Organoboranes. 37. Synthesis and Properties of (Z)-1-Alkenylboronic Esters

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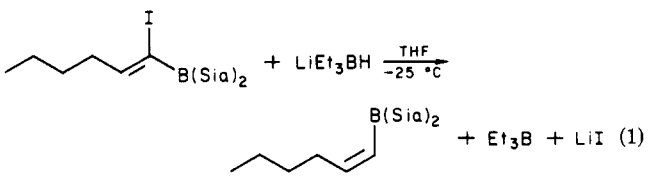
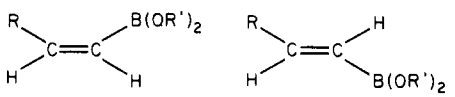
The treatment of (Z)-(1-bromo-1-alkenyl)boronic esters, readily obtained by the hydroboration of 1-bromo-1-alkynes with $BHBr_2{\cdot}SMe_2$ followed by alcoholysis, with potassium triisopropoxyborohydride in ether affords the (Z)-1-alkenylboronic esters cleanly in high chemical yields and excellent stereochemical purities. The isomeric (E)-1-alkenylboronic esters are readily obtained by the hydroboration of 1-alkynes with $BHBr_2{\cdot}SMe_2$, followed by alcoholysis. The spectral properties of the Z and E isomers are compared. The ^{13}C NMR spectra indicate essentially the same degree of B–C resonance contribution in these isomeric pairs. UV irradiation results in a rapid photochemical interconversion between the isomers, producing an equilibrium of 9 parts of E to 1 part of Z isomer.

Alkenylboranes are highly important synthetic intermediates.[2-5] Among the several possible structural types, (E)-1-alkenylboranes are readily obtained by the hydroboration of 1-alkynes and have found extensive applications in organic synthesis.[2] The synthesis of the isomeric (Z)-1-alkenylboranes is less direct and has been achieved by the hydroboration of 1-halo-1-alkynes with a dialkylborane, followed by addition of a hydride to boron, which then transfers with inversion of configuration at the vinylic carbon (eq 1). Lithium triethylborohydride[6] and *tert*-



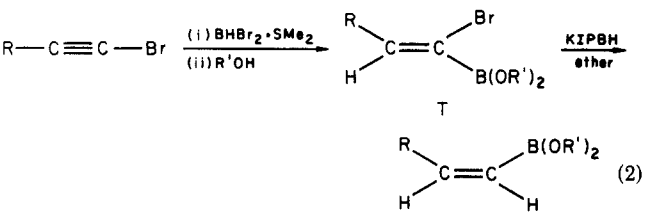
butyllithium[7] have been employed as hydride sources. It was subsequently noted that these (Z)-alkenylboranes easily isomerized to the E isomers on storage at room temperature.[8]

Recent developments in the synthetic utilization of alkyl- and alkenylboronic acids and esters[4,9-11] led us to undertake the development of a convenient method for the preparation of (Z)-1-alkenylboronic acids and esters, 1.



Indeed, they have been prepared earlier by the selective oxidation of (Z)-1-alkenyldisiamylborane[10] and by the dioxyborylation of (Z)-1-alkenyllithium.[12] Recently, a predominant formation of (Z)-alkenylboronic esters by the reaction of lithio(trimethylsilyl)methaneboronic ester with aldehydes was also described (Z:E = 70:30).[4] However, these procedures are not really satisfactory, either because of low chemical yields or because of low stereochemical purities.

We wish to report that the treatment of (Z)-(1-bromo-1-alkenyl)boronic esters with potassium triisopropoxyborohydride[13] (KIPBH) in ether at room temperature offers a rapid procedure for the synthesis of (Z)-1-alkenylboronic esters (1) in high chemical yields and excellent stereochemical purities (eq 2). Since the corresponding



E isomers 2 are also readily obtainable in stereochemically pure form,[14,15] we are now in position to apply these useful intermediates to stereospecific reactions for obtaining products of opposite configuration conveniently. we also report in this paper a study of some of the properties of these 1-alkenylboronic esters.

