Vinylic Organoboranes. 12. Synthesis of (Z)-1-Halo-1-alkenes via Hydroboration of 1-Halo-1-alkynes Followed by Protonolysis[1]

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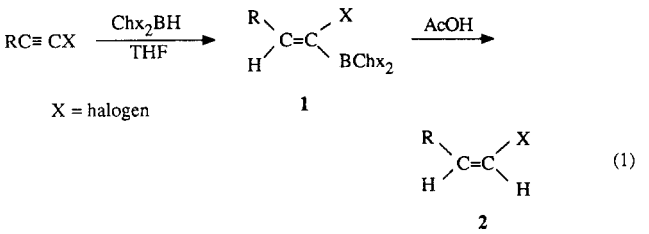
Received February 22, 1989

Practical conditions have been developed for synthesizing (Z)-1-halo-1-alkenes from 1-halo-1-alkynes. The reaction of 1-halo-1-alkynes with dicyclohexylborane (Chx_2BH) or with 9-borabicyclo[3.3.1]nonane (9-BBN) gives exclusively the corresponding B-((Z)-1-halo-1-alkenyl)dialkylboranes 1. No dihydroboration products were found. A general procedure is reported for protonolyzing 1 with AcOH, yielding the (Z)-1-halo-1-alkenes. The synthesis of these haloalkenes is particularly convenient using Chx_2BH in pentane. In this solvent, the synthesis of Chx_2BH, the subsequent hydroboration and protonolysis, and the removal of the borane residue with ethanolamine all go smoothly and rapidly with nearly quantitative yields.

In 1967, Zweifel and Arzoumanian reported a highly stereoselective synthesis of (Z)-1-halo-1-alkenes **2** from 1-halo-1-alkynes via hydroboration with dicyclohexylborane, followed by protonolysis with acetic acid (eq 1).[3]



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Since then, many new hydroborating agents have been introduced.[4] Also, protonolysis of 1-alkenylboranes giving alkenes often occurs under much milder conditions than typical for saturated organoboranes; for example, alcohols and water, instead of AcOH, have proved effective as protonolyzing agents for certain 1-alkenylboranes.[5] Consequently, we undertook to apply these developments in hydroboration and protonolysis to produce a practical general synthesis of (Z)-1-halo-1-alkenes.

A variety of substituted boranes has been used to hydroborate 1-halo-1-alkynes, with the substituents generally having specific functions.[6]

In this study, any substituents would remain unused, aside from a possible steric effect on the regioselectivity of hydroboration. Thus, the choice of hydroborating agents was guided by convenience and availability. Accordingly, dicyclohexylborane (Chx_2BH) and 9-borabicyclo[3.3.1]nonane (9-BBN) were compared in the synthesis of (Z)-1-halo-1-alkenes. (Chx_2BH and 9-BBN will be referred to as monomers instead of the actual hydrogen-bridged dimers.)

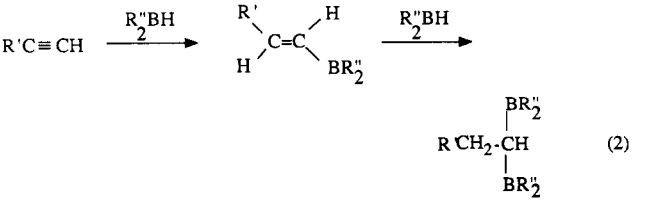
Table I. ^1H NMR Shifts[a] for the Alkene Protons of Alkenylboranes 3 and 5 and 1-Halo-1-alkenylboranes 4[b] and 6[b]

	chemical shift			
	3 or 4, RCH=CXBChx$_2$		5 or 6, RCH=CX-(9-BBN)	
starting alkyne	$CDCl_3$	THF	$CDCl_3$	THF
1-hexyne	H^1 6.73	H^1 6.77	H^1 6.83	H^1 6.68
	H^2 6.14	H^2 6.17	H^2 6.17	H^2 6.06
1-octyne	H^1 6.70	H^1 7.78	H^1 6.80	H^1 6.68
	H^2 6.12	H^2 6.18	H^2 6.15	H^2 6.05
1-chloro-1-hexyne	6.32	6.08	6.86	5.82
1-chloro-1-octyne	6.31	6.07	6.87	5.82
1-bromo-1-hexyne	6.05	6.02	7.07	6.04
1-bromo-1-octyne	6.04	6.02	7.06	6.04
1-iodo-1-hexyne	5.52	5.58	6.90	5.90
1-iodo-1-octyne	5.51	5.59	6.90	5.90

[a] In parts per million downfield from internal TMS. [b] ^1H NMR spectra of all of the compounds showed a triplet for vinylic protons (J = ~7 Hz).

