(11) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, N.Y., 1967, Chapter 1.
(12) J. A. Zoltewicz and J. F. Bunnett, *J. Am. Chem. Soc.*, **87**, 2640 (1965).
(13) R. A. Rossi, R. H. de Rossi, and A. F. López, *J. Am. Chem. Soc.*, **98**, 1253 (1976).
(14) It is unlikely that chloride ion comes from nucleophilic displacement by CH_3O^- on the hydrazide or CB, because it is known that nucleophilic aromatic substitution with unactivated benzene rings is very slow, and this reaction was carried out at very low temperature and for a short time (30 min).
(15) I. P. Fisher and F. P. Lossing, *J. Am. Chem. Soc.*, **85**, 1018 (1963); R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1003, 1011 (1965); R. H. de Rossi, H. E. Bertorello, and R. A. Rossi, *J. Org. Chem.*, **35**, 3328, 3332 (1970); R. G. Bergman, *Acc. Chem. Res.*, **6**, 25 (1973); S. Wawzonek and J. H. Wagenknecht, *J. Electrochem. Soc.*, **110**, 420 (1963).
(16) R. W. Hoffmann, *Chem. Ber.*, **98**, 222 (1965).

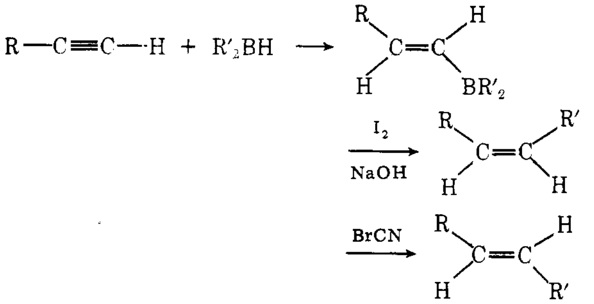
A Stereospecific Route to Trisubstituted Olefins via Organoboranes

Nicholas J. LaLima, Jr., and Alan B. Levy*

Department of Chemistry, State University of New York, Stony Brook, New York 11794

Received August 15, 1977

The Zweifel syntheses of cis[1] and trans[2] olefins (eq 1) via vinylboranes have found limited applications in organic synthesis in large part because of the limited availability of stable dialkylboranes.[3] A further limitation is the requirement imposed by hydroboration that a hydrogen be cis to boron in the initial borane, thus limiting the applicability of this reaction to cis and trans disubstituted olefins.



(1)

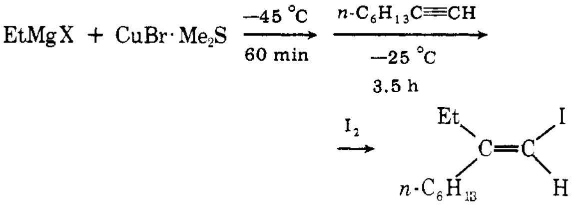
Since the common intermediate in these reactions appears to be a vinyl-substituted borate salt, it appeared reasonable to investigate alternative methods of obtaining the intermediates. In analogy with the lithium alkynyltrialkylborate complexes,[4] formation of a vinyltrialkylborate complex[5] from a vinyllithium and a trialkylborane followed by iodination should lead to olefins. Herein, we report the utility of this sequence in the synthesis of stereospecifically defined trisubstituted olefins[6,7] and the somewhat surprising stereochemistry of this reaction.

Initially, we found that treatment of tri-n-hexylborane with vinyllithium or vinylmagnesium bromide followed by iodination gives moderate yields of 1-octene[8] (eq 2). In order to ascertain the overall stereochemistry and the potential synthetic applications to stereospecifically defined olefins, we undertook a systematic study of this reaction using 2,2-disubstituted vinyl iodides as precursors of stereospecifically defined vinyllithiums.

