the formation of the one-carbon homologated borepane moiety. This then undergoes a rapid deiodoboronation to afford the corresponding (6-alkyn-1-yl)boronate ester. Oxidation of these esters produces the desired 6-alkyn-1-ols in excellent yields (85%). An attempt to extend this reaction to di-*n*-alkylborinates to prepare the corresponding unsymmetrical alkynes did not achieve satisfactory results. Alternatively, the iodination of the "ate" complex from *B*-methylborinane and 1-alkynyllithium, followed by oxidation, provides the required 6-alkyn-1-ols in high yields. This procedure has been successfully extended to the seven-membered borepane moiety to provide the corresponding 7-alkyn-1-ols. Extension of this reaction to the di-*n*-alkylmethylboranes provides the corresponding unsymmetrical alkynes in good yields. Thus, these procedures constitute a simple, general and one-pot synthesis of the desired alkyn-1-ols, valuable synthons in organic synthesis. Insect pheromones, (*Z*)-7-tetradecenal and (*Z*)-7-hexadecenal, were readily prepared in excellent yields by utilizing this convenient procedure.

The increasing importance of alkyn-1-ols as valuable synthons in the synthesis of insect pheromones[1] has warranted the search for simple methods to synthesize this interesting class of compounds. In continuation of our interest in the synthesis of insect pheromones,[2-5] we herein report a simple synthesis of 6- and 7-alkyn-1-ols using organoborane chemistry and its application to the synthesis of (*Z*)-7-tetradecenal (1), the insect pheromone of the citrus flower moth (*Prays citri*),[6] and (*Z*)-7-hexadecenal (2), which elicits the significant activity of the trail-following pheromone of the Argentine ant (*Iridomyrmex humilis*).[7]



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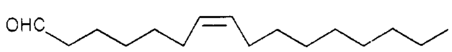

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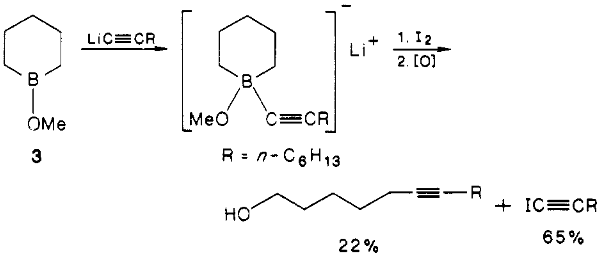
## Results and Discussion

The regio- and stereospecific construction of carbon–carbon bonds is a vital part of organic synthesis and the key role of organoboranes for this operation has been elegantly demonstrated in recent years.[8,9] We previously reported a novel synthesis of acetylenes via the iodination of lithium (1-alkynyl)triorganoborates (eq 1).[10]

$$R_3B \xrightarrow{LiC\equiv CR'} [R_3BC\equiv CR']^-Li^+ \xrightarrow{I_2} RC\equiv CR' + R_2BI \quad (1)$$

It appeared to us that the use of boracyclanes might provide us with a convenient synthesis of the desired alkyn-1-ols. The readily available borinane,[11] the six-membered boracyclane, was first selected for the study. Iodination of the "ate" complex from *B*-methoxyborinane and 1-alkynyllithium was first investigated. We observed that 1-iodo-1-alkyne was formed as a major product, 65%, with only ~22% of the desired 6-alkyn-1-ols (eq 2).



(2)

We thought that the creation of greater steric hindrance about the boron atom might reduce attack of iodine on C1 of the acetylene and thereby improve the yield of 6-alkyn-1-ols. Accordingly, experiments were carried out with representative *B*-alkoxyborinanes containing alkoxy groups of increasing steric requirements. The best results were realized with *B*-(triphenylmethoxy)borinane. In this case a reduction of the yield of 1-iodo-1-alkyne to 5% was achieved (Table I) (eq 3).

Representative 6-alkyn-1-ols were prepared in high yields (Table II).

