Diastereo- and Enantioselective Synthesis of *syn*-α-Vinylchlorohydrins and *cis*-Vinylepoxides

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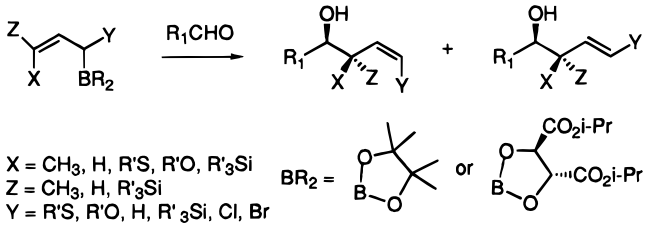
A new method to generate chiral *syn*-vinylchlorohydrins and *cis*-vinyloxiranes is reported. Reaction of (α-haloallyl)lithiums with methoxy-9-BBN or Ipc_2BOMe followed by treatment with $BF_3{\cdot}OEt_2$ leads to (*Z*)-(γ-haloallyl)boranes which react with aldehydes to yield *cis*-vinylepoxides (de ≥ 90%) upon oxidative workup. Alternatively, addition of ethanolamine to the allylboration product yields *syn*-α-halohydrins (de ≥ 90%) that are also easily cyclized to *cis*-vinylepoxides. Extension of this protocol using [(*Z*)-γ-chloroallyl]$BIpc_2$ leads to chiral *syn*-α-chlorohydrins and *cis*-vinylepoxides in high de (≥90%) and ee (90−99%). Enantioselectivity of reactions of chiral (*Z*)-(γ-chloroallyl)boranes with aldehydes are more sensitive to reaction conditions than enantioselectivity of reactions of other α-or γ-substituted allylboranes. The effects of proportion of $BF_3{\cdot}OEt_2$ and the relative efficacies of $LiNR_2$ bases on diastereo- and enantioselectivity of the chloroallylation are reported.

Introduction

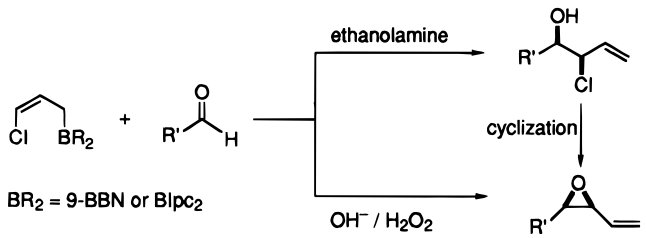
Addition of allyl organometallic reagents to carbonyl compounds is an important method for the stereocontrolled formation of carbon−carbon bonds,[1] and allylic organoboranes are particularly versatile members of this class of reagents (Scheme 1).[2−6]

We have applied the allylboration of aldehydes to the preparation of *syn*-α-halohydrins and *cis*-vinylepoxides (Scheme 2). When boron possesses chiral ligands, the reaction sequence is enantioselective. The present route to *syn*-chlorohydrins[7] is superior to other methods such as asymmetric reduction of α-halo-substituted ketones[8] and opening of chiral epoxides.[7a] Under our allylboration conditions, *syn*-α-halohydrins are easily converted to vinyloxiranes.[9−13] The primary advantage of the new methodology is in the ease of preparation of chiral *cis*-vinyloxiranes which are obtainable only *via* Sharpless epoxidation of (*Z*)-allylic alcohols. Although Sharpless epoxidation proceeds with high enantioselectivity with (*E*)-allylic alcohols it gives variable enantioselectivity with the (*Z*)-isomers.[14]

Scheme 1. Allylboration Employing α- and γ-Substituted Allylic Boron Compounds



Scheme 2



Results and Discussion

Synthesis of (*Z*)-(γ-chloroallyl)boranes. Sterically encumbered trialkylboranes normally react with α-substituted allyllithiums at the less substituted position to provide the corresponding γ-substituted allylboron ate complex.[15] By contrast, (α-chloroallyl)lithium, generated *in situ* from allyl chloride and LDA, reacts with borate esters to produce ate complexes which yield (α-chloroallyl)boronate esters by dealkoxylation.[16] The latter react with aldehydes to yield γ-chlorohydrins. If the borate reagent contains sterically demanding ligands, reaction with (α-chloroallyl)lithium leads to (α- and (γ-chloroallyl)-boronates (Scheme 3).[17b] Sterically less demanding 9-methoxy-9-BBN reacts with (α-chloroallyl)lithium to give predominantly the (α-chloroallyl)boron ate complex.[18] Regioselectivity in allylborane formation thus