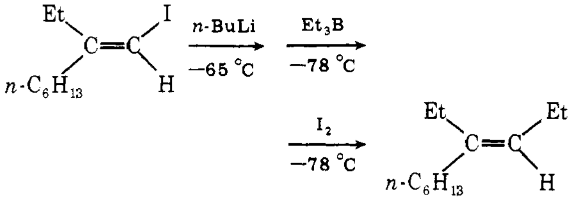
$$(n\text{-}C_6H_{13})_3B + MCH{=}CH_2 \longrightarrow \xrightarrow{I_2} n\text{-}C_6H_{13}CH{=}CH_2 \qquad (2)$$

M = Li 60–65%
M = MgBr 40–50%

Reaction of ethylmagnesium bromide in the presence of $CuBr{\cdot}Me_2S$ with 1-octyne leads upon iodination to a 63% yield of (E)-2-ethyl-1-iodo-1-octene (eq 3).[9] Sequential treatment of the iodide with n-butyllithium, triethylborane, and iodine at low temperature leads to a 75% yield of (E)-4-ethyl-3-decene (eq 4).[10] In view of these encouraging results, a number of the iodides were synthesized by the Normant procedure. From these derivatives the corresponding trisubstituted olefins **1a–j** were prepared. The results are summarized in Table I.

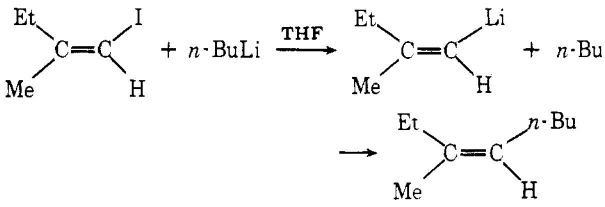


(3)

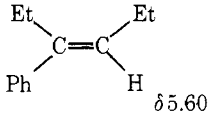


(4)

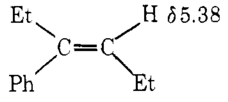
Comparison of the proton-decoupled ^{13}C NMR spectra of Z and E isomers **1g** and **1h** clearly indicates that the two isomers are different. The stereochemistry of the products was determined in two ways. Treatment of (Z)-2-methyl-1-iodo-1-butene with n-butyllithium in THF at −78 °C leads to halogen-metal exchange. Subsequent displacement of the iodide with retention at the vinyl carbon[11] gives (Z)-3-methyl-3-octene (eq 5), identical in all respects with **1i**. Further support for this stereochemical assignment comes from the proton NMR spectrum of **1j**. Comparison of the vinyl proton's adsorption at δ 5.56 in **1j** with those reported for (Z)- and (E)-3-phenyl-3-hexene[12] (**2a,b**) confirms the stereochemical assignment of **1j** as the E isomer.



(5)



2a



2b

The stereochemical purity of the resultant trisubstituted olefins remains a difficult problem. In all cases, by proton-decoupled ^{13}C NMR spectroscopy we appear to have only one isomer. In the case of **1g** and **1h**, each isomer is clearly different, uncontaminated by detectable amounts of the opposite isomer. Furthermore, in the proton NMR of **1j** we cannot detect any of the opposite isomer. Based on careful NMR analysis of **1j**, we have determined this isomer to be at least 97% stereochemically pure. Unfortunately, preliminary attempts to analyze **1g** and **1h** by capillary gas chromatography have failed to separate the isomers.[13] However, the ^{13}C NMR spectra indicate each isomer to be at least 95% stereochemically pure.

Presumably, this reaction involves a mechanism similar to the halogenation reactions of vinylboranes. Initial complexation of the vinyllithium with the trialkylborane gives an "ate" complex (eq 6). Subsequent formation of the iodonium ion

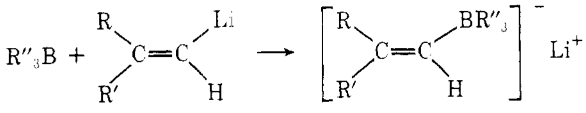
0022-3263/78/1943-1279$01.00/0

Table I. Iodination of Lithium Trialkylvinylborates to Give Trisubstituted Olefins