We also investigated the iodination of the "ate" complex obtained via the treatment of *B*-methylborinane with 1-alkynyllithium as an alternate route for the 6-alkyn-1-ols. Indeed, the desired 6-alkyn-1-ols were obtained in excellent yields with methyl-migrated product produced in only

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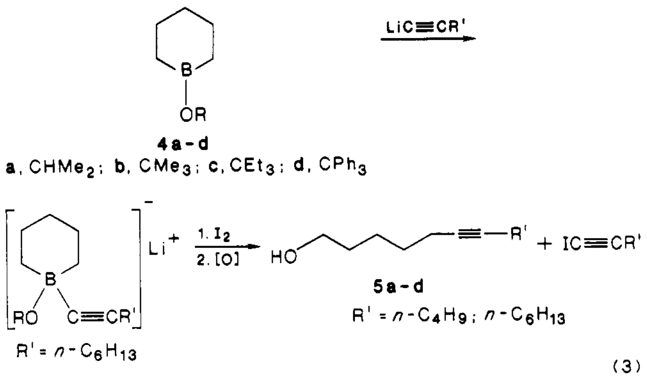
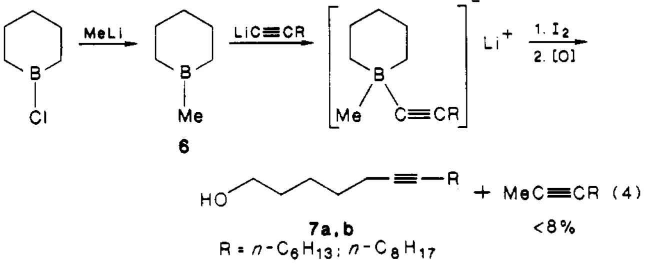


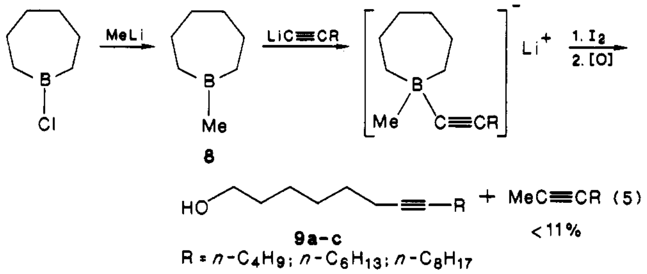
4a-d
a, CHMe2; b, CMe3; c, CEt3; d, CPh3
5a-d
R' = n-C4H9; n-C6H13
R' = n-C6H13



6
7a,b
R = n-C6H13; n-C8H17

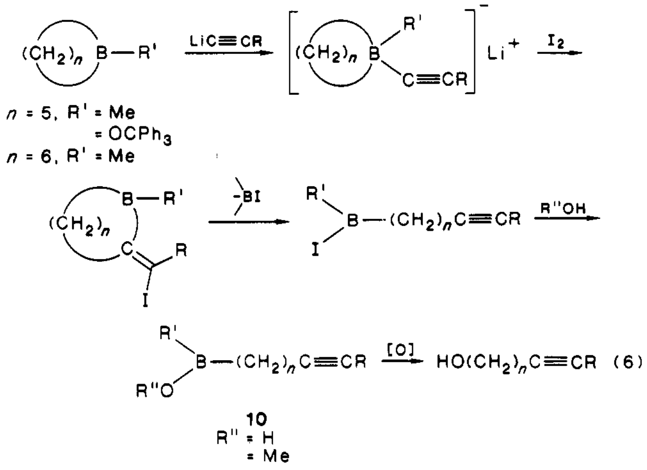
minor amounts (<8%) (eq 4).

This procedure proved more convenient than the previous one. It avoids the need to remove triphenylcarbinol from the product. This reaction sequence was successfully extended to the seven-membered boracyclane, borepane (eq 5). Representative 6- and 7-alkyn-1-ols were prepared in excellent yields (Table II).



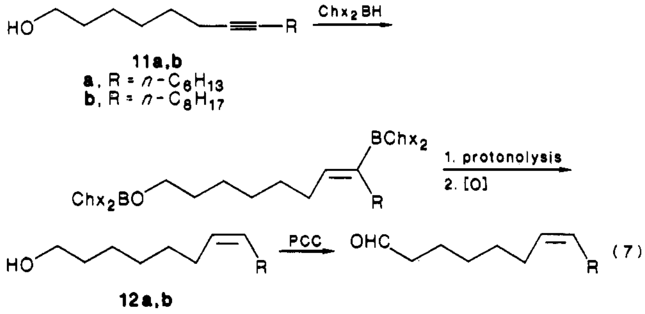
8
9a-c
R = n-C4H9; n-C6H13; n-C8H17

These results indicate that the iodination of the "ate" complex results in the migration of one end of the cycloalkyl chain from boron to the adjacent carbon, producing an intermediate containing one-carbon homologated borepane (when $n = 5$) or borocane (when $n = 6$) moiety. This then undergoes a rapid deiodoboronation to afford the corresponding (6- or 7-alkyn-1-yl)boronate esters. Subsequent oxidation provides the desired 6- or 7-alkyn-1-ols (eq 6).



