7 Hz, Z), 5.78 (d, J = 13 Hz, E), 5.16 (d, J = 7 Hz, Z), 3.94 (t, Z), 3.83 (t, E), 1.7 (m), 1.5 (m), 0.97 (t). Anal. Calcd for $C_{12}H_{15}ClO$: C, 68.40; H, 7.18. Found: C, 68.5; H, 7.12.

(E)-/(Z)-1-(2-Butoxyethenyl)-4-acetoxybenzene (16): colorless oil (40%, $E/Z \approx 2/1$); eluent, pentane/methylene chloride, 1/1; ^1H NMR δ 8.1-7.0 (m, aryl), 6.20 (d, J = 7 Hz, Z), 5.82 (d, J = 13 Hz, E; the other component of the vinylic resonance was obscured by the aryl multiplet), 5.19 (d, J = 7 Hz, Z), 3.92 (t, Z), 3.83 (t, E), 2.28 (s, CH_3COO), 1.7 (m), 1.5 (m), 0.98 (t). Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.4; H, 7.73.

(E)-/(Z)-1-(2-Butoxyethenyl)-3-chlorobenzene (17): colorless oil (43%, $E/Z \approx 2/1$); eluent, pentane; ^1H NMR δ 7.7-7.1 (m, aryl), 7.03 (d, J = 13 Hz, E), 6.25 (d, J = 7 Hz, Z), 5.78 (d, J = 13 Hz, E), 5.17 (d, J = 7 Hz, Z), 3.96 (t, Z), 3.85 (t, E), 1.7 (m), 1.5 (m), 1.0 (t). Anal. Calcd for $C_{12}H_{15}ClO$: C, 68.40; H, 7.18. Found: C, 68.4; H, 7.13.

(E)-/(Z)-1-(2-Butoxyethenyl)-3-nitrobenzene (18): colorless oil (44%, $E/Z \approx 2/1$); eluent, pentane/chloroform, 7/2; ^1H NMR δ 8.5-7.3 (m, aryl), 7.08 (d, J = 13 Hz, E), 6.31 (d, J = 7 Hz, Z), 5.80 (d, J = 13 Hz, E), 5.21 (d, J = 7 Hz, Z), 3.96 (t, Z), 3.83 (t, E), 1.7 (m), 1.4 (m), 0.95 (t). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83. Found: C, 65.3; H, 6.75.

Acknowledgment. We thank the Swedish Natural Science Research Council for financial support.

Registry No. **1a**, 98-88-4; **1b**, 591-50-4; **2**, 111-34-2; (E)-**3**, 36586-17-1; (Z)-**3**, 36586-16-0; **4**, 56750-84-6; **5a**, 122-04-3; **5b**, 586-78-7; **5c**, 636-98-6; (E)-**6**, 97826-86-3; (Z)-**6**, 97826-85-2; **7**, 109125-23-7; **8**, 696-62-8; **9**, 100-06-1; **10**, 108-05-4; **11**, 100-42-5; **12**, 103-30-0; **13**, 940-14-7; (E)-**14**, 111615-85-1; (Z)-**14**, 111615-86-2; (E)-**15**, 111615-87-3; (Z)-**15**, 111615-88-4; (E)-**16**, 111615-89-5; (Z)-**16**, 111615-90-8; (E)-**17**, 111615-91-9; (Z)-**17**, 111615-92-0; (E)-**18**, 111615-93-1; (Z)-**18**, 111615-94-2; p-BrC_6H_4COCl, 586-75-4; p-ClC_6H_4COCl, 122-01-0; p-$AcOC_6H_4COCl$, 27914-73-4; m-ClC_6H_4COCl, 618-46-2; m-$NO_2C_6H_4COCl$, 121-90-4; o-$AcOC_6H_4COCl$, 5538-51-2; o-$NO_2C_6H_4COCl$, 610-14-0; CH_2=CHOMe, 107-25-5; (E)-BuOCH=CHCOPh, 111615-95-3.

Vinylic Organoboranes. 9. A General Stereospecific Synthesis of (Z)- and (E)-Disubstituted Alkenes via Organoboranes[1]

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A general and stereospecific synthesis of (Z)-disubstituted alkenes using mono- and dihaloboranes is presented. The hydridation of dialkylhaloboranes in the presence of 1-alkynes provides the corresponding dialkylvinylboranes (1), representing the first general synthesis of such derivatives. Treatment with iodine in the presence of sodium methoxide induces the migration of one of the alkyl groups from boron to the adjacent carbon, followed by a rapid deiodoboronation to afford (Z)-disubstituted alkenes (2) in high yields. Similarly, the hydroboration of 1-alkynes with alkylbromoboranes ($R^1BHBr\cdot SMe_2$, 4) followed by iodination in the presence of sodium methoxide in methanol affords (Z)-disubstituted alkenes (2) in good yields. Both procedures constitute a general one-pot synthesis of (Z)-disubstituted alkenes from an alkene and 1-alkyne. A simple synthesis of Muscalure (7), the sex pheromone of the housefly (*Musca domestica*), is achieved in good yields. An alternative general stereospecific synthesis of (Z)- and (E)-disubstituted alkenes based on alkenylboronic esters is also described.

The stereospecific synthesis of insect sex attractants is one of the most timely problems today in organic synthesis. Both (Z)- and (E)-disubstituted alkenes with hydroxy or acetate functionalities constitute a major segment of these insect pheromones.[3] Since the presence of minor isomers inhibits the biological activity in most cases,[4] the stereospecific synthesis of the most active isomer is of paramount importance, both scientifically and economically. Organoboranes play an important role in bringing latitude to organic synthesis.[5] The applications of organoboranes to carbon-carbon bond formation has been well documented, and a wide variety of synthetic methods for carbon skeletal assemblage is becoming available.[6] Now we report the stereospecific synthesis of (Z)-disubstituted alkenes using mono- and dihaloborane reagents and its application to the synthesis of Muscalure (7), the sex pheromone of the housefly (*Musca domestica*). We also herein report a general stereospecific synthesis of (Z)- and (E)-disubstituted alkenes utilizing alkenylboronic esters.

Results and Discussion

An elegant approach to the synthesis of both (Z)-[7] and (E)-[8]1,2-disubstituted olefins has been reported by Zweifel (eq 1 and 2).

However, the utility of this elegant Zweifel synthesis depends on the availability of dialkylboranes. Direct hydroboration leads cleanly to the formation of dialkylboranes only in the case of relatively hindered alkenes. More generally, hydroboration fails to stop cleanly at the

(1) Preliminary results were reported In (a) Kulkarni, S. U.; Basavaiah, D.; Brown, H. C. *J. Organomet. Chem.* **1982**, *225*, C1. (b) Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 3806.

(2) (a) Postdoctoral research associate on Grant GM-10937 from the National Institutes of Health. (b) Postdoctoral research associate, Purdue University, 1978-1982. (c) Postdoctoral research associate on a National Science Foundation grant, CHE 8414171. (d) Postdoctoral research associate on a grant, GM 10937-23, from the National Institutes of Health.

(3) Mori, K. *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley-Interscience: New York, 1981; Vol. 4, pp 1-183.

(4) (a) Jacobson, M. *Science (Washington, D.C.)* **1969**, *163*, 190. (b) Roelofs, W. L.; Tette, J. P. *Nature (London)* **1970**, *226*, 1172.

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(6) (a) Brown, H. C. *Pure Appl. Chem.* **1976**, *47*, 49. (b) Cragg, G. M. L. *Organoboranes in Organic Synthesis*; Marcel Dekker: New York, 1973.