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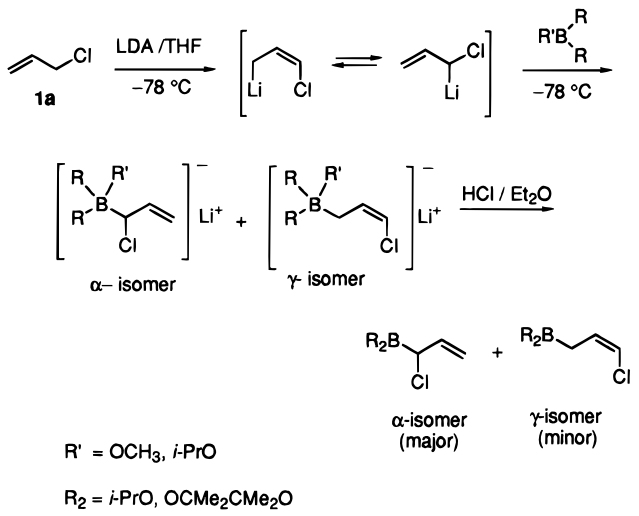
Scheme 3



appears to be influenced by the steric requirements of the boron substituents.

We reinvestigated the reaction between (α-chloroallyl)-lithium and 9-methoxy-9-BBN. At −78 °C BF_3·OEt_2-promoted decomposition of the resultant ate complex **3** produces a mixture of chloroallylboranes **4** and **5** which upon reaction with aldehydes and treatment with ethanolamine[19] yields *syn*-chlorohydrins **7** and γ-chlorohydrins **6** in a ratio of 89−85:11−15 (de 84−88%, Scheme 4; Table 1). The inferior diastereoselectivity is attributed to the formation of minor amounts of (*E*)-(γ-chloroallyl)-borane **5c** along with major (*Z*)-γ-isomer **5a**. Lowering the temperature (−95 °C) for the formation and decomposition of the ate complex improves the regio- and diastereoselectivities (Table 1). Use of a more sterically demanding base, lithium dicyclohexylamide [LiN(c-$Hex)_2$], further improves regioselectivity in favor of the *syn*-chlorohydrin **7** and dramatically improves diastereoselectivity (de = 98%) (Table 2, entry 1). Formation of *syn*-chlorohydrins **7** requires (*Z*)-(γ-chloroallyl)borane **5a** whereas **6** is derived from the (α-chloroallyl)borane **4**.

Regio- and stereoselectivities of reactions of the reagent formed from (α-chloroallyl)lithium, **2a**, and BF_3·OEt_2 are relatively insensitive to reaction conditions (Table 2, entries 1−6). Reaction of (α-chloroallyl)lithium with **2a** at −95 °C followed by demethoxylation of the complex with BF_3·OEt_2 at −95 °C and reaction with benzaldehyde at temperatures between −41 °C and −95 °C consistently yields *syn*-chlorohydrin **7** with 99:1 diastereoselectivity, suggesting **5a** is configurationally stable over this temperature range.

We anticipated that introduction of a bulky chiral auxiliary would improve regioselectivity and yield chiral *syn*-chlorohydrins (Scheme 5). Use of Brown's chiral auxiliary, (−)-*B*-methoxydiisopinocampheylborane (^{d}Ipc_2-BOMe, **2b**) in the chloroallylboration reaction (−78 °C) with LDA as base enhances the regioselectivity (**13**:**12**, ratio 98:2), but the diastereoselectivity (*syn vs anti*) is only 91:9 (Table 2, entry 8). When the entire reaction sequence is conducted at −95 °C using LiN(c-$Hex)_2$, regioselectivity increases to the point that no γ-chlorohydrin is detectable and the de increases to 98% (Table 2, entries 13−16).

Preparation of (chloroallyl)borane **13a** at −95 °C, followed by warming to room temperature, stirring for 2 h, and recooling to −95 °C for 0.5 h, before reaction at −95 °C with benzaldehyde (Table 2, entry 12), did not lower diastereoselectivity. This experiment provides additional evidence that (γ-chloroallyl)boranes are configurationally stable. Similarly, no decrease in diastereoselectivity is observed when **13a** is prepared at −95 °C, warmed to −78 °C, and reacted with PhCHO at the latter temperature (Table 2, entry 15).

The formation of (*Z*)-(γ-chloroallyl)boranes may be due to attack of the boron at the γ-position of (α-chloroallyl)-lithium or *via* rearrangment of an initially formed (α-chloroallyl)borane. Evidence for the formation of (α-chloroallyl)boranes from (α-chloroallyl)lithiums comes from the observation that treatment of (α-chloroallyl)-lithium with methoxy-9-BBN results in a ring-expansion that is most feasible *via* an (α-chloroallyl)boron ate complex.[18] It is well known that decomposition of allylboron ate complexes with Lewis acids such as BF_3·OEt_2 is accompanied by allylic rearrangement.[20] Thus, precedents exist which suggest that (γ-chloroallyl)boranes **5** could arise from BF_3·OEt_2-promoted decomposition of α-ate complexes **4** with a concomitant [1,3]-boron shift (Scheme 4). Since previous reports suggest that the [1,3]-rearrangement of α-methylallyl-9-BBN to (*Z*)- and (*E*)-isomers of crotyl-9-BBN occurs at low temperatures,[21] we examined formation of **4** by low temperature ^{1}H NMR. In initial experiments we were unable to determine if both (α- and (γ-chloroallyl)boranes were present. The driving force for formation of the (*Z*)-(γ-chloroallyl)borane may be due to Lewis base behavior of γ-chlorine.