Results and Discussion

Preparation of (Z)-(1-Bromo-1-alkenyl)boronic Esters. The hydroboration of 1-bromo-1-alkynes with $BHBr_2{\cdot}SMe_2$ in dichloromethane proceeded cleanly to afford (Z)-(1-bromo-1-alkenyl)dibromoboranes (8–10 h). They were converted into the corresponding boronic esters 3 by the procedure developed in this laboratory.[15] The cyclic esters were also prepared by a hydrolysis–esterification sequence (eq 3) or by transesterification of the methyl ester (eq 4). All of the esters were isolated in good yields. Table I provides the pertinent data for these compounds.

Preparation of (Z)-1-Alkenylboronic Esters. Preliminary experiments indicated that KIPBH was far superior to *t*-BuLi or $LiEt_3BH$ for effecting the necessary

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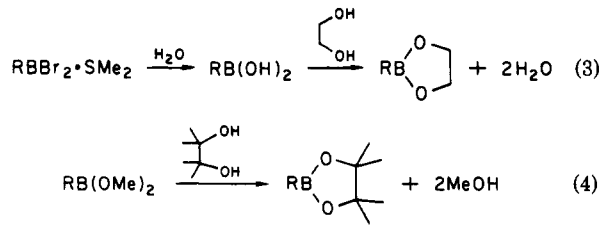
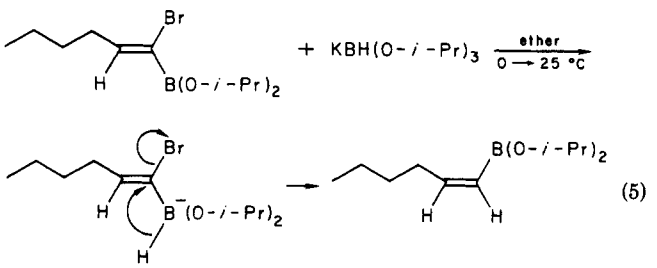


(3)

(4)

hydride transfer in the (1-halo-1-alkenyl)boronic esters. The byproduct, isopropyl borate, $(i\text{-PrO})_3B$, is readily removed from the desired products.

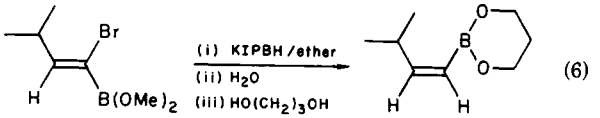
In fact, diisopropyl (Z)-(1-bromo-1-alkenyl)boronates were smoothly converted to the diisopropyl (Z)-1-alkenylboronates by KIPBH in ether or THF. Potassium bromide started precipitating at early stages of KIPBH addition, indicating a rapid reaction. The reaction was complete in 0.5 h (see Experimental Section). The product was isolated simply by removing the precipitated potassium bromide, followed by fractionation. Obviously, the reaction involves a H^- transfer from KIPBH to the boronate ester, followed by H^- migration from boron to the vinylic carbon (eq 5).



(5)

Treatment of dimethyl (Z)-(1-bromo-1-alkenyl)boronate with KIPBH results in scrambling of the ester groups. However, such scrambling rarely causes difficulties.

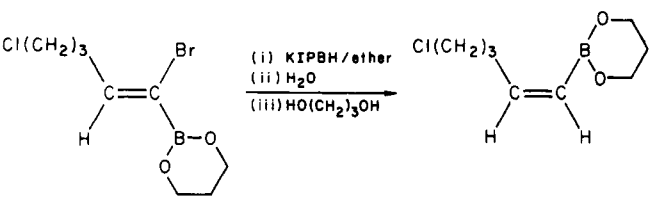
The cyclic esters, particularly the pinacol ester, had a distinct advantage in the ease of workup. $(i\text{-PrO})_3B$ could be simply removed by washing the ether solution of the reaction mixture with water, selectively hydrolyzing $(i\text{-PrO})_3B$ and extracting the components into water, while the pinacol ester remained in the ether layer, unaffected. Although the ethylene and trimethylene glycol esters were partially hydrolyzed during the workup, the resulting boronic acid–ester mixture also remained in the ether phase and could be readily reesterified by treatment with the corresponding diol prior to distillation. With the same procedure, methyl esters could be converted to cyclic esters during the workup stage (eq 6). The yield and analytical