Results and Discussion

Hydroboration Regiochemistry and Stoichiometry. On hydroboration with dialkylboranes, terminal alkynes give a boron-substituted alkene with the boron attached to C-1. The addition of a second R''_2BH gives the 1,1-dibora compound (1,1-dihydroboration, eq 2).[6a,7] With



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equimolar quantities of alkyne and R''_2BH, dihydroboration is often significant and is indicated if starting alkyne is found after the disappearance of R''_2BH. The hydroboration of 1-halo-1-alkynes also occurs to place the boron on C-1, as shown by the appearance of a triplet (J

(1) Presented in part at the 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 1982; American Chemical Society: Washington, DC, 1982; ORGN 38.

(2) (a) Postdoctoral research associate on Grant CHE-79-18881 from the National Science Foundation. (b) Postdoctoral research associate on Grant CHE-76-20846 from the National Science Foundation. (c) Postdoctoral research associate on Grant CHE-8706102 from the National Science Foundation.

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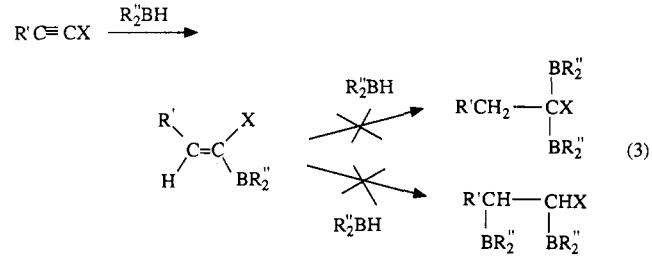
Table II. Reaction Times for 1-Halo-1-alkynes with Chx_2BH and 9-BBN in Various Solvents[a]

	reaction conditions			
alkyne	Chx_2BH[b] (1.3 M pentane)	Chx_2BH[b] (1.3 M THF)	9-BBN[c] (0.4 M CCl_4)	9-BBN (0.5 M THF)
1-chloro-1-hexyne	<1 min		172 h	~50 h
1-chloro-1-octyne	<1 min	<1 min	99 h	~75 h
1-bromo-1-hexyne	<1 min	<1 min	68 h	30 h
1-bromo-1-octyne	<1 min			30 h
1-iodo-1-hexyne	<1 min	<1 min	12 h	4 h
1-iodo-1-octyne	<1 min			4 h

[a] Reactions were run at 25 °C. Unless otherwise indicated, a 2–5% excess of the hydroborating agent was used. [b] The Chx_2BH was used as a slurry. [c] Data from ref 8b. Stoichiometric amounts of 9-BBN and 1-halo-1-alkyne were used.

= 7 Hz) in the ^1H NMR spectra of the reaction product (eq 3, Table I). This is consistent with the previous ex-



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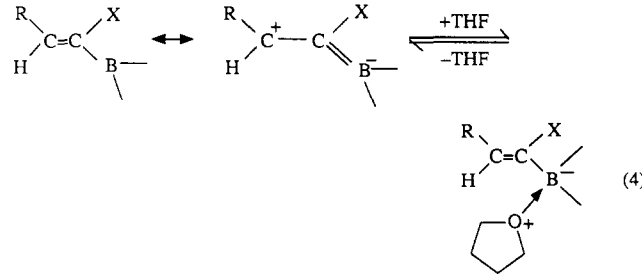
amples of the hydroboration of 1-halo-1-alkynes.[6] However, in this study, no evidence of dihydroboration of haloalkynes was found. The nearly quantitative yields of (*Z*)-1-halo-1-alkenes (**2**) obtained upon the protonolysis of the hydroboration products (eq 1) with AcOH limit any possible dihydroboration or other side reactions to a very small amount. Hydroboration could potentially place the boron on C_2 and rapid β elimination of halogen and borane would then be expected.[8] Starting with a 1-halo-1-alkyne, various sequences of hydroboration and/or elimination, then protonolysis, could be envisioned, which could result in the corresponding 1-alkyne, 1-alkene, alkane, or 1-haloalkane. None of these products were detected, again indicating clean monohydroboration with boron at C_1.