(7) Zweifel, G.; Arzoumanian, H.; Whitney, C. C. *J. Am. Chem. Soc.* **1967**, *89*, 3652.

(8) (a) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 5086. (b) Zweifel, G.; Fisher, R. P.; Snow, J. T.; Whitney, C. C. *Ibid.* **1971**, *93*, 6309.

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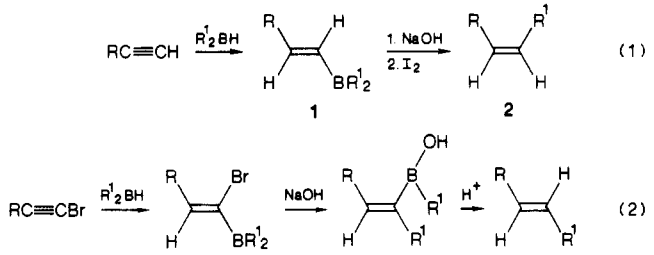
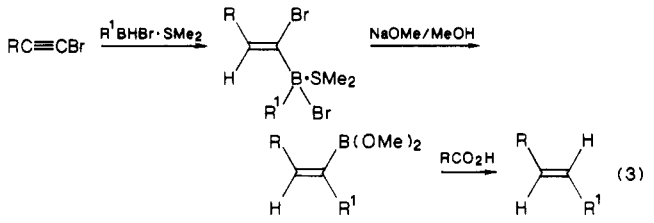


(1)

(2)

R^1_2BH stage.[5] Consequently, these procedures have been severely handicapped by the limited availability of dialkylboranes. Another disadvantage of this procedure is that one of the two alkyl groups (R^1) from dialkylborane is not utilized. Such a loss is undesirable when the alkyl group is derived from an expensive or difficultly synthesized alkene. Recently, we have surmounted these difficulties by utilizing haloboranes,[1,9] particularly monoalkylbromoboranes,[1b,9b] as hydroborating agents in the stereospecific synthesis of (*E*)-disubstituted alkenes (eq 3).



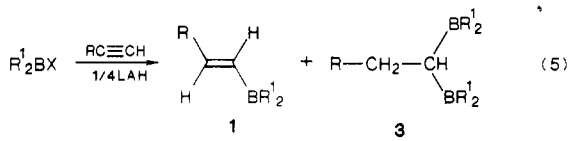
(3)

In this paper, we report solutions to the problems involved in Zweifel's (*Z*)-olefin synthesis, thus providing a more practical synthesis for (*Z*)-disubstituted alkenes.

Synthesis of (*Z*)-Disubstituted Alkenes via Dialkylboranes. The first problem has been circumvented by the general method, developed recently in our laboratory, for the preparation of a wide variety of dialkylboranes via hydridation of the corresponding dialkylhaloboranes.[10] It occurred to us that the hydridation of dialkylhaloboranes in the presence of 1-alkynes, followed by iodination in the presence of a base, might provide the desired (*Z*)-alkene **2** (eq 4), where R is general and X = Cl, Br. Consequently, we examined this reaction sequence as a potential route to the synthesis of (*Z*)-alkenes.

$$R^1_2BX \xrightarrow[{}^1/_4LAH]{RC{\equiv}CH} 1 \xrightarrow[I_2]{NaOMe/MeOH} 2 \qquad (4)$$

Hydroboration of 1-Alkynes with Dialkylboranes. Unfortunately, we encountered two difficulties in this reaction sequence. First, the monohydroboration of 1-alkynes with relatively unhindered dialkylboranes is accompanied by competing dihydroboration resulting in the concurrent formation of 2%–25% 1,1-dibora derivatives (eq 5).[11] We studied the hydroboration of 1-octyne with



(5)

a variety of dialkylboranes of varying steric requirements and established that relatively less hindered dialkylboranes produce considerable amounts of 1,1-dibora derivatives, whereas sterically more demanding reagents form insignificant amounts of dihydroboration.[11] The amount of dihydroboration can be noticeably decreased by carrying out the hydroboration of 1-alkynes with dialkylboranes at lower temperatures, generally at −25 °C.[11] Unfortunately, at this temperature, the rate of hydroboration is inconveniently slow. Alternatively, the use of excess alkyne, generally 100%, reduces the amount of dihydroboration to an insignificant factor. If desired, the excess alkyne can be recovered by distillation from the hydroboration product. In this way, the problem of dihydroboration has been overcome.

Table I. Reaction of Dialkyl-1-octenylboranes[a] with Iodine in the Presence of Base[b]

R^1 in R^1_2BX	1-octyne,[c] mmol	iodination temp, °C	R^1I,[d] %
3-hexyl	10	−5	2
	20	−5	0
	10	−25	0
	10	−78	0
2-butyl	10	−5	5
	20	−5	0
	10	−25	0
	10	−78	0
cyclopentyl	10	−5	9
	20	−5	0
	10	−25	tr
	10	−78	0
n-hexyl	20	−5	35
	20	−25	16
	20	−50	1
	20	−78	tr

[a] Prepared by the addition of $LiAlH_4$ (2.5 mmol) to R^1_2BX (10 mmol) in the presence of appropriate quantities of 1-octyne at 0 °C, in THF, and then allowing to react for 2 h at 0 °C. [b] Aqueous NaOH for the reaction at −5 °C, and NaOMe in MeOH for the reactions at low temperatures. [c] When a stoichiometric amount (10 mmol) of 1-octyne was used, 2%–8% of 1,1-dibora derivatives were formed. In the case of di-*n*-hexylchloroborane, use of 10 mmol of 1-octyne afforded only ~50% of the alkenyldialkylborane; therefore, 100% excess of octyne was utilized. [d] Determined by GC.

Iodination of Dialkylvinylboranes. Second, the iodination of such dialkylvinylboranes containing alkyl groups of low steric requirements and appreciable amounts of 1,1-dibora derivatives as side products produce considerable amounts of alkyl iodides along with the desired (*Z*)-alkenes (eq 6). The formation of such alkyl iodides

$$1 + 3 \xrightarrow[I_2]{NaOMe/NaOH} 2 + R^1I \qquad (6)$$

presumably arises from a reaction similar to that involved in converting trialkylboranes into the corresponding iodides.[12,13] The formation of such derivatives is undesirable. They both decrease the yield and the purity of (*Z*)-alkene.

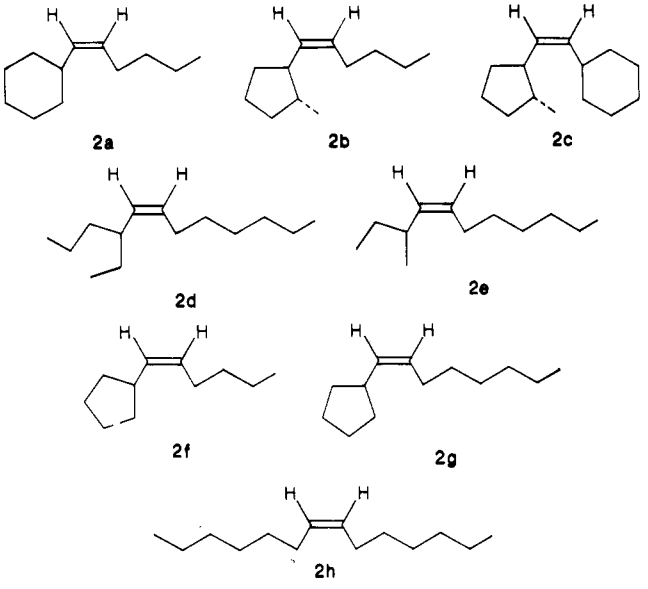
The iodination of these various dialkylvinylboranes (**1**) was examined. The iodination of **1** (R^1 = cyclopentyl) containing 1,1-dibora compound (8%) at −5 °C produced ≈9% of cyclopentyl iodide (Table I), while the iodination of the same vinylborane free from dibora compound, obtained with 100% excess 1-alkyne, at −5 °C reveals the absence of any significant amount of cyclopentyl iodide. These results indicate that the formation of cyclopentyl iodide is due to 1,1-dibora compound. However, in the case of di-*n*-hexylvinylborane, prepared with 100% excess alkyne (free from 1,1-dibora compound), iodination at −5 °C produced ≈35% *n*-hexyl iodide. Obviously, in this case,