(6)

data for the various (Z)-1-alkenylboronic esters prepared are given in Table II. Since KIPBH is highly inert toward alkyl halides,[16] (Z)-(1-bromo-5-chloro-1-pentenyl)boronic ester was readily converted into (Z)-(5-chloro-1-pentenyl)boronic ester in 89% yield (eq 7).

As seen from Table II, all of the (Z)-1-alkenylboronic esters were obtained in excellent stereochemical purities. The stereochemical purities were determined by GC analysis, except in the case of acyclic esters, which decomposed partially under the conditions employed for the analysis. In those cases, ^{13}C NMR was employed. The Z and E isomers of 1-alkenylboronic esters separated nicely



(7)

on an SE-30 column. Since the Z isomers had lower boiling points than the E isomers, the former had shorter retention times. As low as 0.1–0.2% of the minor isomer could be detected. The ^{13}C NMR method involved monitoring the peak heights of the allylic carbon peaks [C(3)] that were distinctly separate ($\Delta\delta \approx 3$–4 ppm) for the two isomers. The limit of detectability was ~3% by ^{13}C NMR.

The (E)-1-alkenylboronic esters needed for the purpose of comparison were prepared as described earlier.[15]

The (Z)-1-alkenylboronic esters prepared in this study are stable without detectable isomerization when stored for a week at room temperature under nitrogen. However, on prolonged storage (1–3 months), small amounts (0.3–2.3%) of isomerization were observed in several samples.

Spectral Properties of (Z)- and (E)-1-Alkenylboronic Esters. (a) IR. The out-of-plane deformation vibrations of (Z)-1-alkenylboronic esters appear at 730–780 cm^{-1} as single or double broad absorption bands, as compared with a single peak at 1000–1005 cm^{-1} for the E compounds.[17] The double-bond stretching vibration was observed at 1640–1650 cm^{-1} for the E and at 1630–1635 cm^{-1} for the Z esters. This difference of 10–15 cm^{-1} between the E and Z isomers is the same as that observed for simple E- and Z-disubstituted alkenes.[18]

(b) ^1H NMR. In ^1H NMR, the C(1) and C(2) protons of the Z and E isomers show distinctly different patterns. They are well-resolved ABX patterns for the E isomers and unresolved multiplets for the Z isomers (J_{trans} = 17–18 Hz and J_{cis} = 13–14 Hz[19]). The data are given in Table III.

(c) ^{13}C NMR. The ^{13}C NMR data are given in Table III. The chemical shifts of C(2) of the Z and E isomers do not differ significantly, probably indicating that the B–C resonance contribution does not differ significantly in these compounds.[20] In several compounds C(3) and C(4) resonated close to each other, and the assignment was difficult. This problem was solved by assuming that there is consistency in the difference in the chemical shifts of C(3) in the Z and E isomers. Thus when the Z compounds were compared with the corresponding E isomers, C(3) was shielded by 3.1–3.9 ppm for the former (Table III). Thus $\Delta\delta_{C(3)} = \delta[C(3)_Z] - \delta[C(3)_E] = -3.1$ to -3.9 ppm. At the same time, $C(4)_Z$ was always found deshielded slightly $\Delta\delta_{C(4)} = \delta[C(4)_Z] - \delta[C(4)_E] = 1.1$–1.3 ppm. Such an assumption seems to be reasonable because a similar pattern is observed in the isomeric pairs of simple 1,2-disubstituted alkenes; the carbons α to the double bond are always shielded by 5–6 ppm in the Z isomers than in the E isomers.[21]