Evidence for the structures of the products from hydroboration of 1-halo-1-alkynes comes from NMR spectra of **4** and **6** (Table I). Proton NMR shows the expected alkenyl triplet (J = 7 Hz), and ^{13}C NMR also indicates an alkene, with the boron-substituted carbon giving very broad signals, which were not always observed.[9a] Other compounds are included in these tables for comparison.

Hydroboration Rate. The time required for the hydroboration of some 1-halo-1-alkynes with 1 equiv of Chx_2BH or 9-BBN is shown in Table II. 1-Halo-1-alkynes were added dropwise to a solution or suspension of the hydroborating agent. The reaction rates were determined by GC or ^1H NMR analysis for unreacted haloalkyne, except as noted. The 1-halo-1-alkenylboranes, which were the products of hydroboration, slowly decomposed at room temperature, as previously reported.[8]

Protonolysis of 1-Halo-1-alkenylboranes. The rates of protonolysis of the 1-halo-1-alkenylboranes **4** and **6** under various conditions are given in Table III. The Chx_2BH derivatives **4** protonolyze rapidly with AcOH in a variety of solvents. The 9-BBN derivatives **6** protonolyze much slower, especially in THF. Slow protonolysis of **4** or **6** with MeOH was observed only in nonpolar solvents, such as CCl_4. For the Chx_2BH compounds **4**, the reaction with MeOH was slow enough so that the rearrangement reaction occurred in competition with the protonolysis, resulting in mixtures of products.[9a] In contrast to the corresponding nonhalogenated compounds **3e** and **5e**, the Chx_2BH compound protonolyzes only slightly faster than the 9-BBN compound.[10]

An explanation of the differences in protonolysis rates can be found in the ^1H and ^{11}B NMR data (Tables I and IV). In the ^{11}B NMR, most of the compounds show upfield shifts on changing from $CDCl_3$ to THF. However, the shifts for the halogen-containing 9-BBN compouds (**6**, 56–63 ppm) are much larger than for the equivalent Chx_2BH (**4**, 1–18 ppm) or nonhalogenated (**3** and **5**, 1–12 ppm) compounds. This indicates that THF forms a stronger complex with the 9-BBN compounds (**6**), which interferes with the protonolysis reaction (eq 4). Similar



(4)

results are found in the ^1H NMR spectra.[11] Compounds **3** and **5** both show small shifts for H^2 on changing from $CDCl_3$ to THF. However, for the halogen-containing compounds **4** and **6**, the 9-BBN derivatives show much greater shifts than the Chx_2BH derivatives on changing from $CDCl_3$ to THF. This is again consistent with a greater interaction of the THF with the 9-BBN compounds.

Synthesis of (*Z*)-1-Halo-1-alkenes. On the basis of the results in Tables II and III, the practical conditions for synthesizing (*Z*)-1-halo-1-alkenes from 1-halo-1-alkynes were developed, and the details are given in the Experimental Section. The results are summarized in Table V.

The following are some general comments on the choice of reaction conditions. In all cases a slight excess, 2–5%, of the hydroborating agent was used to ensure that all of the starting alkyne was consumed, eliminating any separation problems. A general workup was desired, that would minimize potential interferences. For example, an oxidative workup after using Chx_2BH would produce cyclohexanol, which could interfere in the distillation of the product. Thus, after protonolysis, the borane residue was removed via the adduct with ethanolamine[12] (eq 5).