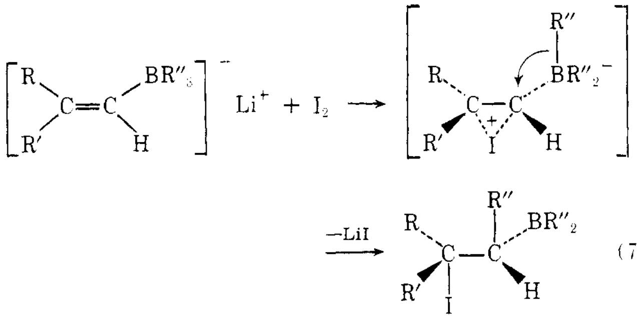
Vinyl iodide[a]			R''_3B,[b,c]				
R	R′	Registry no.	R″ =	Registry no.	Product	Registry no.	Yield,[d,e] %
Ethyl	*n*-Hexyl	64705-58-4	Ethyl	97-94-9	(*E*)-4-Ethyl-3-decene (**1a**)	64705-61-9	75 (61)
			n-Butyl	122-56-5	(*E*)-6-Ethyl-5-dodecene (**1b**)	64705-62-0	82
			Isobutyl	1116-39-8	(*E*)-5-Ethyl-2-methyl-4-undecene (**1c**)	64705-63-1	72
			sec-Butyl	1113-78-6	(*E*)-5-Ethyl-3-methyl-4-undecene (**1d**)	64705-64-2	66
			Cyclohexyl	1088-01-3	(*E*)-1-Cyclohexyl-2-ethyl-1-octene (**1e**)	64705-65-3	76
			Cyclopentyl	23985-40-2	(*E*)-1-Cyclopentyl-2-ethyl-1-octene (**1f**)	62134-95-6	82
n-Propyl	Ethyl	64705-59-5	Ethyl		(*Z*)-4-Ethyl-3-heptene (**1g**)	64705-66-4	80
Ethyl	*n*-Propyl	64705-60-8	Ethyl		(*E*)-4-Ethyl-3-heptene (**1b**)	64705-67-5	87
Ethyl	Methyl	52812-57-4	*n*-Butyl		(*Z*)-3-Methyl-3-octene (**1i**)	34213-99-5	79
Ethyl	Phenyl	64245-21-2	Ethyl		(*E*)-3-Phenyl-3-hexene (**1j**)	39857-50-6	38

[a] 5.0 mmol of the iodide treated with 5.0 mmol of *n*-BuLi at −80 °C in 5.0 mL of ether and stirred for 15 min at −60 °C. [b] 5.0 mmol added dropwise at −80 °C and stirred for 10 min. [c] 5.0 mmol of I_2 added in 3 mL of THF. [d] Analysis by GLPC (isolated yields in parentheses). [e] All compounds exhibited spectral data in accordance with their structure and gave satisfactory elemental composition by high-resolution mass spectrometry and/or elemental analysis.

followed by migration of an alkyl group from boron to carbon with concurrent anti opening of the iodonium ion leads to **3** (eq 7). β-Haloboranes similar to **3** are known to eliminate R_2BX in an anti manner in the presence of excess base.[1] In the absence of base, a thermal syn elimination similar to that previously reported for the cyanobromination of vinylboranes[2] must occur, leading directly to the trisubstituted olefin **1** (eq 8).

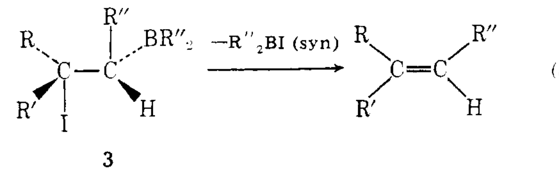


(6)



(7)

3



(8)

3

These results are in sharp contrast to the recent report of Evans and co-workers[5a,b] wherein the reaction of a vinyllithium with an alkylboronate ester followed by iodination leads to net inversion of the carbon originally bearing iodine. Presumably, the change in mechanism is due to the increased electrophilicity of **3** vs. the borinate and boronate intermediates investigated by Zweifel and Evans and to the absence of nucleophiles such as sodium methoxide or sodium hydroxide present in their reactions.