Haloallylborations with 13. The (*Z*)-halo-substituted allylboranes **13a**−**d** react rapidly with aldehydes at −95 °C to give halohydrins upon ethanolamine workup,[19] and *cis*-vinyloxiranes after oxidative workup.[22] High diastereo- and enantioselectivities are realized in these experiments (Scheme 5; Table 3). Routine oxidation (OH^-/H_2O_2) of the carbon−boron bond[22] lowers optical purities of base-sensitive oxiranes compared to their halohydrin precursors and is not recommended (Table 3, entries 3, 4, 7, and 8). Such oxiranes are best obtained by cyclization of corresponding chlorohydrins in a separate step. We successfully employed K_2CO_3/MeOH or KO-*t*-Bu/THF to generate base-sensitive oxiranes with no diminution of optical purity compared to the chlorohydrin precursors.

The absolute configurations of chlorohydrins, **16** [R = (*E*)-PhCH=CH, c-Hex] obtained from **2b** were determined by hydrogenolysis to alcohols, **21**, of known configuration[23] (Scheme 6). The configurations of the hy-

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Scheme 4

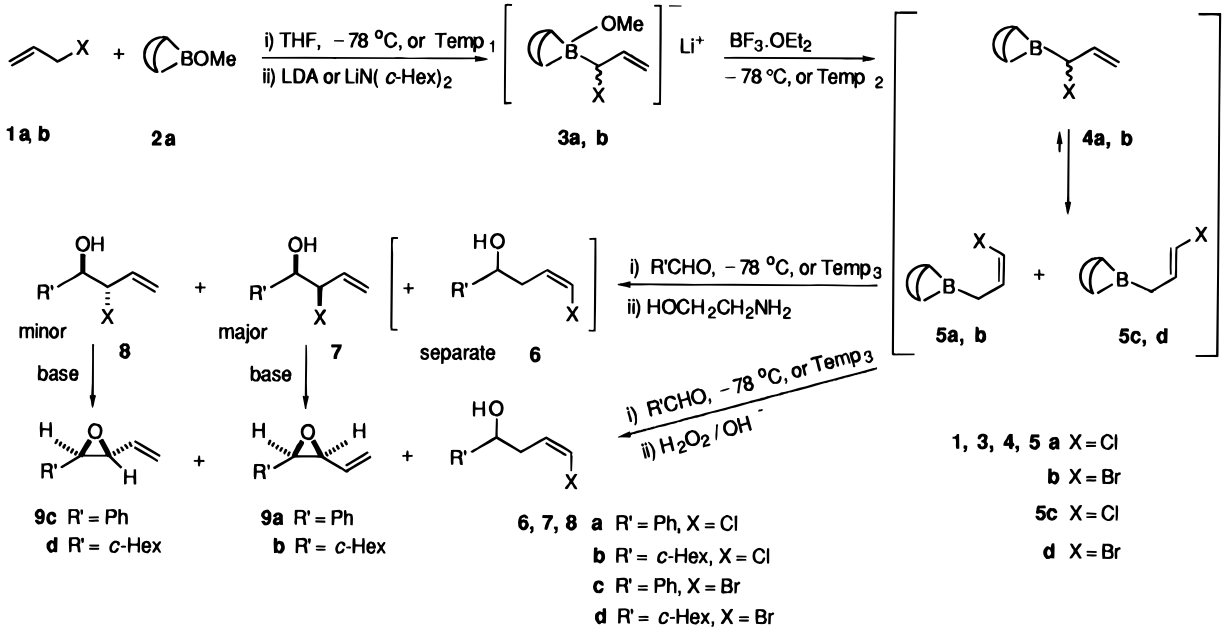

Table 1. Reaction of (Chloroallyl)boranes 4 and 5 with Aldehydes at Low Temperatures[a]

			chlorohydrin[b]		vinyloxirane **9**[c]	
entry	**1**	R′CHO R′ =	yield (%)[d]	α vs γ **7+8:6**	yield (%)[d,e]	*cis vs trans*[f]
1	**1a**	Ph	79	85:15	95	92:8
2	**1a**	$PhCH_2$	86	87:13	97	94:6
3	**1b**	Ph	76	88:12	96	94:6
4	**1b**	c-Hex	78	89:11	97	93:7
5[g]	**1a**	Ph	77	91:9	98	95:5
6[g]	**1a**	c-Hex	76	95:5	98	94:6

[a] Unless noted reactions were carried out at −78 °C, using 1.2 equiv of LDA and 2.6 equiv of $BF_3{\cdot}OEt_2$. [b] Ratios determined by product isolation. [c] Obtained by direct oxidative workup or cyclization of **7** and **8**. [d] Isolated yields. [e] Yields of chlorohydrin cyclization. [f] Ratios determined by ^1H NMR and capillary GC analyses. Capillary GC analyses of chlorohydrins (*syn vs anti*) gave the same ratio. [g] Reactions carried out at −95 °C.

drogenation products **21** (R_1 = $PhCH_2CH_2$, c-Hex) were further established by synthesis from ^{d}Ipc_2B(allyl). The absolute configurations of other halohydrins and vinyloxiranes resulting from γ-haloallylborations using **2b** and **2c** were assigned by analogy with these two correlations.