(9) (a) Brown, H. C.; Basavaiah, D. *J. Org. Chem.* **1982**, *47*, 754. (b) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U. *Ibid.* **1982**, *47*, 3808.
(10) Brown, H. C.; Kulkarni, S. U. *J. Organomet. Chem.* **1981**, *218*, 299.
(11) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U. *J. Organomet. Chem.* **1982**, *225*, 63.
(12) Brown, H. C.; Rathke, M. W.; Rogić, M. M. *J. Am. Chem. Soc.* **1968**, *90*, 5038.
(13) De Lue, N. R.; Brown, H. C. *Synthesis* **1976**, 114.

the attack of iodine on unhindered primary alkyl groups competes with the desired migration of the R^1 group to the vinylic carbon. We also examined the effect of temperature on the formation of alkyl iodides. The iodination of **1** (R^1 = secondary alkyl group) at −25 °C with sodium methoxide as a base produced (*Z*)-alkenes free from alkyl iodides (even when 2%–8% 1,1-dibora compound was present along with **1**). However, di-*n*-hexylvinylborane (**1**, R^1 = *n*-C_6H_{13}) free from the corresponding 1,1-dibora derivative produced 16% *n*-hexyl iodide. Iodination at −50 °C provided the desired (*Z*)-alkene almost free from *n*-hexyl iodide (only 1%, Table II).

Therefore, it appears that the iodination of **1** derived from unhindered primary alkyl groups under the reaction conditions (−5 °C) results in the formation of a considerable amount of primary alkyl iodide. This competing reaction can be totally suppressed at −50 °C. This observation is in agreement with the previous reports that in the iodination of trialkylboranes the formation of primary alkyl iodides is much more facile than the formation of secondary alkyl iodides.[12,13] In this way, we established that the second difficulty, the concurrent formation of alkyl iodides, can be circumvented by carrying out the treatment of dialkylvinylboranes (**1**) with sodium methoxide and iodine at lower temperatures (−25 °C when R is secondary alkyl, −50 °C when R^1 is primary alkyl). In fact, a temperature of −78 °C proved to be generally satisfactory for all dialkylvinylboranes to form the desired (*Z*)-alkenes with negligible formation of alkyl iodides (Table I).

Thus, both of these difficulties were overcome and a variety of (*Z*)-alkenes (**2a–h**) were prepared by this procedure (Table II).



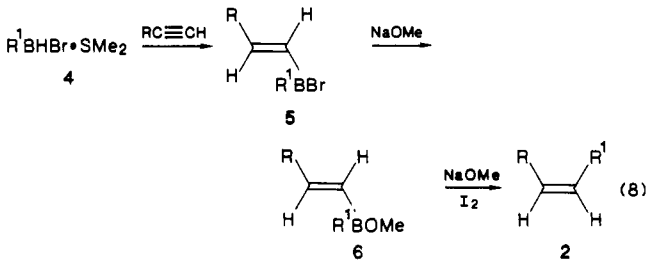
These examples clearly demonstrate the applicability of this procedure to the utilization of relatively hindered alkenes such as 1-methyl-1-cyclopentene, as in the synthesis of (*Z*)-1-cyclohexyl-2-(*trans*-2-methylcyclopentyl)-ethylene (**2c**), alkenes with intermediate steric requirements such as cyclopentene, as in the synthesis of (*Z*)-1-cyclopentyl-1-octene (2g), and alkenes of low steric requirements such as 1-hexene, as in the case of (*Z*)-7-tetradecene (**2h**). Thus, this modification greatly extends the scope and the applicability of Zweifel's original synthesis of (*Z*)-disubstituted alkenes.

However, this procedure suffers from two significant disadvantages: (1) Monohydroboration of 1-alkynes with dialkylboranes, particularly when the alkyl group is primary, is often complicated by the competing dihydroboration. This can be avoided by using a large excess of 1-alkyne. But such use of a large excess of alkyne is not practical in cases where the alkyne has a high boiling point. (2) One of the two alkyl groups on boron is lost, thus rendering this procedure undesirable when the alkyl group is derived from an expensive or difficultly synthesized alkene. Therefore, our attention was next drawn to overcoming these difficulties.

Synthesis of (*Z*)-Disubstituted Alkenes via Alkylbromoboranes. Recently, we reported the preparation of a new class of partially alkylated bromoborane reagents, alkylbromoborane ($R^1BHBr{\cdot}SMe_2$, **4**) via controlled hydridation of the corresponding alkyldibromoborane ($R^1BBr_2{\cdot}SMe_2$) for the synthesis of mixed dialkylbromoboranes and trialkylboranes (eq 7).[14]

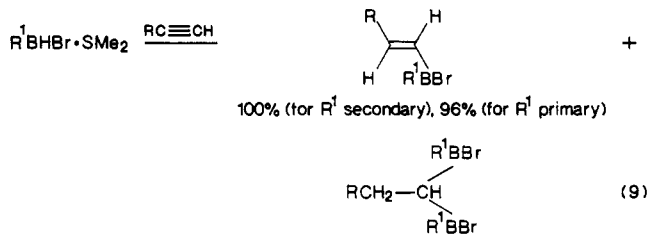
$$R^1BBr_2{\cdot}SMe_2 \xrightarrow[Et_2O]{^1/_4LAH} \underset{\mathbf{4}}{R^1BHBr{\cdot}SMe_2} \xrightarrow{\text{alkene}} R^1R^2BBr \xrightarrow{MeOH} R^1R^2BOMe \xrightarrow[\text{alkene}]{^1/_3LAH} R^1R^2R^3B \quad (7)$$

It appeared to us that the treatment of the vinylborane **5**, obtained via hydroboration of 1-alkynes with alkylbromoborane **4** with iodine in the presence of base, might provide the desired (*Z*)-disubstituted alkenes (**2**) (eq 8).



Consequently, we examined this reaction sequence as a potential route for the synthesis of (*Z*)-disubstituted alkenes.

Monohydroboration of 1-alkynes with a variety of alkylbromoboranes ($R^1BHBr{\cdot}SMe_2$, **4**) was first examined. It was established that there was no significant dihydroboration for a secondary alkyl group and only 2% dihydroboration for a primary group (eq 9).[15]



Thus, this new hydroborating agent, $R^1BHBr{\cdot}SMe_2$ (**4**), solves the problem of dihydroboration that was involved in the case of dialkylboranes (R^1_2BH, eq 5), providing a clean monohydroborated vinylborane (**5**).

However, we encountered difficulty in the iodination reaction. Iodination of the vinylborane **6** produced considerable amounts of vinyl iodides (≈40%) along with the

(14) Kulkarni, S. U.; Basavaiah, D.; Zaidlewicz, M.; Brown, H. C. *Organometallics* **1982**, *1*, 212.