In summary, the present development provides a convenient stereospecific route to trisubstituted olefins in two steps from a terminal acetylene, a Grignard reagent, and a trialkylborane. While alternative procedures are available for the synthesis of olefins from vinyl iodides, the ready availability of trialkylboranes via hydroboration and the known limitation of other reactions to relatively unhindered alkyl derivatives suggest that his procedure may be the method of choice in many cases. To enhance the utility of this sequence, work is in progress to develop a "blocked" borane for use in this reaction[14] and to apply this sequence to the synthesis of naturally occurring compounds.

Experimental Section

Infrared spectra were recorded on a Pye Unicam SP 1000 using a thin film on sodium chloride. ^1H NMR spectra were determined on a Varian EM-360 or a Varian PFT-80 spectrometer using $CDCl_3$ as solvent and Me_4Si as an internal standard. ^{13}C NMR data were obtained on a Varian CFT-20 instrument in $CDCl_3$ solvent and using Me_4Si as an internal standard. Low-resolution mass spectra were recorded on a Hewlett-Packard 5980A mass spectrometer. High-resolution data were obtained on an AEI MS-30 instrument.

GLC analyses were carried out on a Varian 1400 chromatograph equipped with a flame detector and a Hewlett-Packard 3380 integrating recorder using 6 ft × 0.125 in. stainless steel columns filled with 10% loaded packing on AW-DMCS treated 80–100 Chromosorb W. Either Se-30 or Xe-60 liquid phases were used. All yields based on GLC were determined using an internal standard. Preparative gas chromatography was carried out on a Varian 920 instrument equipped with 6 ft × 0.5 in. stainless steel columns filled with 20% loaded packing on AW-DMCS treated 40–60 Chromosorb W. Either Se-30 or Xe-60 liquid phases were employed.

Air-sensitive materials were handled via the standard techniques described in Chapter 9 of ref 3c. All glassware was dried at 150 °C for 4 h, assembled hot, and allowed to cool under a nitrogen purge. The reaction flasks were fitted with a side arm capped with a rubber septum. All reactions were carried out under a static pressure of nitrogen.

Materials. Triethyl- and triisobutylborane were obtained from Callery Chemical Co. and used without further purification. Tri-*n*-butyl-, tricyclopentyl-, and tricyclohexylborane were prepared by hydroboration with borane methylsulfide in THF.[3c] Tri-*sec*-butylborane was obtained from Aldrich Chemical Co. and standardized by oxidation with alkaline hydrogen peroxide. The *n*-alkanes (Phillips) employed as internal standards were used as received. All solvents were distilled from benzophenone ketyl under nitrogen. The vinyl iodides were prepared by the method of Normant using $CuBr\cdot Me_2S$ as the source of copper. The solvent used was a 50:50 mixture of ether and dimethyl sulfide. All other conditions are identical with those reported.[9] The iodides were consistently isolated in ca. 60% yields using this procedure. The lithium reagents were prepared by the method of Normant.[15]

(*E*)-4-Ethyl-3-decene (1a). A dry 250-mL flask equipped with a septum-capped inlet, reflux condenser, and magnetic stirring bar was flushed with nitrogen. The flask was charged with 60 mL of ether and 15.96 g (60 mmol) of (*E*)-2-ethyl-1-iodo-1-octene and cooled to −80 °C. To this mixture 25.64 mL of *n*-butyllithium (2.34 M) was added. The solution was placed in a −60 °C bath ($CHCl_3/CO_2$) for 30 min and cooled to −80 °C. Triethylborane (5.87 g, 60 mmol) was added, and the solution was stirred for 10 min. Finally, 15.24 g (60 mmol) of iodine dissolved in 60 mL of THF was added over a 15-min period. The solution was stirred for 1 h at −80 °C and then allowed to warm to room temperature. The reaction was hydrolyzed with 75 mL of 3 N NaOH under nitrogen. The residual borane was washed three times with 50 mL of 3 N NaOH then oxidized in the presence of 75 mL of 3 N NaOH by the slow dropwise addition of 15 mL of 30% hydrogen peroxide. The organic layer was washed with water and dried, and the solvent was removed by distillation through a 6-in. Vigreux column. Subsequent distillation through a Teflon-coated microspinning band column at 77 mmHg gave 6.43 g of *n*-butyl iodide. The pressure was reduced to 15 mmHg and further distillation gave 6.19 g (61%) of analytically pure (*Z*)-4-ethyl-3-decene; bp 81–83 °C (15 mm); IR 1378, 1465, 2860, 2940, 2970, 3040 cm^{-1}; NMR ($CDCl_3$) δ 0.8–1.6 (m, 17 H), 1.98 (m, 6 H), 5.08 (t, 1 H); high-resolution mass spectrum; *m/e* 168.1881 ($M^{+\cdot}$) ($C_{12}H_{24}$ requires 168.1913).