The enantiopreferences of γ-haloallylborations using **2b** and **2c** are consistent with those for allylboration reagents derived from (+)- and (−)-α-pinene, respectively (Table 3).[24] The enantiopreference observed for (γ-haloallyl)boranes derived from ^{d}Ipc_2BOMe involves *si face* attack, which is in agreement with previous reports,[22a,24] for related reagents (Scheme 7).

Allylborations proceed *via* initial rapid formation of a carbonyl−boron ate complex and rate-determining formation of a new carbon−carbon bond *via* a cyclic six-membered chair transition state. Stereocontrol is manifested during the formation of the new carbon−carbon bond (Scheme 7). Transition states[25a] for this process are expected to be earlier for (γ-haloallyl)borane analogs compared to unsubstituted allylboranes or allylboranes substituted at the γ-position with electron-donating groups since the former are less nucleophilic at the reacting allyl carbon. Thus, although high stereoselection is observed for reactions of (γ-haloallyl)boranes it would be expected to be much more sensitive to temperature and solvent than allylborations with more electron-rich analogs.

In agreement with these expectations reaction of (γ-chloroallyl)borane **13a** with benzaldehyde at −78 °C generates *syn*-chlorohydrin of 78% ee. Lowering the temperature to −95 °C improves the ee to 97% (Table 3, entry 3).

To test the influence of solvent(s) on the enantioselectivity, we added LiN(c-Hex)$_2$ in THF to a mixture of Ipc_2-BOMe and allyl chloride in diethyl ether at −95 °C. Addition of benzaldehyde followed by workup gives α-chlorohydrin of 97% ee. When the same reaction is conducted using only THF, the ee is lowered to 75% (Table 3, entry 4). In contrast, allylborations with unsubstituted allyl- and (*Z*)-(γ-alkoxyallyl)boranes proceed with high enantioselectivity which is independent of solvent and is maximum at −78 °C in THF.[25b]

Reaction of benzaldehyde with (*Z*)-(γ-bromoallyl)boranes **13b, d**, prepared by *in situ* deprotonation of allyl bromide, generated α-bromohydrins with *syn* selectivity of 90:10 when benzaldehyde was added at −78 °C (Table 2, entry 9). The (α/γ-bromoallyl)borane reagent was less regio- and diastereoselective than the analogous (α/γ-chloroallyl)boranes (Table 2, entries 10 and 11). Lower diastereoselectivity is attributed to steric conjestion and lower Lewis base character of the (*Z*)-γ-bromine which increases the proportion of (*E*)-isomer.

Effect of Stoichiometry of $BF_3{\cdot}OEt_2$. Decomposition of allylboron ate complexes usually requires excess $BF_3{\cdot}OEt_2$.[26] Treatment of ate complexes **10, 11** with 1.33 equiv of $BF_3{\cdot}OEt_2$ followed by immediate condensation with aldehydes generates mixtures of chlorohydrin and

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Table 2. Haloallylboration of Benzaldehyde under Different Conditions[a]

entry	X	temp$_1$ (°C)[b]	temp$_2$ (°C)[c]	temp$_3$ (°C)[d]	BF_3·OEt_2 (equiv)	**2**	halohydrin α:γ[e]	epoxide *cis:trans*[f]	ee, % (*cis*)[g]
1	Cl	−95	−95	−95	2.63	**2a**	95:5	99:1	
2[h]	Cl	−95	−95	−95	2.63	**2a**	98:2	95:5	
3	Cl	−95	−95	−78	1.33	**2a**	99:1	99:1	
4	Cl	−95	−95	−62	1.33	**2a**	99:1	99:1	
5	Cl	−95	−95	−41	1.33	**2a**	>99:<1	99:1	
6	Cl	−95	−95	−95	1.33	**2a**	>99:<1	99:1	
7	Cl	−95	−95	−95	1.5	**2a**	96:4	99:1	
8[i]	Cl	−78	−78	−78	2.63	**2b**	98:2	91:9	78
9	Br	−78	−78	−78	2.63	**2b**	96:4	90:10	74
10	Cl	−78	−95	−95	2.63	**2b**	99:1	99:1	88
11	Br	−78	−95	−95	2.65	**2b**	98:2	94:6	86
12	Cl	−95	−95[j]	−95	2.65	**2b**	>99:<1	99:1	87
13	Cl	−95	−95	−95	1.33	**2b**	>99:<1	99:1	98
14	Cl	−95	−95	−95	1.66	**2b**	>99:<1	99:1	97
15	Cl	−95	−95	−78	2.63	**2b**	>99:<1	99:1	86
16	Cl	−95	−95	−78	1.33	**2b**	>99:<1	99:1	85