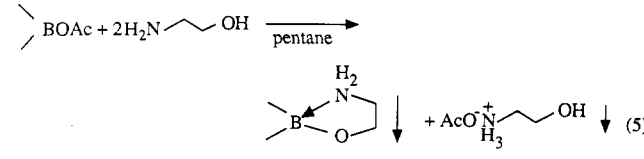


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Table III. Rates of Protonolysis of 1-Alkenylboranes 3 and 5 and 1-Halo-1-alkenylboranes 4 and 6 under Various Conditions[a]

	time required for protonolysis, 25 °C						
	3 and 4, RCH=CXBChx$_2$			5 and 6, RCH=CX(9-BBN)			
	AcOH	MeOH		AcOH		MeOH	
starting alkyne	CCl_4 or THF	CCl_4	THF	CCl_4	THF	CCl_4	THF
1-octyne[b]	<1 min	0.75 h	8 h	<1 min	<1 min	1 h	10 h
1-octyne[b]	<0.3 h[c]				0.75 h		
1-chloro-1-hexyne	<1 min		no rxn	3 min	30 h	10 h	no rxn
1-chloro-1-octyne	<1 min				30 h		
1-bromo-1-hexyne	<1 min		no rxn	3 min	30 h	2 h	no rxn
1-bromo-1-octyne	<1 min				30 h		
1-iodo-1-hexyne	<1 min		no rxn	1 min	20 h	1 h	no rxn
1-iodo-1-octyne	<1 min				20 h		

[a] Reactions followed by ^{1}H NMR or GC. See Experimental Section. [b] Data from ref 9. [c] Protonolyzed with MeOH + 1 mol % AcOH.

Table IV. ^{11}B NMR Shifts[a] for 1-Alkenylboranes 3 and 5 and 1-Halo-1-alkenylboranes 4 and 6

	chemical shift			
	3 and 4, RCH=CX-BChx$_2$		5 and 6, RCH=CX-(9-BBN)	
starting alkyne	$CDCl_3$	THF	$CDCl_3$	THF
1-hexyne	73	72	77	64
1-octyne	73	72	77	66
1-chloro-1-hexyne	76	58	72	16
1-chloro-1-octyne	73	56	72	16
1-bromo-1-hexyne	72	61	78	15
1-bromo-1-octyne	72	61	78	15
1-iodo-1-hexyne	67	67	78	17
1-iodo-1-octyne	68	67	77	17

[a] In parts per million downfield from external TMS.

Hydrocarbon solvents minimize the solubility of the adduct. This is especially advantageous in the case of Chx$_2$BH since the synthesis of Chx$_2$BH and the subsequent hydroboration and protonolysis all go smoothly and rapidly in pentane. For 9-BBN, the hydroboration was done in THF, and then to significantly reduce the time for protonolysis, the THF was removed under vacuum and replaced with pentane. Upon distillation of the (*Z*)-1-halo-1-alkenes **2b** and **2c**, some isomerization (≤20%) to the trans compound was often found.[13] This was reducded to less than 2% by adding a small amount of $NaHCO_3$ and BHT to the mixture before distillation.[14] This was adopted as a general procedure, even though no similar difficulties were found with the corresponding chloro or iodo compounds (**2a,d–j**).

Conclusion

The hydroboration of 1-halo-1-alkynes with Chx$_2$BH or with 9-BBN yields exclusively C-1 monohydroboration products, which can be easily protonolyzed with AcOH to give (*Z*)-1-halo-1-alkenes. The overall yields of these reactions are nearly quantitative, indicating that this reaction sequence has excellent prospects for synthetic applications.

Experimental Section

General Comments. The techniques described in Chapter 9 of ref 4 were used extensively. Glassware was assembled hot or flamed out while flushing with prepurified nitrogen. The reactions were carried out under a slight static pressure of nitrogen. The CCl_4 and $CDCl_3$ were distilled from P_2O_5 and stored over 4-Å molecular sieves, and the $CDCl_3$ was kept in the dark. MeOH was distilled from $Mg(OMe)_2$, and THF and pentane were distilled from LAH. The pentane was pretreated with concentrated H_2SO_4 to remove unsaturated material and then washed with dilute NaOH and then water and passed through a column of Al_2O_3. AcOH and ethanolamine were used as received after flushing with nitrogen. 9-BBN was prepared as previously described, and solutions in THF and CCl_4 were standardized by measurement of the H_2 evolved on hydrolysis with MeOH/THF.[4] Chx$_2$BH was prepared from BH_3·SMe_2 immediately before use by a modification of the previously described procedure.[15] the 1-halo-1-alkynes were prepared by standard literature procedures[16] with improvements reported earlier.[9b]