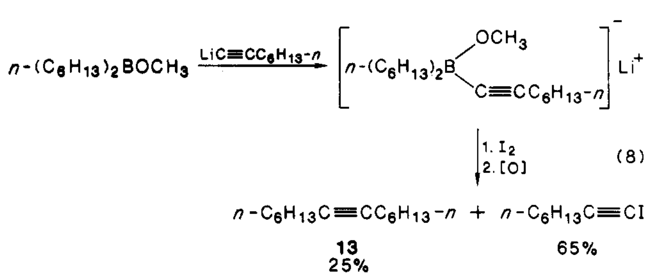
10
R'' = H
= Me

The *Prays citri* pheromone, (*Z*)-7-tetradecenal (1), and (*Z*)-7-hexadecenal (2), which elicits the significant activity of the trail-following pheromone of the Argentine ant (*Iridomyrmex humilis*), were synthesized by utilizing **11a** and **11b** respectively (R = *n*-Hex, $n = 5$; *n*-Oct, $n = 6$) (eq 7) in excellent yields (Table II).



11a,b
a, R = n-C6H13
b, R = n-C8H17
12a,b

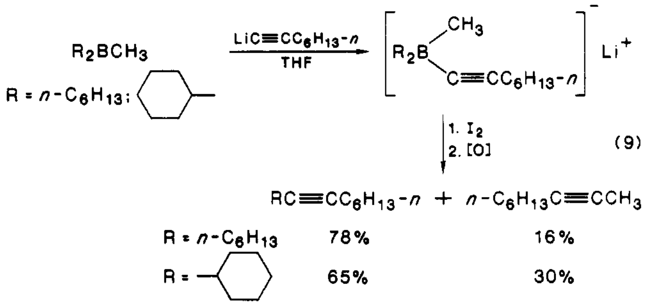
To test the generality of the reaction, we also explored the reaction of lithium methyl octynyldi-*n*-hexylborinate with iodine. It was observed that the desired 7-tetradecyne was formed only in 25% yield, along with 65% of 1-iodo-1-octyne (eq 8).



13
25%

The above reaction was carried out with various lithium alkyl octynyldi-*n*-hexylborinates and the best results were obtained when triethylmethoxydi-*n*-hexylboranes were utilized. The results are summarized in Table III.

We also investigated the reaction of iodine on the "ate" complexes derived from dialkylmethylboranes and octynyllithium. The corresponding unsymmetrical alkynes were formed in good yields, along with methyl-migrated products (eq 9).



In the above reactions, only one of the two alkyl groups is utilized. This difficulty can be overcome by putting two blocking groups on boron. Accordingly, reactions were carried out on thexylalkoxyalkylboranes where thexyl and alkoxy groups serve as blocking groups. The results are discussed in the following paper.

In summation, we now have a simple, general method to synthesize 6- and 7-alkyn-1-ols via boracyclanes, which offer great promise in the synthesis of insect pheromones. We are presently exploring the possibilities of utilizing these valuable boron intermediates (**10**) in organic transformations with the objective of applying them to the synthesis of insect pheromones and other biologically active molecules.

**Table I. Synthesis of 6-Alkyn-1-ols via *B*-Alkoxyborinane Derivatives**

| boracyclane | 1-alkyne for alkynyllithium | yield[a] of 6-tridecyn-1-ol, % | yield[a] of 1-iodo-1-octyne, % |
|---|---|---|---|
| *B*-methoxyborinane (**3**) | 1-octyne | 22 | 65 |
| *B*-isopropoxyborinane (**4a**) | 1-octyne | 50 | 38 |
| *B*-*tert*-butoxyborinane (**4b**) | 1-octyne | 58 | 34 |
| *B*-(triethylmethoxy)borinane (**4c**) | 1-octyne | 65 | 21 |
| *B*-(triphenylmethoxy)borinane (**4d**) | 1-octyne | 85 | 5 |

[a] GC yields using *n*-hexadecane as an internal standard. All of the reactions were carried out on a 10-nmol scale and the products were analyzed on a 6 ft 10% SE-30 column.