General Procedure for the Preparation of Olefins 1b–j. A dry 50-mL round-bottom flask equipped with a septum-capped side arm and reflux condenser was connected to an oil bubbler. The system was purged with nitrogen and maintained under nitrogen until after the oxidation. To this flask was added 5 mL of THF and 5.0 mmol of the iodide. The solution was cooled to −80 °C, and 5.5 mmol of *n*-butyllithium was added. The solution was stirred at −60 °C for 30 min and cooled to −80 °C, and 5.0 mmol of the appropriate borane was added. The solution was stirred for 10 min, and then 1.26 g (5 mmol) of I_2 in 5 mL of THF was added. The solution was stirred for 1 h at −80 °C and allowed to warm to room temperature. The residual borane was washed three times with 5 mL of 3 N NaOH then oxidized by addition of 2 mL of 3 N NaOH followed by the dropwise addition of 2 mL of 30% hydrogen peroxide. The organic layer was separated and dried, and the trisubstituted olefin content was measured by GLC vs. an internal standard. Purification by preparative gas chromatography afforded essentially pure (<98%) trisubstituted olefins.

(*E*)-6-Ethyl-5-dodecene (1b). Isolation by preparative gas chromatography gave 0.61 g of pure material; IR 1465, 2840, 2940, 2965 cm^{-1}; NMR ($CDCl_3$) δ 0.6–1.75 (m, 21 H), 2.0 (m, 6 H), 5.10 (t, 1 H); high-resolution mass spectrum, *m/e* 196.2213 ($M^{+\cdot}$) ($C_{14}H_{28}$ requires 196.2190).

(*E*)-5-Ethyl-2-methyl-4-undecene (1c). Isolation by preparative gas chromatography gave 0.53 g of pure material; IR 1370, 1385, 1470, 2960, 2980, 3060 cm^{-1}; NMR ($CDCl_3$) δ 0.70–2.30 (m, 27 H), 5.10 (t, 1 H); high-resolution mass spectrum, *m/e* 196.2202 ($M^{+\cdot}$) ($C_{14}H_{28}$ requires 196.2190).

(*E*)-5-Ethyl-3-methyl-4-undecene (1d). Isolation by preparative gas chromatography gave 0.49 g of pure material; IR 1378, 1465, 2865, 2940, 2975 cm^{-1}; NMR ($CDCl_3$) δ 0.60–1.68 (m, 22 H), 1.8–2.4 (m, 5 H), 4.82 (d, 1 H); high-resolution mass spectrum, *m/e* 196.2179 ($M^{+\cdot}$) ($C_{14}H_{28}$ requires 196.2190).

(*E*)-1-Cyclohexyl-2-ethyl-1-octene (1e). Isolation by preparative gas chromatography gave 0.61 g of pure material; IR 1450, 2860, 2935, 2965 cm^{-1}; NMR ($CDCl_3$) δ 0.5–2.5 (m, 29 H), 4.96 (d, 1 H); high-resolution mass spectrum, *m/e* 222.2327 ($M^{+\cdot}$) ($C_{16}H_{30}$ requires 222.2346).

(*E*)-1-Cyclopentyl-2-ethyl-1-octene (1f). Isolation by preparative gas chromatography gave 0.51 g of pure material; IR 1380, 1460, 2870, 2950; NMR ($CDCl_3$) δ 0.5–3.0 (m, 27 H), 4.98 (d, 1 H); high-resolution mass spectrum, *m/e* 208.2190 ($M^{+\cdot}$) ($C_{15}H_{28}$ requires 208.2214).