(15) In the present experiment, about 5%–10% of 1-octyne remained unreacted corresponding to the amount of ether-cleaved product; $R^1B(OEt)_2$ formed during the hydridation step (estimated by ^{11}B NMR of $R^1BHBr{\cdot}SMe_2$, **4**). The amount of dihydroboration was estimated by the amount of 1-octanol formed after the oxidation. For experimental details, see ref 11.

Table II. Synthesis of (*Z*)-Disubstituted Alkenes from Dialkylhaloboranes and Terminal Alkynes[a]

alkene for R^1_2BX	X	alkyne, mmol	iodination temp, °C	product[b,c]	yield,[d] %	bp, °C (mm)	n^{20}_D
cyclohexene	Cl	1-hexyne (50)	−5	**2a**	78	52–54(1.2) [lit.[7a] 44–45(1.0)]	1.4590 [lit.[7a] 1.4586]
1-methylcyclopentene	Cl	1-hexyne (50)	−25	**2b**	69	70–71(3.0)	1.4544
	Br	1-cyclohexylethyne (50)	−25	**2c**[e]	67	58–60(0.6)	1.4803
cis-3-hexene	Cl	1-octyne (50)	−25	**2d**	70	78–79(1.8)	1.4384
cis-2-butene	Br	1-octyne (50)	−25	**2e**	64	58–59(1.5)	1.4305
	Br	1-octyne (100)	−5	**2e**	72	58–59(1.5)	1.4310
cyclopentene	Cl	1-hexyne (50)	−5	**2f**	67[f]	56–57(2.0)	1.4549
	Cl	1-hexyne (100)	−5	**2f**	76	55–57(2.0)	1.4555
	Br	1-octyne (50)	−78	**2g**	62	80–81(1.6)	1.4580
1-hexene	Cl	1-octyne (100)	−78	**2h**[g]	66	75–76(0.8)	1.4399

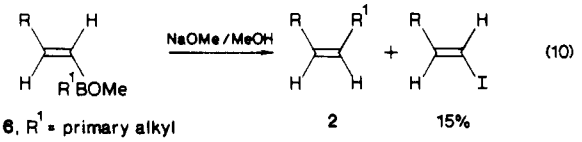
[a] All reactions were carried out with 50 mmol of R_2BX. [b] Structures were confirmed by ^1H and ^{13}C NMR spectral analyses; chemical purities of all products were >97% by GC analysis on a 6-ft SE-30 column (impurities are the dienes corresponding to the alkynes, <3%). [c] Isomeric purities are ~99% unless mentioned otherwise (determined by ^{13}C NMR analysis[26]). [d] Yields of pure products isolated by distillation, based on R^1_2BX. [e] Contains 2–3% of trans isomer (by ^{13}C NMR[26]). [f] The crude material contained 9% cyclopentyl iodide, removed by treatment with ethanolic KOH prior to distillation. [g] Distilled R^1_2BCl was utilized in order to minimize the formation of diene, which presumably arises from $RBCl_2$.

Table III. Synthesis of (*Z*)-Disubstituted Alkenes from Alkyldibromoboranes and 1-Alkynes[a]

alkene for $R^1BBr_2{\cdot}SMe_2$	1-alkyne	product[b,c]	yield,[d] %	bp, °C (mm)	n^{20}_D	amounts of vinyl iodide formation,[e] %
cyclohexene	1-pentyne	**2i**	74	77–79 (12)	1.4612	3
cis-3-hexene	1-pentyne	**2j**	69	70–71 (12)	1.4319	6
cyclopentene	1-pentyne	**2k**	62	66–68 (12)	1.4565	10
2-methyl-1-pentene	1-pentyne	**2l**	67[f]	71–72 (12)	1.4321	14
1-octene	1-pentyne	**2m**	61	82–83 (2.5)	1.4357	15
1-hexene	1-octyne	**2h**	68[f]	76–77 (0.8)	1.4392	15
1-tridecene	1-decyne	**7**	59	140–142 (0.01) [lit.[18] 157–158 (0.1)]	1.4559 [lit.[18] n^{26}_D 1.4517]	16

[a] All reactions were carried out in 30-mmol scale (except **2l** and **2h**). [b] Chemical purities of all distilled compounds are >98% by GC analysis on a 6-ft SE-30 column. [c] Isomeric purities are >99% by ^{13}C NMR analysis.[26] [d] Yields of pure products isolated by distillation (except **2l** and **2h**). [e] GC yields of vinyl iodides determined by separate experiments with suitable internal standard. [f] GC yields of the alkenes.

desired (*Z*)-alkenes. The formation of such vinyl iodides presumably was due to a reaction similar to that involved in the preparation of vinyl iodides from the corresponding vinylboronic acids.[16] However, the best yields of the desired (*Z*)-alkene were realized when the iodination of the vinylborane **6** was carried out in methanol (as a solvent) with sodium methoxide as a base at room temperature, thus reducing to 15% the formation of the undesired vinyl iodides when the alkyl group on boron is primary (eq 10).

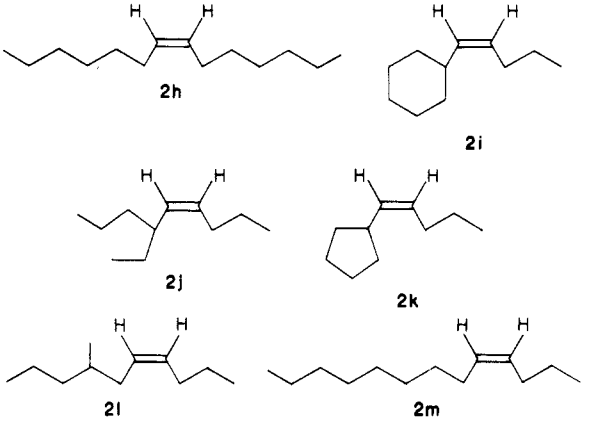


(10)

Similar results were realized in the related prostaglandin synthesis.[17]

We examined the effect of alkyl groups of varying steric bulk on the formation of vinyl iodides and established that the formation of vinyl iodides varies inversely with the steric bulk of the alkyl group on boron, with sterically more hindered alkyl groups leading to the decreased amounts of the vinyl iodide. Thus, in the case of the relatively hindered cyclohexyl group, there is only 3% vinyl iodide formation, whereas the less hindered *n*-hexyl group provides 15% vinyl iodide formation (Table III). We also studied the effect of temperature on the formation of vinyl iodides. We observed that lower reaction temperatures caused only minor changes in the formation of vinyl iodides. However, at −78 °C, the formation of vinyl iodide was diminished to 6–7%, but the reaction becomes very sluggish, requiring 18 h to achieve 70% completion.

A variety of (*Z*)-disubstituted alkenes (**2h–m**) were prepared by this procedure (Table III).



We have successfully applied this procedure for the synthesis of Muscalure (**7**),[18] the sex pheromone of the housefly (*M. domestica*) from tridecene and 1-decyne (eq 11).

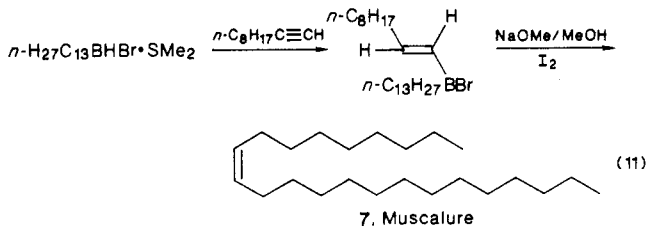
This new hydroborating agent, $R^1BHBr{\cdot}SMe_2$ (**4**), solves both significant problems that are associated with the use of dialkylboranes (R^1_2BH, eq 5), thus providing a general one-pot, more practical, and stereospecific synthesis of (*Z*)-disubstituted alkenes.