[a] $LiN(c\text{-}Hex)_2$ was used, unless noted. [b] Temp$_1$, temperature of ate complex formation. [c] Temp$_2$, temperature of ate complex decomposition using BF_3·OEt_2. [d] Temp$_3$, temperature of R′CHO addition. [e] Ratios of α *vs* γ-halohydrins by isolation. *Syn vs anti* ratios of α-halohydrins by capillary GC analysis. This was same as the *cis vs trans* ratios of epoxides. [f] Obtained by cyclization of chlorohydrins. Ratios by ^1H NMR and capillary GC analyses. [g] ee's by GC (Cyclodex B, 30 m × 0.25 mm i.d. column) analyses of *syn*-α-halohydrins and epoxides were identical. [h] Cyclohexanecarboxadehyde was used. [i] LDA was used. [j] After decomposition of ate complex, the reaction was warmed to rt for 2 h, and then recooled to −95 °C for 0.5 h before addition of aldehyde.

vinyloxirane (ratio 90:10). The formation of vinyloxirane may result from the presence of dialkylamine. This procedure is suitable for BF_3·OEt_2-sensitive substrates and products. Use of 2.6 equiv of BF_3·OEt_2 results in exclusive chlorohydrin formation (Table 2). Although excess BF_3·OEt_2 increases the proportion of γ-chlorohydrins, it prevents formation of vinyloxirane by complexation with dialkylamine.

Reactions of **13** with benzaldehyde are more sensitive to the amount of BF_3·OEt_2 (Table 4, entries 3−5) than are reactions with aliphatic aldehydes. For reactions in which LDA is used as the base, lowering the amount of BF_3·OEt_2 from 2.5 equiv to 1.33 equiv increases the ee of chlorohydrin from 84% to the maximum obtained in this work, 95%.

Effect of Structure of $LiNR_2$ Bases on the EE of Chlorohydrins. LDA, $LiN(c\text{-}Hex)_2$, LiTMP, and LiN(c-Hex)*i*-Pr are reported to efficiently metalate allyl chloride.[18] We briefly examined the effect of base on the enantioselectivity of *syn*-chlorohydrin formation (Table 5). With the exception of LDA, which gave lower diastereo- and enanatioselectivities, all bases examined gave chlorohydrin with comparable diastereo- and enantiomeric composition.

Conclusions

In summary, (α-chloroallyl)lithium, generated *in situ*, is trapped by 9-MeO-9-BBN. Subsequent treatment with BF_3·OEt_2 leads to (*Z*)-(γ-chloroallyl)borane **5**, which condenses with aldehydes to yield (±) *syn*-α-chlorohydrins **7** and (±) *cis*-vinyloxiranes **9**.[27] Use of ^{d}Ipc$_2$BOMe or ^{l}Ipc$_2$BOMe in this process leads to (*Z*)-(γ-chloroallyl)boranes **13a**−**d** which yield chiral chlorohydrins and *cis*-vinyloxiranes in high de and ee. A similiar sequence using (bromoallyl)lithium provided chiral *syn*-α-bromohydrins with slightly lower de and ee.

Experimental Section

General Chemical Procedures. THF and diethyl ether were distilled from sodium−benzophenone ketyl. Diisopropylamine, dicyclohexylamine [$(c\text{-}Hex)_2NH$], *N*-isopropylcyclohexylamine, and 2,2,6,6-tetramethylpiperidine were freshly distilled from CaH_2 prior to use. Allyl chloride was freshly distilled over P_2O_5 prior to use. Aldehydes were distilled prior to use. The ^{d}Ipc$_2$BOMe, ^{l}Ipc$_2$BOMe, and 9-BBN were purchased from Aldrich and used without purificaton. Moisture- and air-sensitive reactions were conducted under argon in vacuum-dried glassware. A nitrogen glove-bag was used to weigh moisture-sensitive compounds. Syringes and cannulas were used to transfer air-sensitive reagents.[28] Unless otherwise stated, standard workup refers the combination of organic extracts, washing with ice-cold brine, drying over anhydrous $MgSO_4$, and concentration *in vacuo*. ^1H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively. GC analyses were conducted using a 30-m × 0.25-mm i.d. fused silica column coated with DB-1 with FID detection.