Photochemical Interconversion of (Z)- and (E)-1-Alkenylboronic Esters. It has been repoted that (E)-1-heptenylboronic ester, on direct UV irradiation, failed

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Table I. Preparation of (*Z*)-(1-Bromo-1-alkenyl)boronic Esters, (*Z*)-RCH=CBrB(OR')$_2$

R	(OR')$_2$	bp, °C/torr	n^{20}D	isolated yield, %	analysis: calcd C	calcd H	calcd B	calcd Br	found C	found H	found B	found Br
C_4H_9	$(OMe)_2$	46-48/0.1	1.4644	84	40.89	6.87	4.61	34.01	41.07	6.93	4.79	33.76
C_4H_9	$(O\text{-}i\text{-}Pr)_2$	64-65/0.2	1.4448	87	49.52	8.31	3.71	27.46	49.34	8.37	3.41	27.21
C_4H_9	$-O(CH_2)_3O-$	86-88/0.1	1.4943	94	43.77	6.53	4.38	32.36	43.83	6.79	4.12	32.57
C_4H_9	$-O(CH_2)_2O-$	76-78/0.1	1.4864	91	41.25	6.06	4.65	34.31	41.13	6.00	4.81	34.25
C_4H_9	$-O[C(CH_3)_2]_2O-$	84-86/0.1	1.4723	95	49.86	7.67	3.74	27.65	49.70	7.84	3.92	27.44
$(CH_3)_2CH$	$(OMe)_2$	77-79/14	1.4558	82	38.06	6.39	4.89	36.17	38.13	6.37	4.75	36.12
$(CH_3)_2CH$	$-O(CH_2)_3O-$	64-66/0.1	1.4921	86	41.25	6.06	4.65	34.31	41.26	5.79	4.44	34.07
$Cl(CH_2)_3$	$-O(CH_2)_3O-$	112-114/0.1	1.5175	89	35.94	4.90	4.04		36.01	4.84	3.84	

Table II. Preparation of (*Z*)-1-Alkenylboronic Esters, (*Z*)-RCH=CHB(OR')$_2$

R	(OR')$_2$	bp, °C/torr	n^{20}D	isolated yield, %	analysis: calcd C	calcd H	calcd B	found C	found H	found B	^{11}B NMR, δ
C_4H_9	$(OMe)_2$	78-90/15[a]									27.7
C_4H_9	$(O\text{-}i\text{-}Pr)_2$	86-88/14	1.4158	89	67.94	11.88	5.10	68.08	12.14	4.83	27.4
C_4H_9	$-O(CH_2)_3O-$	98-99/13	1.4528	94	64.32	10.20	6.43	64.27	10.55	6.29	26.7
C_4H_9	$-O(CH_2)_2O-$	79-82/13	1.4462	89	62.39	9.82	7.02	62.04	9.73	6.94	30.5
C_4H_9	$-O[C(CH_3)_2]_2O-$	97-98/13	1.4353	92	68.54	11.03	5.15	68.63	11.13	5.02	30.0
$(CH_3)_2CH$	$-O(CH_2)_3O-$	76-77/13	1.4490	74	62.39	9.82	7.02	62.40	9.79	6.95	26.6
$Cl(CH_2)_3$[b]	$-O(CH_2)_3O-$	56-58/0.05	1.4768	94	50.98	7.49	5.74	51.20	7.43	5.49	26.5

[a] Contaminated with the isopropyl esters formed by exchange with the reagent. [b] Anal. Calcd: Cl, 18.81. Found: Cl, 18.65.