**Table II. Synthesis of 6- and 7-Alkyn-1-ols[a] and the Corresponding (*Z*)-7-Alken-1-ols[b] and (*Z*)-7-Alkenals[b]**

| boracyclane | 1-alkyne for 1-alkynyllithium | product[c] | yield,[d] % | bp °C/mm[e] | $n^{20}{}_D$[e] |
|---|---|---|---|---|---|
| *B*-(triphenylmethoxy)borinane | 1-hexyne | 6-undecyn-1-ol (**5a**) | 71 | 108–110/2<br>(90–92/0.03)[13] | 1.4635<br>($n^{24}{}_D$ 1.4582)[13] |
| | 1-octyne | 6-tridecyn-1-ol (**5b**) | 70 | 103–104/0.10<br>(107–109/0.10)[15] | 1.4630<br>($n^{25}{}_D$ 1.4608)[15] |
| *B*-methylborinane | 1-octyne | 6-tridecyn-1-ol (**7a**) | 72 | 104–105/0.10 | 1.4628 |
| | 1-decyne | 6-pentadecyn-1-ol (**7b**) | 72 | 123–125/0.05 | 1.4592 |
| *B*-methylborepane | 1-hexyne | 7-dodecyn-1-ol (**9a**) | 74 | 110–112/0.4<br>(99–100/0.2)[18] | 1.4596<br>($n^{25}{}_D$ 1.4614)[18] |
| | 1-octyne | 7-tetradecyn-1-ol (**9b**) | 73 | 117–118/0.10<br>(104–105/0.01)[15] | 1.4612<br>($n^{25}{}_D$ 1.4627)[15] |
| | | (*Z*)-7-tetradecen-1-ol (**11a**) | 85[f,g] | 112–113/0.03<br>(110–112/0.02)[4] | 1.4551<br>(1.4566)[4] |
| | | (*Z*)-7-tetradecenal (**1**) | 80[f,h] | 87–89/0.05 | 1.4499 |
| | 1-decyne | 7-hexadecyn-1-ol (**9c**) | 72 | 135–136/0.01 | 1.4609 |
| | | (*Z*)-7-hexadecen-1-ol (**11b**) | 86[f,g] | 132–134/0.01 | 1.4579 |
| | | (*Z*)-7-hexadecenal (**2**) | 80[f,h] | 110–111/0.05 | 1.4525 |

[a] Preparation of alkyn-1-ols were carried out on a 30-mmol scale. [b] These reactions were carried out on a 20-mmol scale. [c] Chemical purities of all the compounds were >97% by GC analysis on a 6 ft SE-30 column. [d] Yields of pure distilled products. [e] Literature values are given in parentheses. [f] Isomeric purities are >99% by $^{13}C$ NMR analysis.[19] [g] Isolated yields from the corresponding 7-alkyn-1-ols. [h] Isolated yields from the corresponding (*Z*)-7-alken-1-ols.

**Table III. Synthesis of Unsymmetrical Alkynes via "Ate" Complexes Derived from ($n$-$C_6H_{13})_2BOR$ and 1-Octynyllithium**

| ($c$-$C_6H_{13})_2BOR$, R = | yield[a] of 7-tetradecyne, % | yield[a] of 1-iodo-1-octyne, % |
|---|---|---|
| $CH_3$ | 25 | 65 |
| $CHMe_2$ | 38 | 44 |
| $CMe_3$ | 56 | 34 |
| $CEt_3$ | 65 | 22 |
| $CPh_3$[b] | 35 | 25 |

[a] All of the reactions were carried out on a 10-mmol scale. GC yields using *n*-hexadecane as an internal standard. GC analyses were performed on 10% SE-30 on Chromosorb W column. [b] In this case, the reaction product contained about 20% of a high boiling material.

## Experimental Section

All boiling points are uncorrected. The GC analyses were carried out by using *n*-hexadecane as an internal standard, either on a Varian 1400 gas chromatograph (column 12 ft × 1/8 in. packed with 10% SE-30 on Chromosorb W AW DMCS) or on a Hewlett-Packard 5750 research chromatograph (column 6 ft × 1/4 in. packed with 10% SE-30 on Chromosorb W AW DMCS). IR spectra were recorded on a Perkin-Elmer 137 spectrophotometer. $^1H$ NMR and $^{13}C$ NMR spectra were recorded on Varian T-60 and FT-80A spectrometers, respectively. 1-Alkynes were obtained from Farchan Acetylenes. All alcohols were dried over molecular sieves (3 Å). All manipulations of the boron compounds were done under nitrogen by using standard procedures.