(*Z*)-4-Ethyl-3-heptene (1g). Isolation by preparative gas chromatography gave 0.22 g of pure material; IR 855, 875, 900, 1390, 1465, 2880, 2940, 2975, 3020 cm^{-1}; NMR ($CDCl_3$) δ 0.50–1.65 (m, 11 H), 1.70–2.30 (m, 6 H), 5.16 (t, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.98, 14.12, 14.66, 21.03, 21.74, 29.64, 32.37, 125.63, 140.48; high-resolution mass spectrum, *m/e* 126.1422 ($M^{+\cdot}$) (C_9H_{18} requires 126.1408).

(*E*)-4-Ethyl-3-heptene (1h). Isolation by preparative gas chromatography gave 0.178 g of pure material; IR 1390, 1465, 2880; 2940, 2975, 3020 cm^{-1}; NMR ($CDCl_3$) δ 0.5–1.67 (m, 11 H), 1.70–2.40 (m, 6 H), 5.10 (t, 1 H); ^{13}C NMR ($CDCl_3$) δ 13.28, 13.86, 14.75, 20.90, 21.44, 23.11, 38.89, 126.13, 140.49; high-resolution mass spectrum, *m/e* 126.1417 ($M^{+\cdot}$) (C_9H_{18} requires 126.1408).

(*Z*)-3-Methyl-3-octene (1i). Isolation by preparative gas chromatography gave 0.32 g of pure material; IR 1378, 1460, 2860, 2940, 2970; NMR ($CDCl_3$) δ 0.60–1.50 (m, 10 H), 1.68 (d, 3 H), 1.80–2.40 (m, 4 H), 5.17 (t, 1 H); high-resolution mass spectrum, *m/e* 126.1420 ($M^{+\cdot}$) (C_9H_{18} requires 126.1408).

(*E*)-3-Phenyl-3-hexene (1j). Isolation by preparative gas chromatography gave 0.18 g of pure material; IR 700, 765, 865, 1038, 1075, 1380, 1460, 1600, 2880, 2940, 2980, 3040, 3065; NMR (CCl_4) δ 0.7–1.3 (m, 6 H), 2.0–2.7 (m, 4 H), 5.57 (t, 1 H), 7.23 (s, 5 H); high-resolution mass spectrum, *m/e* 160.1244 ($M^{+\cdot}$) ($C_{12}H_{16}$ requires 160.1251).

Acknowledgment. We wish to thank Professor Paul Helquist for many fruitful discussions concerning this project. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation, and to the Research Foundation of the State University of New York for support of this work.

References and Notes

(1) The base-catalyzed iodination of vinylboranes has been proposed to proceed via a trans-addition, trans-elimination sequence: G. Zweifel, H. Arzoumanian, and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 3652 (1967).

(2) The treatment of vinylboranes with cyanogen bromide has been proposed to proceed via a trans-addition, cis-elimination sequence: G. Zweifel, R. P. Fisher, J. T. Snow, and C. C. Whitney, *J. Am. Chem. Soc.*, **94**, 6560 (1972).

(3) H. C. Brown, "Hydroboration", W. A. Benjamin, New York, N.Y., 1962; (b) "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972; (c) H. C. Brown, G. W. Kramer, A. B. Levy, and M. M. Midland, "Organic Syntheses via Boranes", Wiley-Interscience, New York, N.Y., 1975; (d) T. Onak, "Organoborane Chemistry", Academic Press, New York, N.Y., 1975; (e) G. M. L. Gragg, "Organoboranes in Organic Synthesis", Marcell Dekker, New York, N.Y., 1973.