General Procedure for Chloroallylboration of Aldehydes Using Ipc$_2$BOMe *syn*-(1*R*,2*R*)-2-Chloro-1-cyclohexyl-3-buten-1-ol (16a). To a stirred and cooled (−95 °C) mixture of ^{d}Ipc$_2$BOMe (11.5 mmol) and allyl chloride (15 mmol) in anhyd ether (50 mL) was added a solution of $LiN(c\text{-}Hex)_2$ (15 mmol) in THF (25 mL). After stirring for 1 h, BF_3·OEt_2 (30 mmol) was added followed by cyclohexanecarboxaldehyde (11.5 mmol). The reaction was continued at −95 °C for 4 h. All solvents were removed *in vacuo* at rt, and the residue was triturated with *n*-pentane (40 mL) and allowed to settle (12 h). The supernatant was transferred to another predried flask by cannula. The residue was further treated with pentane (2 × 30 mL), and the pentane extracts were combined. Removal of pentane *in vacuo* furnished a semisolid. (For direct oxidative workup, see synthesis of *cis*-vinylepoxides). This residue was dissolved in ether and treated with ethanolamine following the reported procedure.[19] Standard workup followed by flash chromatography (hexane:ether, 95:5) yielded **16a** as a colorless liquid (1.5 g, 72% yield): ^{13}C NMR and ^1H NMR spectral data are in agreement with those reported.[17b] $[\alpha]^{23}_D$ +56.68 (c = 2.41, $CHCl_3$).

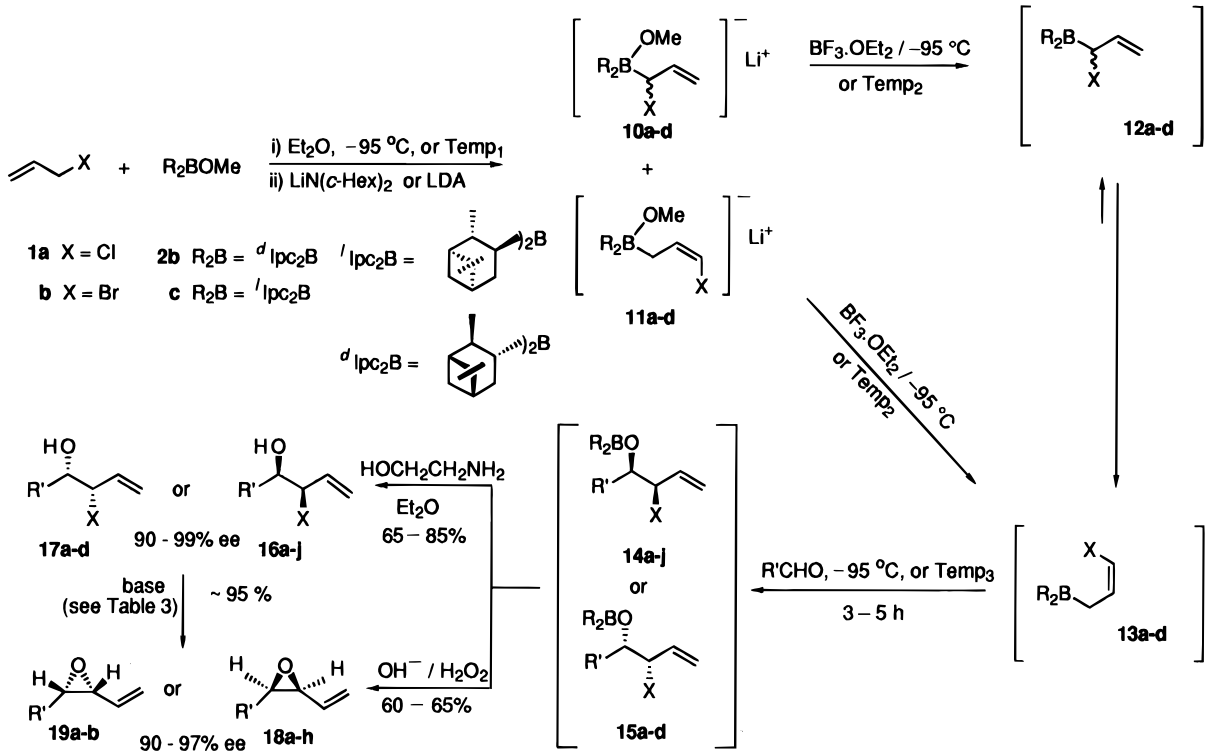
***syn*-(1*R*,2*R*)-2-Chloro-1-phenyl-3-buten-1-ol (16b).** ^1H NMR and ^{13}C NMR spectral data are in agreement with reported values.[17b] $[\alpha]^{23}_D$ +18.86 (c = 1.92, $CHCl_3$).