Table III. ^{1}H NMR and ^{13}C NMR Spectral Data of the (*Z*)- and (*E*)-1-Alkenylboronic Esters, RCH=CHB(OR')$_2$

R	(OR')$_2$	isomer	^{1}H NMR data, δ: C(1)H	^{1}H NMR data, δ: C(2)H	^{13}C NMR data,[a] δ: C(2)	C(3)	C(4)	Δδ[C(3)] Z − E	Δδ[C(4)] Z − E
C_4H_9	$(OMe)_2$	*E*	5.55 (d)	6.58 (d/t)	152.4	35.3	30.5		
C_4H_9	$(O\text{-}i\text{-}Pr)_2$	*Z*	5.42 (d)	6.0-6.45 (m)	148.9	32.1	31.7	−3.2	1.1
		E	5.50 (d)	6.60 (d/t)	151.4	35.3	30.6		
C_4H_9	$-O(CH_2)_3O-$	*Z*	5.20 (d)	6.0-6.6 (m)	152.3	31.2	31.8	−3.9	1.1
		E	5.50 (d)	6.6 (d/t)	151.3	35.1	30.7		
C_4H_9	$-O(CH_2)_2O-$	*Z*	5.35 (d)	6.2-6.7 (m)	155.7	31.9	31.5	−3.4	1.2
		E	5.40 (d)	6.7 (d/t)	154.9	35.3	30.3		
$(CH_3)_2CH$	$-O(CH_2)_3O-$	*Z*	5.04 (d)	5.8-6.3 (m)	149.6	28.9	32.6	−3.5	1.2
		E	5.26 (d)	6.48 (d/d)	148.7	32.4	31.4		
$Cl(CH_2)_3$	$-O(CH_2)_3O-$	*Z*	5.25 (d)	5.9-6.5 (m)	159.2	30.1	22.9	−3.1	1.3
		E			157.8	33.2	21.6		

[a] The C(1) was observed as a very broad peak at 115-125 ppm in most cases.

to yield any detectable change in its IR spectrum.[17] It has also been reported that (*Z*)-(2-chloro-2-phenyl-1-ethenyl)boronic ester does not isomerize on UV irradiation, attributed to a large energy difference between the two isomers.[22] Our spectral study, however, suggested that a large steric interaction between a dioxyboryl group and a β-cis substitutent is unlikely.

In fact, when the trimethylene glycol esters of (*Z*)- and (*E*)-1-hexenylboronic acid were separately irradiated in quartz tube under an argon atmosphere by a high-pressure Hg lamp with a Vycor filter, isomerization took place and the ratio of *Z*:*E* = 1:9 was reached in approximately 20 h from both isomers with high material balance. Evidently, the interconversion between the *Z* and *E* isomers of 1-alkenylboronic esters is a facile primary process under direct photolysis conditions.

Experimental Section

Materials. The starting 1-bromo-1-alkynes were prepared by the reported procedure[23] and carefully fractionated to be free from the parent 1-alkynes. Solutions of $BHBr_2{\cdot}SMe_2$ in dichloromethane[24] and KIPBH in ether[13] were prepared by the procedures developed in this laboratory. All of the solvents were of analytical reagent grade and were stored over molecular sieves. Manipulation of borane reagents was done under a nitrogen atmosphere by using hypodermic syringes and double-ended needles.[25]

Gas chromatographic analyses were performed with a Hewlett-Packard Model 5750A instrument coupled with a H-P 3390A digital integrator. SE-30 (5%) on Chromosorb W (60–80 mesh) column (9 ft × 0.25 in.) was used. The ^{1}H NMR spectra were recorded on Perkin-Elmer R-32 (90 MHz) and Varian T-60 spectrometers. ^{11}B NMR and ^{13}C NMR spectra were recorded on a Varian FT-80A spectrometer. Chemical shift values, all in $CDCl_3$, are given in parts per million (δ) relative to Me_4Si in ^{1}H and ^{13}C NMR and relative to $BF_3{\cdot}OEt_2$ in ^{11}B NMR. IR spectra (neat liquid) were recorded with a Perkin-Elmer 137 spectrophotometer.