**6-Undecyn-1-ol (5a).** To triphenylmethanol (30 mmol) in tetrahydrofuran (15 mL) was added a solution of borinane in tetrahydrofuran (30 mmol) at 0 °C, and the solution was stirred at room temperature for 1 h. 1-Hexynyllithium (30 mmol), obtained by the reaction of *n*-butyllithium (30 mmol) with 1-hexyne (30 mmol) in tetrahydrofuran at 0 °C, was added to *B*-(triphenylmethoxy)borinane (**4d**) at 0 °C and the resulting "ate" complex was cooled to −78 °C. To this solution at −78 °C was added iodine (30 mmol, 7.62 g) in tetrahydrofuran (30 mL), and the reaction mixture was stirred for 3 h at −78 °C. Any excess iodine was destroyed by adding an aqueous solution of sodium thiosulfate, and the reaction mixture was allowed to warm up to room temperature. The reaction mixture was then treated with an aqueous solution of sodium hydroxide (3 M) and 30% hydrogen peroxide. After oxidation, the product was extracted with *n*-pentane (3 × 25 mL), washed with water (2 × 30 mL), and dried over magnesium sulfate. The solvent was removed and the distillation[12] of the product afforded pure 6-undecyn-1-ol (**5a**): yield; 3.58 g, 71%; bp 108–110 °C/2 mm; $n^{20}{}_D$ 1.4635 [lit.[13] bp 90–92 °C/0.03 mm; $n^{24}{}_D$ 1.4582]; GC analysis, >98% chemical purity; IR (neat) $\nu$ 3320 cm$^{-1}$ (OH); $^1H$ NMR ($CDCl_3/Me_4Si$) $\delta$ 0.71–1.83 (m, 13 H), 1.85–2.41 (*m*, 4 H), 2.51 (br *s*, 1 H), 3.69 (distorted *t*, 2 H); $^{13}C$ NMR ($CDCl_3/Me_4Si$) $\delta$ 79.89, 80.31 (C≡C), 62.41, 32.22, 31.29, 28.99, 25.07, 21.91, 18.72, 18.40, 13.53 (alkyl C).

**7-Tetradecyn-1-ol (9b).** The procedure from *B*-methylborepane (**8**) is representative. To 30 mmol of *B*-chloroborepane[14] in ether at −78 °C was added 30 mmol of methyllithium. After 0.5 h at room temperature, 30 mmol of 1-octynyllithium was added at 0 °C, and the resulting "ate" complex was cooled to −78 °C. Iodination and oxidation were carried out as described in the previous procedure. The crude material contained 11% of 2-nonyne, which could be separated by careful distillation to afford 4.6 g (73%) of 7-tetradecyn-1-ol (**9b**): bp 117–118 °C/0.01 mm; $n^{20}{}_D$ 1.4612 [lit.[15] bp 104–105 °C/0.01 mm, $n^{25}{}_D$ 1.4627]; GC analysis, >97% chemical purity; IR (neat) $\nu$ 3310 cm$^{-1}$ (OH); $^1H$ NMR ($CDCl_3/Me_4Si$) $\delta$ 0.71–1.85 (m, 19 H), 1.96–2.37 (*m*, 5 H), 3.57 (*t*, 2 H, *J* = 7 Hz); $^{13}C$ NMR ($CDCl_3/Me_4Si$) $\delta$ 80.34, 80.05 (C≡C), 65.52, 32,73, 31.51, 29.26, 28.76, 28.65, 25.51, 22.68, 18.88, 14.06.

**(*Z*)-7-Tetradecenal (1).** 7-Tetradecyn-1-ol (20 mmol) was treated with dicyclohexylborane (40 mmol) for 1 h at 0 °C, followed by 2 h at room temperature, to afford the corresponding vinyl-

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(12) In this distillation, triphenylcarbinol remains as pot residue.
(13) Svirskaya, P. I.; Leznoff, C. C. *J. Chem. Eng. Data* **1979**, *24*, 152.
(14) Brown, H. C.; Zaidlewicz, M. *J. Am. Chem. Soc.* **1976**, *98*, 4917.
(15) Voaden, D. J.; Jacobson, M. *J. Med. Chem.* **1972**, *15*, 619.

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); $^1$H 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 (CHO), 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); $^1$H 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).

**Acknowledgment.** We are indebted to the National Institutes of Health (Grant GM 10937-23) and the National Science Foundation (Grant CHE 8414171) for support of this work.

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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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