However, it should be pointed out that in these procedures the alkyl group on the boron has been obtained via

(16) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786.

(17) (a) Evans, D. A.; Thomas, R. C.; Walker, J. A. *Tetrahedron Lett.* **1976**, 1427. (b) Evans, D. A.; Crawford, T. C.; Thomas, R. C.; Walker, J. A. *J. Org. Chem.* **1976**, *41*, 3947.

(18) Carlson, D. A.; Mayer, M. S.; Silhacek, D. L.; James, J. D.; Beroza, M.; Bierl, B. A. *Science (Washington, D.C.)* **1971**, *174*, 76.

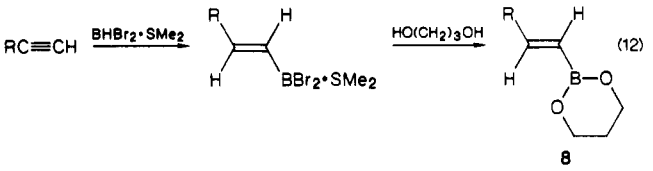


(11)

7, Muscalure

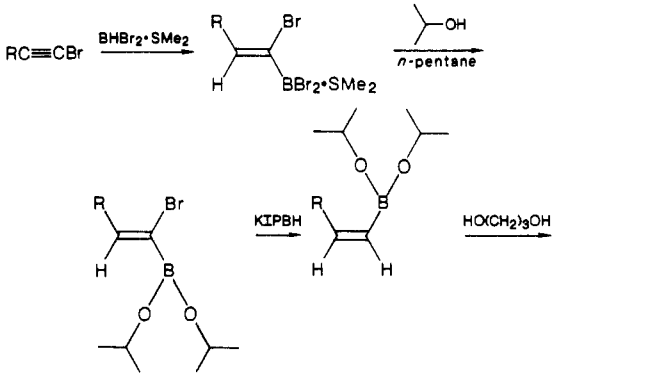
hydroboration of the corresponding olefin with dibromoborane–dimethyl sulfide. Groups that are not available via hydroboration cannot be introduced by this procedure. Consequently, we undertook to develop a more general stereospecific synthesis of (*Z*)- and (*E*)-disubstituted olefins via alkenylboronic esters that permits the introduction of an organyl group not available via hydroboration.

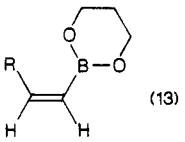
Synthesis of (*Z*)- and (*E*)-Disubstituted Olefins via Alkenylboronic Esters. Recently we have developed simple, convenient procedures to prepare both (*E*)- and (*Z*)-2-(1-alkenyl)-1,3,2-dioxaborinane derivatives[19,20] viz. **8** and **9** (eq 12 and 13).



(12)

8

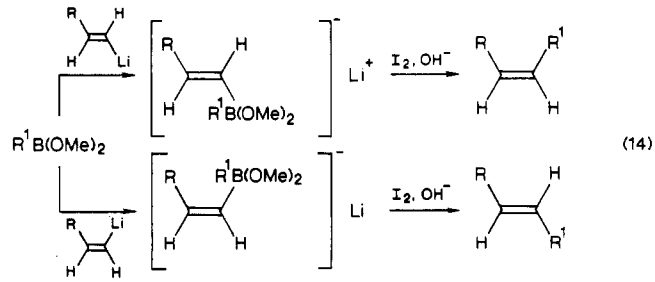




(13)

9

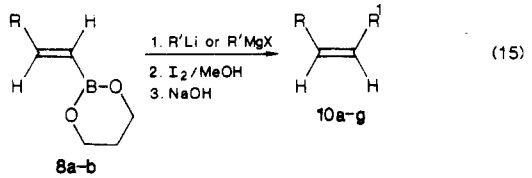
Evans et al.[17b] have reported the synthesis of (*Z*)- and (*E*)-olefins based on organoboranes (eq 14) and applied the strategy for the construction of prostanoid olefin models.



(14)

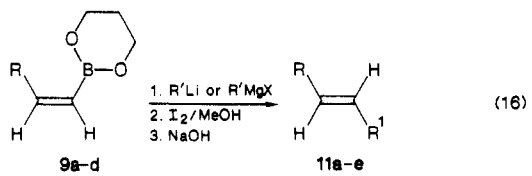
In this method, the R group has been introduced via hydroboration, and the procedure often requires prior stereoselective synthesis of alkenyllithium reagents.[21]

Matteson et al.[22] have obtained the boron intermediate **8** by a different route, and the trans geometry of the isomer was proved by B-butylation with *n*-butyllithium followed by rearrangement with iodine and base to form (*Z*)-disubstituted alkenes. However, no systematic investigation of this reaction sequence seems to have been undertaken. Consequently, we undertook a systematic study to synthesize (*Z*)- and (*E*)-disubstituted olefins via **8** and **9** utilizing organolithium or Grignard reagents (eq 15 and 16). It should be noted that it is possible to introduce



(15)

8a–b **10a–g**



(16)

9a–d **11a–e**

organyl groups not available via hydroboration by the present procedure, thus generalizing the synthesis of (*Z*)- and (*E*)-disubstituted alkenes[23] via organoboranes.

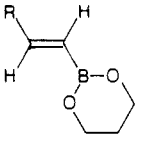
The boron intermediate viz. **8** and **9** have been prepared as described previously.[6,7] We have chosen **8** and **9** for the present study because of the stability of the cyclic ester group.[23c] The intermediate **8** was reacted with an alkyllithium or a Grignard reagent in diethyl ether at −78 °C. In a typical experiment, the boron intermediate **8a** was treated with *n*-butyllithium at −78 °C in diethyl ether, stirred for 0.5 h at −78 °C, and then brought to 0 °C. After removal of the solvents, the residue was dissolved in methanol at 0 °C. The ^{11}B NMR spectrum showed a broad single peak at δ +4.38, indicative of an "ate" complex. Iodination in methanol at 0 °C, followed by treatment with a base, produced (*Z*)-5-decene (**10f**) in 65% yield (GC), along with (*E*)-1-iodo-1-hexene (25–30%). The formation of such vinyl iodides presumably was due to a reaction similar to that involved in the preparation of vinyl iodides from the corresponding vinylboronic acids.[16]

The reaction was much cleaner when **8a** was treated with phenyllithium. In this case, no 1-iodo-1-alkenes were formed. When methyllithium was used, poor yields of methyl-substituted alkenes were obtained. This indicates that the methyl group possesses poor migratory aptitude in these reactions. Better results were realized when 2-lithiothiophene and 3-lithiopyridine were reacted at −78 °C. Compounds **10c** and **13d** were obtained in good yields with excellent stereochemical purities. The reaction gave a mixture of isomers with 2-lithiofuran and **8b** (71% *Z* + 29% *E*). Representative (*Z*)-disubstituted alkenes (**10a–g**) were prepared by the reaction sequence as shown in eq 15. The results are summarized in Table IV.