GC analyses were carried out on the following columns: (a) Carbowax 20M, 10% on 60/80 Chromosorb W, 12 ft × 0.25 in.; (b) trixylyl phosphate, 10% on 60/80 Chromosorb W, 12 ft × 0.25 in; (c) tricresyl phosphate, 20% on 60/80 Firebrick, 6 ft × 0.25 in; (d) methylsilicone 50-m column on 5890A capillary GC. The NMR spectra were obtained on a Varian T-60 (^{1}H, 60 MHz), a Varian FT-80A (^{11}B, 25.517 MHz), a Varian XL-200 (^{1}H, 200 MHz), and a Nicolet NT-470 (^{1}H, 470 MHz).

Rate of Hydroboration of 1-Halo-1-alkynes with Chx$_2$BH. Chx$_2$BH is almost insoluble in THF, CCl_4, or pentane. When 1 equiv of a 1-halo-1-alkyne is added dropwise to a stirred slurry of Chx$_2$BH at room temperature, the solution becomes homogeneous as the last few drops of the alkyne are added, much like a titration endpoint. GC analysis shows no remaining alkyne. This indicates that the hydroboration of 1-halo-1-alkynes with Chx$_2$BH is very fast.

Rate of Hydroboration of 1-Halo-1-alkynes with 9-BBN. In a typical reaction, 33.9 mL of a 0.59 M 9-BBN/THF solution (20 mmol) was placed in a flask that was in a 25 ± 0.5 °C water bath and equipped with a magnetic stirring bar. THF (2.5 mL), *n*-dodecane (0.7388 g, 1.0 mL, GC internal standard), and 1-bromo-1-hexyne (3.11 g, 19.3 mmol, 2.6 mL) were then added.

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(17) For ^{1}H NMR data of compounds (**2c**, **2g**, **2j**), see the Experimental section in Vinylic Organoboranes, part 13 in this series. ^{1}H NMR ($CDCl_3$/TMS): **2a** β 6.10–5.53 (m, 2 H), 2.43–2.03 (m, 2 H), 1.50–1.20 (m, 8 H), 1.00–0.76 (m, 3 H); **2b** δ 6.43–5.64 (m, 2 H), 2.17 (m, 2 H), 1.33 (m, 4 H), 0.86 (m, 3H); **2d** δ 6.16–5.83 (m, 2 H), 3.13–2.70 (m, 1 H), 2.10–1.10 (m, 8 H); **2e** δ 6.93 (δ, *J* = 8 Hz, 1 H), 6.26 (d, *J* = 8 Hz, 1 H), 7.73–7.20 (m, 5 H); **2f** δ 6.33–5.76 (m, 2 H), 2.30–1.96 (m, 2 H), 1.56–1.20 (m, 4 H), 1.06–0.76 (m, 3 H); **2h** δ 6.13–5.76 (m, 2 H), 2.93–2.33 (m, 1 H), 1.03 (d, *J* = 6 Hz, 6 H); **2i** δ 6.53 (d, *J* = 8 Hz, 1 H), 6.10 (d, *J* = 8 Hz, 1 H), 1.20 (s, 9 H).
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Table V. Synthesis of (Z)-1-Halo-1-alkenes from 1-Halo-1-alkynes

compound[a]	hydroborating agent	% yield[b] (GC)	purity,[c] %	bp, °C/mmHg
[Z]-1-chloro-1-octene (2a)	Chx_2BH	93	>99	84–7/45[d]
[Z]-1-chloro-1-octene (2a)	9-BBN	73	>99	85–7/47[d]
[Z]-1-bromo-1-hexene (2b)	Chx_2BH	85 (>99)	98	59–61/40[e]
[Z]-1-bromo-1-octene (2c)	Chx_2BH	91	98	75–78/16[f]
[Z]-1-bromo-1-octene (2c)	9-BBN	92	98	75–78/16[f]
[Z]-1-bromo-2-cyclopentyl-1-ethene (2)[i]	9-BBN	82	>98	64–66/9
[Z]-1-bromo-2-phenylethene (2e)	Chx_2BH	84	>98	60–62/1.20[g]
[Z]-1-iodo-1-hexene (2f)	Chx_2BH	94	>99	58–60/16[h]
[Z]-1-iodo-1-hexene (2f)	9-BBN	84 (>99)	>99	58–60/16[h]
[Z]-1-iodo-1-octene (2g)[22]	Chx_2BH	98	>99	55–7/1
[Z]-1-iodo-3-methyl-1-butene (2h)[23]	Chx_2BH	75	>98	66–68/65
[Z]-1-iodo-3,3-dimethyl-1-butene (2i)[20]	Chx_2BH	73	>98	70–72/65
[Z]-1-iodo-2-cyclohexyl-1-ethene (2j)[20]	Chx_2BH	80	>98	58–60/1.40