***syn*-(3*R*,4*R*)-3-Chloro-1-dodecen-4-ol (16c).** IR (film) ν 3406, 1077, 987, 927 cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.94 (ddd, J = 17.6, 10.2, 8.6 Hz, 1H), 5.36 (ddd, J = 17.6, 1, 1 Hz, 1H), 5.23 (ddd, J = 10.2, 1, 1 Hz, 1H), 4.32 (dd, J = 8.7, 5.6 Hz, 1H), 3.65 (m, 1H), 2.17 (d, J = 2.0 Hz, 1H), 1.58−0.86 (m, 17H). ^{13}C NMR ($CDCl_3$) δ 135.45, 118.77, 74.27, 68.85, 34.90, 33.80,

(27) Jayaraman, S.; Hu, S.; Oehlschlager, A. C. *Tetrahedron Lett.* **1995**, *36*, 4765.

(28) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes;* Wiley-Interscience: New York, 1975.

Scheme 5



10-13a X = Cl, R_2B = $^{d}Ipc_2B$
b X = Br, R_2B = $^{d}Ipc_2B$
c X = Cl, R_2B = $^{l}Ipc_2B$
d X = Br, R_2B = $^{l}Ipc_2B$

14, 16a X = Cl, R' = *c*-Hex, R_2B = $^{d}Ipc_2B$
b X = Cl, R' = Ph, R_2B = $^{d}Ipc_2B$
c X = Cl, R' = *n*-C_8H_{17}, R_2B = $^{d}Ipc_2B$
d X = Cl, R' = $PhCH_2$, R_2B = $^{d}Ipc_2B$
e X = Cl, R' = (*E*)-EtCH=CH, R_2B = $^{d}Ipc_2B$
f X = Cl, R' = (*E*)-PhCH=CH, R_2B = $^{d}Ipc_2B$
g X = Cl, R' = *i*-Pr, R_2B = $^{d}Ipc_2B$
h X = Cl, R' = *t*-Bu, R_2B = $^{d}Ipc_2B$
i X = Br, R' = *c*-Hex, R_2B = $^{d}Ipc_2B$
j X = Br, R' = Ph, R_2B = $^{d}Ipc_2B$

15, 17 a X = Br, R' = *c*-Hex, R_2B = $^{l}Ipc_2B$
b X = Br, R' = Ph, R_2B = $^{l}Ipc_2B$
c X = Cl, R' = *c*-Hex, R_2B = $^{l}Ipc_2B$
d X = Cl, R' =Ph, R_2B = $^{l}Ipc_2B$

18 a R' = *c*-Hex **b** R' = Ph
c R' = *n*-C_8H_{17} **d** R' = $PhCH_2$
e R' = (*E*)-EtCH=CH **f** R' = (*E*)-PhCH=CH
g R' = *i*-Pr **h** R' = *t*-Bu
19 a R' = *c*-Hex **b** R' = Ph

29.50, 29.46, 29.20, 25.52, 22.62, 14.01. CIMS *m*/*z* (isobutane, rel intensity) 201 [(M^+ − 18) + 1 (8.3)], 183 (54.3), 165 (68.9), 141 (100). $[\alpha]^{23}_D$ +35.18 (*c* = 2.08, $CHCl_3$). Anal. Calcd for $C_{12}H_{23}ClO$: C, 65.88; H, 10.60. Found: C, 65.78; H, 10.39.

***syn*-(2*R*,3*R*)-3-Chloro-1-phenyl-4-penten-2-ol (16d).** IR (film) *ν* 3416, 1604, 1454, 1085, 989, 932 cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.35−7.23 (m, 5H), 6.03 (ddd, *J* = 16.9, 10.2, 7.5 Hz, 1H), 5.37 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.28 (ddd, *J* = 10.2, 1, 1 Hz, 1H), 4.36 (dd, *J* = 7.7, 4.6 Hz, 1H), 3.94 (m, 1H), 2.97 (dd, *J* = 13.8, 5 Hz, 1H), 2.81 (dd, *J* = 13.8, 7.8 Hz, 1H), 2.18 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) *δ* 137.45, 135.27, 129.43, 126.65, 126.76, 119.08, 75.12, 67.06, 40.31. CIMS *m*/*z* (isobutane, rel intensity) 197 [M^+ + 1 (12.7)], 179 (29.8), 161 (27.5), 151 (4.3), 143 (100), 133 (7.3), 121 (36.7). $[\alpha]^{23}_D$ +15.7 (*c* = 2.88, $CHCl_3$). Anal. Calcd for $C_{11}H_{13}ClO$: C, 67.18; H, 6.66. Found: C, 66.99; H, 6.78.

***syn*-(3*R*,4*R*)-3-Chloro-(5*E*)-1,5-octadien-4-ol (16e).** IR (film) *ν* 3396, 1670, 1640, 1101, 968, 927 cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 5.95−5.80 (m, 2H), 5.49−5.43 (m, 1H), 5.35 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.24 (ddd, *J* = 10.2, 1, 1 Hz, 1H), 4.33 (ddd, *J* = 14.4, 1, 1 Hz, 1H), 4.16 (t, *J* = 6.4 Hz, 1H), 2.06 (m, 2H), 1.88 (m, 1H), 0.99 (t, *J* = 3.4 Hz, 3H). ^{13}C NMR ($CDCl_3$) *δ* 136.80, 134.95, 126.78, 118.96, 75.30, 67.91, 25.18, 13.19. CIMS *m*/*z* (isobutane, rel intensity) 143 [(M^+ − 18) + 1 (100)], 125 (29.8), 107 (57.5). $[\alpha]^{23}_D$ +14.50 (*c* = 2.0, $CHCl_3$). Anal. Calcd for $C_8H_{13}ClO$: C, 59.81; H, 8.16. Found: C, 59.69; H, 8.20.