The boron intermediates (**9a–d**) were prepared following literature procedure.[20] Treatment of these boron intermediates with an alkyllithium or a Grignard reagent produced "ate" complexes, which, upon treatment with iodine in methanol at 0 °C, followed by a base, afforded (*E*)-di-

(19) Brown, H. C.; Bhat, N. G.; Somayaji, V. *Organometallics* **1983**, *2*, 1311.
(20) Brown, H. C.; Imai, T. *Organometallics* **1984**, *3*, 1392.
(21) Corey, E. J.; Beames, D. J. *J. Am. Chem. Soc.* **1972**, *94*, 7210.
(22) Matteson, D. S.; Jesthi, P. K. *J. Organomet. Chem.* **1976**, *110*, 25.
(23) (a) Brown, H. C.; Lee, H. D.; Kulkarni, S. U. *Synthesis* **1982**, 195. (b) Negishi, E.; Katz, J.-J.; Brown, H. C. *Ibid.* **1972**, 555. (c) Brown, H. C.; Imai, T.; Bhat, N. G. *J. Org. Chem.* **1986**, *51*, 5277. (d) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U.; Lee, H. D.; Negishi, E.; Katz, J.-J. *Ibid.* **1986**, *51*, 5270.

Table IV. Stereospecific Synthesis of (*Z*)-Disubstituted Alkenes via 8

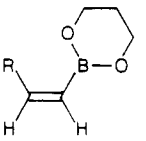


8

R	R^1Li or R^1MgX	product[a]	yield,[b] %	bp, °C (mm)	n^{20}_D
n-C_4H_9	PhLi	1-phenyl-(*Z*)-1-hexene (**10a**)	76	82–84 (2.75)	1.5220
CH_3	PhLi	1-phenyl-(*Z*)-1-propene (**10b**)	(82)[c]		
CH_3		1-(2-thiophenyl)-(*E*)-1-propene (**10c**)[d]	68	66–68 (12)	1.5680
CH_3		1-(3-pyridyl)-(*E*)-1-propene (**10d**)[d]	58	88–90 (20)	1.5250
CH_3		1-(3-thiophenyl)-(*E*)-1-propene (**10e**)[d]	61	76–78 (20)	1.5705
n-C_4H_9	*n*-C_4H_9Li	(*Z*)-5-decene (**10f**)	(65)[c]		
n-C_4H_9		2-methyl-(*Z*)-3-octene (**10g**)	62	76–78 (98)	1.4226

[a] All reactions were carried out on a 10-mmol scale, and stereochemical purity (≥99%) of the products was determined by either GC analyses or ^{13}C spectral data. [b] Yields are based on starting boronate esters viz. 8. [c] Values in parentheses are the GC yields with *n*-hexadecane as an internal standard. [d] Stereochemical purity (>99%) was ascertained by ^{13}C NMR spectroscopy.[29]

Table V. Stereospecific Synthesis of (*E*)-Disubstituted Alkenes via 9



9

R	R^1Li or R^1MgX	product[a]	yield,[b] %	bp, °C (mm)	n^{20}_D
n-C_4H_9	PhLi	1-phenyl-(*E*)-1-hexene (**11a**)	74	84–86 (2.00)	1.5280
CH_3	PhLi	1-phenyl-(*E*)-1-propene (**11b**)	(80)[c]		
c-C_6H_{11}	*n*-C_4H_9Li	1-cyclohexyl-(*E*)-1-hexene (**11c**)	(58)[c]		
c-C_5H_9	*n*-C_4H_9Li	1-cyclopentyl-(*E*)-1-hexene (**11d**)	(60)[c]		
n-C_4H_9	$(CH_3)_2CHMgCl$	2-methyl-(*E*)-3-octene (**11e**)	62	82–84 (80.00)	1.4246

[a] All reactions were carried out on a 10-mmol scale, and stereochemical purity (>99%) of the products was determined by GC analyses. [b] Yields are based on starting boronate esters via. 9. [c] Values in parentheses are the GC yields with *n*-hexadecane as an internal standard.

substituted alkenes (**11a–e**) in good yields. The results are summarized in Table V.

Conclusions

Thus, these new methods describe the development of (*Z*)-disubstituted alkenes with dialkylmonohalo and monoalkyldibromoborane reagents, thus extending the scope and applicability of Zweifel's original synthesis of (*Z*)-disubstituted alkenes. Monoalkyldibromoborane proved to be a better reagent in these syntheses than dialkylmonohaloborane. The stereospecific synthesis of (*E*)-disubstituted alkenes[23d] and regiospecific synthesis of ketones[23d] were also demonstrated with these haloborane reagents. The methodology for preparing (*Z*)- and (*E*)-disubstituted alkenes via alkenylboronic esters is useful for introducing organyl groups not available via hydroboration, thus generalizing the synthesis of (*Z*)- and (*E*)-disubstituted alkenes[3,4,11] via organoboranes. Arylated and heterocyclic-substituted alkenes can be prepared in good yields by the present procedure. We are currently utilizing heterocyclic-substituted alkenes for asymmetric hydroboration with diisopinocampheylborane.

Experimental Section

General Procedures. All of the boiling points are uncorrected. GC analyses were carried out with *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 5890A capillary gas chromatograph (methyl silicone column 50 m in length and 0.25 mm in diameter). Some GC analyses were carried out on a Hewlett-Packard research chromatograph 5750 (6 ft × $^1/_4$ in. column packed with 10% SE-30 on Chromosorb W AW DMCS). IR spectra were recorded on a Perkin-Elmer 1420 ratio-recording infrared spectrophotometer. ^1H NMR and ^{13}C NMR were recorded on a Varian T-60 and FT-80A spectrometer, respectively.

Materials. The boron compounds **8a–b** and **9a–d** were prepared as described in the literature.[19,20] All of the organolithium reagents were purchased and titrated with 1,3-diphenyl-2-propanone *p*-tolylsulfonylhydrazone.[24] All of the Grignard reagents were purchased from Aldrich Chemical Co. Ether (Mallinckrodt, anhydrous) and *n*-pentane (Phillips) were further dried over 4-Å molecular sieves. 1-Alkynes were obtained from Farchan Laboratories. The alkenes were obtained either from Aldrich or from the Chemical Samples Division of Albany International. 2-Lithiothiopnene and 3-lithiopyridine were prepared by the action of *n*-butyllithium on thiophene and 3-bromopyridine, respectively, in diethyl ether at 0 °C for 0.5 h. All manipulations of the boron compounds were done under nitrogen by standard procedures.[5]

Establishment of the Reaction Conditions for the Preparation of (*Z*)-Alkenes via R^1_2BH Reagents. (1) Iodination

(24) Lipton, M. F.; Sorenson, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155.

at −5 °C. To 10 mmol of distilled di-*n*-hexylchloroborane (2.16 g), obtained via hydroboration of 1-hexene with $BH_2Cl{\cdot}SMe_2$,[25] were added 10 mL of THF and 2.96 mL of 1-octyne (20 mmol), followed by a slow addition of 2.55 mL of $LiAlH_4$ (2.5 mmol, 0.98 M) in THF at 0 °C. The reaction mixture was stirred for 2 h at 0 °C and for 0.5 h at room temperature. Excess 1-octyne was removed under reduced pressure. The residual vinylborane was dissolved in 10 mL of THF and cooled to −5 °C. Then, 13.3 mL of aqueous sodium hydroxide (40 mmol, 3 M) was added, followed by a slow addition of 2.54 g of I_2 (10 mmol) in THF. The reaction mixture was warmed to room temperature, and any excess iodine was decolorized with the addition of aqueous $Na_2S_2O_3$ solution. Pentane (15 mL) was added, followed by addition of *n*-hexadecane (1.46 mL, 5 mmol), and stirred well. GC analysis showed the presence of 35% *n*-hexyl iodide (Table I).