Preparation of (*Z*)-(1-Bromo-1-alkenyl)boronic Esters. The procedure was essentially as described earlier.[15] Preparation of dimethyl (*Z*)-(1-bromo-1-hexenyl)boronate is representative. 1-Bromo-1-hexyne (100 mmol) was hydroborated with $BHBr_2{\cdot}SMe_2$ (100 mmol) in dichloromethane. The reaction was complete in about 8 h. Pentane (100 mL) was added. While the flask was cooled (ice–salt bath), methanol (400 mmol) was slowly introduced into the flask with rapid stirring. The stirring was continued for

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an additional 15 min at 0 °C, and the pentane layer was separated from the heavy methanol layer containing most of the HBr evolved in the reaction (the pentane layer may still contain some dissolved HBr, which will go off with the solvent). The methanol layer was extracted with pentane (2 × 20 mL) and the combined pentane extract, upon evaporation of the solvent, followed by fractionation, gave pure dimethyl (*Z*)-(1-bromo-1-hexenyl)boronate. The yield and physical and spectral data are summarized in Table I.

Alternatively, the cyclic esters were prepared by the initial hydrolysis of the hydroboration product, followed by the esterification as exemplified below. 1-Bromo-1-hexyne (100 mmol) was hydroborated with $HBBr_2 \cdot SMe_2$ as described earlier. The product was added to about 100 g of ice water mixture with stirring. After the solution was stirred for an additional 5–10 min, ether (70 mL) was added to dissolve partially solidified boronic acid. The aqueous phase was extracted with ether (2 × 25 mL), and the combined ether extracts were washed with brine (3 × 50 mL) and dried over anhydrous $MgSO_4$. The almost colorless boronic acid, left after the removal of ether, was suspended in pentane (100 mL), and trimethylene glycol (105 mmol) was added to it. Stirring the reaction mixture resulted in an almost instantaneous separation of water. The pentane layer was dried over anhydrous $MgSO_4$. Solvent evaporation and fractionation gave the pure ester.

Preparation of (*E*)-1-Alkenylboronic Esters. These compounds were prepared as described in the earlier paper.[15] Table III summarizes the spectral data for these esters.

Preparation of (*Z*)-1-Alkenylboronic Esters. Two procedures were employed, one involving direct isolation and the other involving the hydrolysis of $(i\text{-PrO})_3B$ and a partial hydrolysis of the product, followed by reesterification using a glycol. Preparation of diisopropyl (*Z*)-1-hexenylboronate is representative of the former procedure.

To an ice-cooled solution of diisopropyl (*Z*)-(1-bromo-1-hexenyl)boronate (25 mmol) in ether (25 mL) in a 100-mL round-bottom flask was added, with stirring, an ethereal solution of KIPBH (25 mmol) over a period of 5 min. The cold bath was then removed, and the stirring was continued at room temperature for 0.5 h. The ^{11}B NMR indicated the completion of the reaction. The solid KBr was removed by centrifugation. The solid KBr was washed twice with ether (20 mL), and the washings were combined with the original mother liquor. Ether was stripped off, and diisopropyl (*Z*)-1-hexenylboronate was fractionated from $(i\text{-PrO})_3B$ by using a Vigreaux column. After a subsequent distillation, an analytically pure sample was obtained.

The preparation of trimethylene (*Z*)-(5-chloro-1-pentenyl)boronate is typical of the hydrolysis–reesterification procedure. The reaction of trimethylene (*Z*)-(1-bromo-5-chloro-1-pentenyl)boronate with KIPBH was done exactly as described above. Then water (10 mL) was added to the reaction mixture at 0 °C, and the mixture was stirred for 10 min to hydrolyze the unwanted $(i\text{-PrO})_3B$. The ether layer was separated, and the aqueous layer was washed with ether (2 × 15 mL).[26] The combined ether extract was washed with brine. Ether was removed by distillation, and trimethylene glycol (12.5 mmol, 50%) was added to the residue, followed by hexane (100 mL). About 50–60 mL of the solvent was distilled out to remove isopropyl alcohol and water. On cooling, the residual hexane layer became turbid, indicating the presence of excess diol, which was easily removed by adding $CaCl_2$ (2 g) and stirring the mixture for 1 h. Decantation and distillation gave the pure product.