[a] All of the compounds (2a–j) gave satisfactory ^1H NMR data.[17] [b] All of the reactions were carried out on a 50-mmol scale, and the yields were based on the starting 1-halo-1-alkynes. [c] Stereochemical purity was established by GC analyses. [d] Lit.[18] bp 69–70 °C/15 mmHg. [e] Lit.[19] bp 96 °C/170 mmHg. [f] Lit.[20] bp 57–59 °C/5 minHg. [g] Lit.[18] bp 49–52 °C/1 minHg. [h] Lit.[21] bp 68 °C/15 mmHg. [i] The compound 2d appears to be new in the literature, and the ^1H NMR spectrum is given in the supplementary material (see the paragraph at the end of the paper).

The solution (40 mL) was then 0.50 M in 9-BBN. The hydroboration reaction was followed by observing the disappearance of the 1-bromo-1-hexyne via GC using column b. the GC samples were prepared by shaking ~0.5 mL of 3 M K_2CO_3 and then drying the THF layer with a small amount of K_2CO_3.

Rate of Protonolysis of 1-Halo-1-alkenylboranes 4 and 6. Typically, the reaction mixture from the determination of the rate of hydroboration of the 1-halo-1-alkyne with 9-BBN in THF was used. The THF solution of 6c (19.3 mmol) was treated with 1.2 mL of AcOH (20.0 mmol) via syringe. The protonolysis reaction was followed by observing the appearance of (Z)-1-bromo-1-hexene (2b) via GC using column b. The GC samples were pretreated as described before. The rates of protonolysis for the other systems were determined by ^1H NMR. Solutions of 4 or 6 in CCl_4 or THF with benzene as an internal standard were treated with 1.04 ± 0.02 equiv of AcOH or MeOH. The reactions were followed by integrating the vinyl signals due to starting materials and products.

Synthesis of [Z]-1-Halo-1-alkenes (2) Using Chx_2BH. A typical example is given here. Chx_2BH (50 mmol) was prepared as in ref 15. Pentane (~50 mL) was added, and the flask was placed in a 20–25 °C water bath. While this stirred, 9.328 g (49.6 mmol) of 1-bromo-1-octyne was added dropwise via syringe through a septum inlet (5–10 min). The mixture became homogeneous, and the flask was briefly shaken to wash the walls of the flask. Immediately following this, AcOH (3.3 mL, 55 mmol) was added dropwise via syringe (~5 min) while stirring. The flask was again shaken, and then 2 equiv of ethanolamine (6.5 mL, 108 mmol) was added via syringe. The best results were obtained if a small part of the ethanolamine (10–20%) was added and the mixture allowed to stir for a few minutes to allow the formation of a solid precipitate. The rest of the ethanolamine was then slowly added (10–15 min). The reaction mixture, including the precipitate, was then poured into a dry chromatography column containing ~20 cm of 60–200 silica gel and a top layer (~10 cm) of 20% ethanolamine on silica gel. In the receiving flask was placed 0.1 g of BHT and 0.2 g of $NaHCO_3$. Pentane (~300 mL) was used to wash the reaction mixture, including the precipitate, into the column and then to elute the column. A slight N_2 pressure was often used to make the column proceed rapidly (~15 min). Most of the eluted pentane was removed by distillation through as short Vigreaux column, and the remaining material, including the $NaHCO_3$, was transferred to a smaller flask via a double-ended needle for distillation through a short-path apparatus. Colorless (Z)-1-bromo-1-octene (2c, 8.70 g, 45.5 mmol, 91%) distilled at 75–78 °C/16 mmHg. Analysis by GC on column b indicated 98% purity with <2% of the trans compound. For lower boiling products, the distillation receiver was cooled in an ice bath. The hydroboration and protonolysis reactions described here are exothermic, and for larger scale reaction, more attention to cooling the reaction mixture would be needed.