(2) Iodination at −25 °C. Iodination of 10 mmol of di-*n*-hexyl-1-octenylborane was carried out in the presence of 9 mL of sodium methoxide (40 mmol, 4.4 M) at −25 °C (1 h) and analyzed on GC with *n*-hexadecane as an internal standard which showed 16% of *n*-hexyl iodide formation.

Similarly, iodinations at −50 °C (2.25 h) and −78 °C (3 h) were carried out and analyzed for the alkyl iodide (Table I).

Preparation of (*Z*)-7-Tetradecene (2h). To 50 mmol of distilled di-*n*-hexylchloroborane (10.8 g) were added at 0 °C 40 mL of THF and 14.8 mL of 1-octyne (100 mmol), followed by a slow addition of 12.8 mL of $LiAlH_4$ (12.5 mmol, 0.98 M) in THF, and the mixture was stirred at 0 °C for 2 h, followed by 0.5 h of stirring at room temperature. Excess 1-octyne was removed under reduced pressure, and the residual vinylborane was dissolved in 60 mL of THF and then cooled to −78 °C. To this reaction mixture at −78 °C were added sequentially with vigorous stirring 45 mL of NaOMe (200 mmol, 4.4 M) in MeOH and 12.7 g of I_2 (50 mmol) in 50 mL of THF. The reaction was allowed to proceed for 3 h at −78 °C, and any excess iodine present was decolorized by adding an aqueous solution of $Na_2S_2O_3$. The reaction flask was then brought to room temperature, and the reaction mixture was extracted with pentane (3 × 75 mL). The organic layer was washed with 3 M NaOH solution (50 mL) and water and dried over anhydrous $MgSO_4$. Solvent was removed, and distillation afforded 6.5 g (66%) of (*Z*)-7-tetradecene (**2h**), bp 75–76 °C (0.8 mm), n^{20}_D 1.4399. GC analysis indicated 99% chemical purity. ^1H NMR ($CDCl_3/SiMe_4$): δ 13.81, 22.52, 27.11, 28.88, 29.66, 31.70 (alkyl C), 129.70 (C=C). The single vinylic carbon (δ 129.27) reveals the absence of any significant amounts of the corresponding *E* isomer.[26]

Preparation of (*Z*)-6-Ethyl-4-nonene (2j) via $R^1BHBr{\cdot}SMe_2$. To 30 mmol of 3-hexyldibromoborane-dimethyl sulfide[27] prepared from 30 mmol of (*Z*)-3-hexene (3.72 mL) and 30 mmol of $BHBr_2{\cdot}SMe_2$ (16.6 mL, 1.81 M) were added at 0 °C 3 mL of SMe_2 and 25 mL of Et_2O, followed by a slow addition of 8.2 mL of $LiAlH_4$ (7.5 mmol, 0.92 M) in Et_2O with stirring under nitrogen. The reaction was allowed to proceed for 3 h at 0 °C and for 1 h at room temperature. The resulting alkylbromoborane was slowly transferred to the solution of 1-pentyne (3 mL, 30 mmol) in Et_2O at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and for 1 h at room temperature. Then, the resulting vinylbromoborane was added to 34.0 mL of NaOMe (150 mmol, 4.4 M) in MeOH at 0 °C. After 0.5 h at room temperature, the solvent ether was removed under vacuum, and 30 mL of MeOH was added. Iodine (30 mmol, 7.6 g) was added to this vinylborane in MeOH at 0 °C and stirred at room temperature for 3 h. Aqueous $Na_2S_2O_3$ solution was now added, the reaction mixture was extracted with pentane, and the extract was dried over anhydrous $MgSO_4$. The crude product showed ≈6% 1-pentenyl iodide. This could be separated by careful distillation to yield pure (*Z*)-6-ethyl-4-nonene (**2j**; 3.18 g, 69%), bp 70–71 °C (12 mm), n^{20}_D 1.4319. GC analysis indicated >99% chemical purity. ^1H NMR ($CDCl_3/SiMe_4$): δ 0.69–1.68 (m, 17 H), 1.78–2.38 (m, 3 H), 4.84–5.61 (m, 2 H). ^{13}C NMR ($CDCl_3/SiMe_4$):[22] δ 11.55, 13.63, 14.05, 20.34, 22.96, 28.52, 29.74, 37.92, 38.59 (alkyl C), 129.42, 134.78 (C=C). Only two signals for two vinylic carbons (nonequivalent) reveal the absence of any significant amounts of the corresponding *E* isomer.[20]

Preparation of Muscalure [(*Z*)-9-Tricosene, 7] via $RBHBr{\cdot}SMe_2$. The crude Muscalure, prepared from 1-tridecene (30 mmol, 7.15 mL) and 1-decyne (30 mmol, 5.4 mL) by the above procedure, contained ≈16% of 1-decenyl iodide. This could be separated by careful distillation to yield 5.7 g (59%) of (*Z*)-9-tricosene (**7**), bp 140–142 °C (0.01 mm), n^{20}_D 1.4559 [lit.[16] bp 157–158 °C (0.1 mm), n^{28}_D 1.4517]. GC analysis indicated 100% chemical purity. ^1H NMR ($CDCl_3/SiMe_4$): δ 0.70–1.66 (m, 40 H), 1.85–2.22 (m, 4 H), 5.33 (m, 2 H). ^{13}C NMR ($CDCl_3/SiMe_4$): δ 13.89, 22.59, 27.15, 29.30, 29.66, 31.88 (alkyl C), 129.70 (C=C). The single vinylic carbon signal reveals the absence of any significant amount of the corresponding *E* isomer.[26]

Preparation of 1-phenyl-(*Z*)-1-hexene (10a) is representative. In a dry, 100-mL flask equipped with a magnetic stirring bar and septum inlet were placed (*E*)-2-(1-hexenyl)-1,3,2-dioxaborinane (**8a**, 10 mmol, 1.76 mL) and diethyl ether (20 mL). The mixture was then cooled to −78 °C, and phenyllithium in cyclohexane–diethyl ether mixture (11 mmol, 5.50 mL) was added dropwise. The reaction mixture was stirred for 0.5 h at −78 °C and at 0 °C for 1 h. The solvents were then pumped off, and methanol (10 mL) was added at 0 °C. Iodine (10 mmol, 2.54 g) in methanol (40 mL) was then added slowly at 0 °C, and the reaction mixture was stirred overnight at room temperature. Sodium hydroxide (10 mL of 3 M solution) was then added and stirred for 15 min. It was then diluted with water (150 mL) and extracted with *n*-pentane (3 × 25 mL). The combined pentane extract was washed with an aqueous 1 M solution of sodium thiosulfate (25 mL) and water (2 × 50 mL) and then dried over anhydrous potassium carbonate. Evaporation of the solvent gave a crude product, which was purified by distillation to afford 1-phenyl-(*Z*)-1-hexene (**10a**; 1.20 g, 76%), bp 82–84 °C (2.75 mm), n^{20}_D 1.5220. GC analysis showed >99% stereochemical purity, IR (neat): ν 1641, 1598, 1488, 910, 767, and 697 cm^{-1}. ^1H NMR ($CDCl_3/TMS$): δ 0.76–0.93 (distorted t, 3 H), 1.16–1.46 (m, 4 H), 2.13–2.46 (m, 2 H), 5.33–5.83 (m, 1 H), 6.33 (d, J = 11 Hz, 1 H), and 7.06–7.26 (m, 5 H). Mass spectrum: m/e (M^+) 160.