Photochemical Interconversion of (*Z*)- and (*E*)-1-Hexenylboronic Ester. A solution of trimethylene (*Z*)-1-hexenylboronate (5 mL, 0.11 M in spectral grade hexane) containing a known amount of dodecane as GC internal standard was bubbled with Ar for 15 min in a quartz tube and irradiated by using a high-pressure Hg lamp through a Vycor filter. Aliquots were analyzed by GC at various time intervals. The time of irradiation, ratio of *Z*:*E*, and the total recovery are as follows: 8 h, 8:92, 99.7%; 18 h, 10:90, 96.7%. Under the same conditions the corresponding *E* isomer also isomerized: 8 h, 13:87, 99.6%; 18 h, 13:87, 96.8%.

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Registry No. KIPBH, 42278-67-1; (*Z*)-$(C_4H_9)CH{=}CHB(OMe)_2$, 91083-19-1; (*Z*)-$(C_4H_9)CH{=}CHB(O\text{-}i\text{-}Pr)_2$, 91083-20-4; (*Z*)-$(C_4H_9)CH{=}CHBO(CH_2)_3O$, 91083-21-5; (*Z*)-$(C_4H_9)CH{=}CHBO(CH_2)_2O$, 91083-22-6; (*Z*)-$(C_4H_9)CH{=}CHBO[C(CH_3)_2]_2O$, 91083-23-7; (*Z*)-$(CH_3)_2CHCH{=}CHBO(CH_2)_3O$, 91083-24-8; (*Z*)-$Cl(CH_2)_3CH{=}CHBO(CH_2)_3O$, 91083-25-9; (*E*)-$(C_4H_9)CH{=}CHB(OMe)_2$, 91083-26-0; (*E*)-$(C_4H_9)CH{=}CHB(O\text{-}i\text{-}Pr)_2$, 91083-27-1; (*E*)-$(C_4H_9)CH{=}CHBO(CH_2)_3O$, 91083-28-2; (*E*)-$(C_4H_9)CH{=}CHBO(CH_2)_2O$, 91083-29-3; (*E*)-$(CH_3)_2CHCH{=}CHBO(CH_2)_3O$, 91083-30-6; (*E*)-$Cl(CH_2)_3CH{=}CHBO(CH_2)_3O$, 91110-41-7; (*Z*)-$(C_4H_9)CH{=}CBrB(OMe)_2$, 91083-31-7; (*Z*)-$(C_4H_9)CH{=}CBrB(O\text{-}i\text{-}Pr)_2$, 91083-32-8; (*Z*)-$(C_4H_9)CH{=}CBrBO(CH_2)_3O$, 91083-33-9; (*Z*)-$(C_4H_9)CH{=}CBrBO(CH_2)_2O$, 91083-34-0; (*Z*)-$(C_4H_9)CH{=}CBrBO[C(CH_3)_2]_2O$, 91083-35-1; (*Z*)-$(CH_3)_2CH{=}CBrB(OMe)_2$, 91083-36-2; (*Z*)-$(CH_3)_2CH{=}CBrBO(CH_2)_3O$, 91083-37-3; (*Z*)-$Cl(CH_2)_2CH{=}CBrBO(CH_2)_3O$, 91083-38-4; $(C_4H_9)C{\equiv}CBr$, 1119-64-8; $(CH_3)_2CHC{\equiv}CBr$, 54105-74-7; $Cl(CH_2)_3C{\equiv}CBr$, 87750-57-0; $HO(CH_2)_3OH$, 57-55-6; $HO(CH_2)_2OH$, 107-21-1; $HO[C(CH_3)_2]_2OH$, 76-09-5; MeOH, 67-56-1; $(CH_3)_2CHOH$, 67-63-0; $BHBr_2 \cdot SMe_2$, 55671-55-1.

(26) Addition of NaCl is recommended when the phase separation is not clear.