(4) For recent examples involving the use of alkynltrialkylborate salts in organic synthesis, see: (a) H. C. Brown, A. B. Levy, and M. M. Midland, *J. Am. Chem. Soc.*, **97**, 5017 (1975); (b) J. Hooz and R. Mortimer, *Tetrahedron Lett.*, 805 (1976); (c) A. Pelter, C. R. Harrison, and D. Kirkpatrick, *J. Chem. Soc., Chem. Commun.*, 544 (1973); (d) N. Miyaura, T. Yoshinari, M. Itoh, and A. Suzuki, *Tetrahedron Lett.*, 2961 (1974); (e) M. M. Midland, J. A. Sinclair, and H. C. Brown, *J. Org. Chem.*, **39**, 731 (1974); (f) K. Utimoto, F. Furubayashi, and H. Nozaki, *Chem. Lett.*, 397 (1975); (g) A. Pelter, C. Subrahmanyan, R. J. Laub, K. J. Gould, and C. R. Harrison, *Tetrahedron Lett.*, 1633 (1975); (h) A. Pelter, K. J. Gould and C. R. Harrison, *ibid.*, 3327 (1975); (i) M. Naruse, T. Tomita, K. Utimoto, and H. Nozaki, *Tetrahedron*, **30**, 835 (1974); (j) M. Naruse, K. Utimoto, and H. Nozaki, *Tetrahedron Lett.*, 2741 (1973); (k) A. Suzuki, N. Miyaura, S. Abiko, M. Itoh, H. C. Brown, J. A. Sinclair, and M. M. Midland, *J. Am. Chem. Soc.*, **95**, 3080 (1973).

(5) For recent examples of reactions involving trialkylvinylborate salts and related derivatives, see: (a) D. A. Evans, T.C. Crawford, R. C. Thomas, and J. A. Walker, *J. Org. Chem.*, **41**, 3947 (1976); (b) D. A. Evans, R. C. Thomas, and J. A. Walker, *Tetrahedron Lett.*, 1427 (1976); (c) H. C. Brown, A. B. Levy, and M. M. Midland, *J. Am. Chem. Soc.*, **97**, 5017 (1975); (d) N. Miyaura, H. Tagami, M. Itoh, and A. Suzuki, *Chem. Lett.*, 1411 (1974); (e) K. Utimoto, K. Uchida, and H. Nozaki, *Tetrahedron Lett.*, 1493 (1974);(f) 4527 (1973).

(6) For reviews of trisubstituted olefin syntheses, see: (a) J. Reucroft and P. G. Summes, *Q. Rev., Chem. Soc.*, **25**, 135 (1971); (b) D. J. Faulkner, *Synthesis*, 175 (1971). For more recent references, see references cited in A. Marfat, R. R. McGuirk, R. Kramer, and P. Helquist, *J. Am. Chem. Soc.*, **99**, 253 (1977).

(7) Biologically active compounds of this class include insect pheromones and insect juvenile hormone.

(8) For a recent report on the iodination of lithium trialkylisopropenylborate complexes, see ref 5d.

(9) The addition of the organocopper reagent to a terminal acetylene is highly dependent on the purity of the copper salt used. We find $CuBr \cdot Me_2S$ to be the method of choice using a 1:1 mixture of dimethyl sulfide–diethyl ether as solvent. All other conditions are identical to those of Normant and coworkers: J. F. Normant, G. Cahiez, C. Chuit, and J. Villieras, *J. Organomet. Chem.*, **77**, 269, 281 (1974).

(10) The only other product observed is the vinyl iodide. Protonolysis of the intermediate vinyllithium indicates the iodide is completely consumed. Therefore, the vinyl iodide appears to be arising via the direct iodination of the "ate" complex. We have not yet determined the stereochemistry of the recovered vinyl iodide. The material balance is on the order of 90% in all cases.

(11) J. Millon, R. Lorne, and G. Linstrumelle, *Synthesis*, 434 (1975).

(12) (a) J. Duboudin and B. Jousseaume, *J. Organomet. Chem.*, **44**, C1 (1972); (b) J. Duboudin and B. Jousseaume, *C. R. Hebd. Seances Acad. Sci., Ser. C*, **276**, 1421 (1973).

(13) Preliminary attempts involved the use of 50 ft SCOT columns using Apiezon L or OV-1 as liquid phase and 150 ft wall-coated capillary columns using squalane or OV-101 as the liquid phase.

(14) In accordance with Suzuki,[5d] our preliminary results suggest that *B*-alkyl-9BBN's undergo this reaction in good yields with the same overall stereochemistry described herein.

(15) G. Cahiez, D. Bernard, and J. F. Normant, *Synthesis*, 245 (1976).