Synthesis of (Z)-1-Halo-1-alkenes (2) Using 9-BBN. To 93 mL of a 0.59 M 9-BBN/THF solution (55 mmol) was added 9.45 g (50 mmol) of 1-iodo-1-hexyne via syringe. After stirring at room temperature for 6 h, the THF was completely removed with vacuum (0.2 mmHg) and replaced with ~50 mL of pentane. AcOH (3.3 mL, 55 mmol) was added via syringe, and the mixture stirred for 10 min. The remainder of the synthesis was the same as when Chx_2BH was used. The ethanolamine precipitate was very sticky and more difficult to handle than in the synthesis with Chx_2BH. Colorless (Z)-1-iodo-1-hexene (8.70 g, 41.7 mmol, 84%) distilled at 58–60 °C/16 mmHg. GC analysis on column b indicated >99% purity with no trans compound.

Acknowledgment. We are indebted to the National Science Foundation (Grants CHE-7918881, 7620846, and 8706102) for support of this work.

Registry No. 2a, 64531-23-3; 2b, 13154-12-6; 2c, 42843-49-2; 2d, 123240-92-6; 2e, 588-73-8; 2f, 16538-47-9; 2g, 52356-93-1; 2h, 64245-25-6; 2i, 64245-24-5; 2j, 67404-69-7; $CH_3(CH_2)_5C{\equiv}CCl$, 64531-26-6; $CH_3(CH_2)_3C{\equiv}CBr$, 1119-64-8; $CH_3(CH_2)_5C{\equiv}Br$, 38761-67-0; $CH_3(CH_2)_3C{\equiv}CI$, 1119-67-1; $CH_3(CH_2)_5C{\equiv}CI$, 81438-46-2; c-$C_5H_9C{\equiv}CBr$, 123240-90-4; $PhC{\equiv}CBr$, 932-87-6; $CH_3CH(CH_3)C{\equiv}CI$, 89323-83-1; $CH_3C(CH_3)_2C{\equiv}CI$, 23700-63-2; $ChxC{\equiv}CI$, 52788-64-4; $CH_3(CH_2)_3CH{=}CHBChx_2$, 37609-12-4; $CH_3(CH_2)_5CH{=}CHBChx_2$, 62072-20-2; $CH_3(CH_2)_3CH{=}CClBChx_2$, 87393-79-1; $CH_3(CH_2)_5CH{=}CClBChx_2$, 87393-82-6; $CH_3(CH_2)_3CH{=}CBrBChx_2$, 87393-80-4; $CH_3(CH_2)_5CH{=}CBrBChx_2$, 87393-83-7; $CH_3(CH_2)_3CH{=}CIBChx_2$, 87393-81-5; $CH_3(CH_2)_5CH{=}CIBChx_2$, 87393-84-8; $CH_3(CH_2)_3CH{=}CH$(9-BBN), 69322-45-8; $CH_3(CH_2)_5CH{=}CH$(9-BBN), 73062-42-7; $CH_3(CH_2)_3CH{=}CCl$(9-BBN), 87411-94-7; $CH_3(CH_2)_5CH{=}C$Cl(9-BBN), 87393-86-0; $CH_3(CH_2)_3CH{=}CBr$(9-BBN), 67826-84-0; $CH_3(CH_2)_5CH{=}CBr$(9-BBN), 87393-87-1; $CH_3(CH_2)_3CH{=}CI$(9-BBN), 87393-85-9; $CH_3(CH_2)_5CH{=}CI$(9-BBN), 87393-88-2; Chx_2BH, 1568-65-6; 9-BBN, 280-64-8.

Supplementary Material Available: ^1H NMR spectrum of compound [Z]-1-bromo-2-cyclopentyl-1-ethene (2d) (1 page). Ordering information is given on any current masthead page.