1-(2-Thiophenyl)-1(*Z*)-propene (10c). By the above procedure, compound **10c** was prepared in 68% yield. The only modifications was to maintain the temperature at −78 °C during the iodination step. IR (neat): ν 3020, 2912, 2854, 1510, 1435, 1365, 1174, 853, 828, and 695 cm^{-1}. ^1H NMR ($CDCl_3/TMS$): δ 1.93 (m, 3 H), 5.33–5.93 (m, 1 H), 6.50 (m, 1 H), and 6.73–7.26 (m, 3 H). ^{13}C NMR ($CDCl_3/TMS$): δ 126.83, 126.59, 124.82, 124.64, 124.34, 122.99, and 14.95. Mass spectrum: m/e (M^+) 124.

1-(3-Pyridyl)-1(*Z*)-propene (10d). IR (neat): ν 3080, 3020, 2957, 1656, 1420, 1023, 828, 797, and 709 cm^{-1}. ^1H NMR ($CDCl_3/TMS$): δ 1.90 (m, 3 H), 5.90 (m, 1 H), 6.40 (m, 1 H), and 7.4–8.5 (m, 4 H). ^{13}C NMR ($CDCl_3/TMS$): δ 150.04, 147.49, 135.69, 129.21, 126.37, 123.02, and 14.53. Mass spectrum: m/e (M^+) 119.

Preparation of 1-phenyl-(*E*)-1-hexene (11a) is representative. In a dry, 100-mL flask were placed (*Z*)-2-(1-hexenyl)-1,3,2-dioxaborinane (**9a**; 10 mmol, 1.93 mL) and diethyl ether (20 mL). The flask was cooled to −78 °C, and phenyllithium in cyclohexane–diethyl ether mixture (11 mmol, 5.50 mL) was added dropwise. The reaction mixture was stirred at −78 °C for 0.5 h and at 0 °C for 1 h. The solvents were then pumped off, and methanol (10 mL) was added at 0 °C. Iodine (10 mmol, 2.54 g) in methanol (40 mL) was added slowly with vigorous stirring at 0 °C, and the reaction mixture was stirred overnight. Sodium hydroxide (10 mL of 3 M solution) was added, and the reaction mixture was stirred for 15 min. It was then diluted with water (150 mL) and extracted with *n*-pentane (3 × 25 mL). The combined pentane extract was washed with an aqueous 1 M solution

(25) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1979**, *44*, 2417.

(26) In a mixture of isomers, the vinylic carbons of the (*Z*)-alkenes can be distinguished from the corresponding carbons of (*E*)-alkenes. Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757.

(27) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1980**, *45*, 384.

(28) Both *Z* and *E* isomers cleanly separate on a 10% SE-30 column on Chromosorb W (12 ft × $^1/_2$ in.) programmed at 50–250 °C (10 °C/min).

(29) In a mixture of isomers, the methyl group on the double bond can be distinguished by ^{13}C chemical shifts.

(30) In our communication, ref 1b we reported the ^{13}C NMR spectrum of neat sample **2j** (with $CDCl_3$ as locking solvent and $SiMe_4$ as external standard). We found in the literature that ^{13}C spectra of samples are generally recorded as solutions in $CDCl_3$. Therefore, we now recorded ^{13}C spectra of sample **2j** as its solution in $CDCl_3$.

of sodium thiosulfate (25 mL) and water (2 × 25 mL) and then dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded a crude product, which was purified by distillation to provide 1-phenyl-(*E*)-1-hexene (**11a**; 1.18 g, 74%), bp 84.86 °C (2 mm), n^{20}_D 1.5280. GC analysis showed >99% stereochemical purity. IR (neat): ν 1645, 1594, 964, 740, and 690 cm^{-1}. ^1H NMR ($CDCl_3$/TMS): δ 0.80–1.03 (distorted t, 3 H), 1.16–1.53 (m, 4 H), 2.00–2.33 (m, 2 H), 5.83–6.10 (m, 2 H), and 7.03–7.26 (m, 5 H).

2-Methyl-(*E*)-3-octene. IR (neat): ν 1655 and 967 cm^{-1} (C=C). ^1H NMR ($CDCl_3$/TMS): δ 0.83–1.03 (m, 9 H), 1.16–1.53 (m, 4 H), 1.83–2.46 (m, 3 H), and 5.26–5.46 (m, 2 H).

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Pheromones via Organoboranes. 3. Vinylic Organoboranes. 10. Stereospecific Synthesis of (*Z*)- and (*E*)-6- and -7-Alken-1-ols via Boracyclanes[1]

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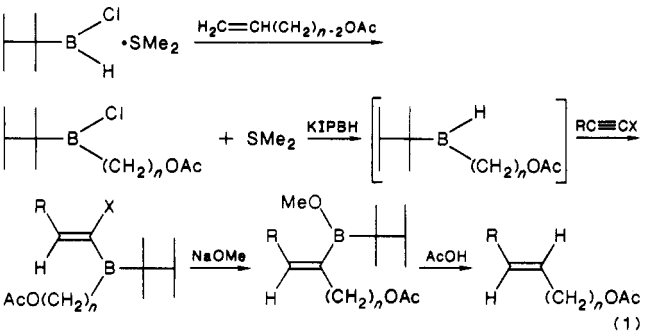
Treatment of *B*-(*E*)-1-alkenylborinanes, obtained via monohydroboration of 1-alkynes with borinane, with iodine in the presence of a base results in the migration of one end of the cycloalkyl chain from boron to the adjacent carbon, producing intermediates containing the seven-membered borepane moiety, which undergo rapid deiodoboronation to afford the (*Z*)-6-alkenyl-1-boronate esters. These boronate esters, upon oxidation, provide (*Z*)-6-alken-1-ols. The procedure is successfully extended to *B*-(*E*)-1-alkenylborepane derivatives to produce (*Z*)-7-alken-1-ols. The preparation of (*E*)-6- and -7-alken-1-ols has been carried out via borinane and borepane derivatives. Borinane, as prepared previously, hydroborates cleanly 1-bromo-1-alkynes to provide the *B*-((*Z*)-1-bromo-1-alkenyl)borinanes. Treatment of these boron intermediates with sodium methoxide results in the displacement of bromine by one end of the boracycloalkyl moiety, producing the corresponding vinylboranes containing the seven-membered borepane moiety. The intermediates, upon controlled protonolysis, followed by oxidation, afford the (*E*)-6-alken-1-ols. The methodology was extended to borepane derivatives to provide (*E*)-7-alken-1-ols. The above procedures constitute a simple, very convenient, stereospecific, and general one-pot synthesis of (*Z*)- and (*E*)-6- and -7-alken-1-ols. The methodology has been applied to the synthesis of representative pheromones containing a (*Z*)- or an (*E*)-alkene moiety in good yields.

Organoboranes play an important role in bringing latitude to organic synthesis.[3] Highly stereospecific syntheses of (*Z*)- and (*E*)-disubstituted alkenes via organoboranes are well documented in the literature.[4,5] Recently we reported applications of the general stereospecific synthesis of (*E*)-disubstituted olefins via thexylchloroborane–dimethyl sulfide to the synthesis of pheromones containing an (*E*)-alkene moiety[6] (eq 1).



(1)

The synthesis[7] of unsaturated alcohols has attracted considerable attention from organic chemists in recent years because such alcohols[8,9] or acetates[8,10] are known to be insect pheromones. For example, (*Z*)-7-dodecen-1-ol (**2a**) is the pheromone of the male moths of lepidoptera, *Raphia frater Grt* (Noctuidae),[9] and (*Z*)-7-dodecen-1-yl

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