***syn*-(3*R*,4*R*)-4-Chloro-1-phenyl-(5*E*)-1,5-hexadien-3-ol (16f).** IR (film) *ν* 3395, 1651, 1494, 1449, 1070, 967, 931 cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 7.42−7.23 (m, 5H), 6.71 (d, *J* = 15.1 Hz, 1H), 6.21 (dd, *J* = 15.1, 6 Hz, 1H), 5.98 (ddd, *J* = 16.9, 10.2, 7.8 Hz, 1H), 5.40 (d, *J* = 16.9 Hz, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 4.65−4.39 (m, 2H), 2.41 (s, 1H). ^{13}C NMR ($CDCl_3$) *δ* 136.27, 134.63, 133.12, 128.65, 128.06, 126.99, 126.70, 119.54, 75.20, 67.71. EIMS *m*/*z* (rel intensity) 208 [M^+ (4.3)], 172 (21), 133 (100), 115 (26.5), 103 (8.1), 91 (5.5), 77 (12), 55 (12.7). HRMS Calcd for $C_{12}H_{13}ClO$: 208.0655. Found: 208.0655.

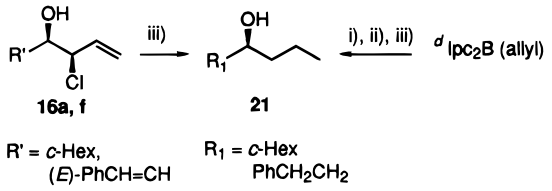
***syn*-(3*R*,4*R*)-4-Chloro-2-methyl-5-hexen-3-ol (16g).** IR (film) *ν* 3363, 1651, 1416, 1087 cm^{-1}. ^1H NMR ($CDCl_3$) *δ* 5.97 (ddd, *J* = 16.9, 10.2, 6.8 Hz, 1H), 5.37 (ddd, *J* = 16.9, 1, 1 Hz, 1H), 5.24 (ddd, *J* = 10.2, 0.7, 0.7 Hz, 1H), 4.50 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.36 (dd, *J* = 8.0, 3.6 Hz, 1H), 2.05 (d, *J* = 6.2 Hz, 1H), 1.87 (m, 1H), 0.97 (dd, *J* = 9.9, 6.8 Hz, 6H). ^{13}C NMR ($CDCl_3$) *δ* 135.75, 118.4, 78.90, 67.45, 31.02, 19.67, 16.47. CIMS *m*/*z* (isobutane, rel intensity) 149 [(M^+ + 1 (12.3)], 131 (100). $[\alpha]^{23}_D$ +55.0 (*c* = 2.0, $CHCl_3$). Anal. Calcd for C_7H_{13}-OCl: C. 56.57; H, 8.82. Found: C, 56.72; H, 8.77.

Table 3. Haloallylboration of Aldehydes with Reagents 13a-d[a]

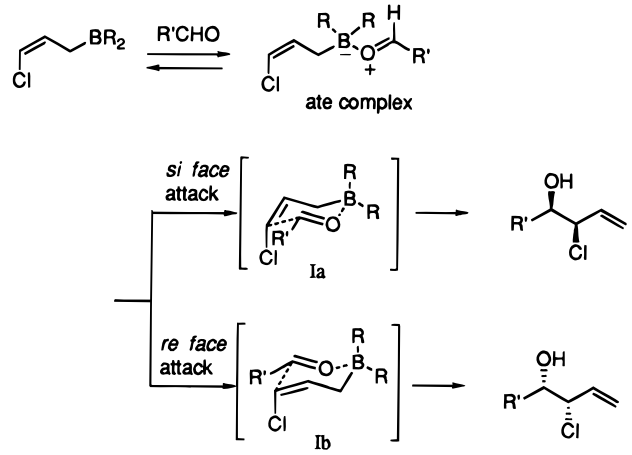
			syn-halohydrin,			*cis*-vinyloxirane[b]		
entry	R′CHO R′ =	**1**	**2**	yield, %[c]	ee, %[d]	yield, %[c]	ee, %[d]	*cis*/*trans*[e]
1	*n*-C_8H_{17}	**1a**	**2b**	70	98	95	98[f]	99:1
2	*i*-Pr	**1a**	**2b**	68	95	99	95[f]	98:2
3	Ph	**1a**	**2b**	78	98	96	97	98:2
4[g]	Ph	**1a**	**2b**	77	76	97	75	99:1
5	c-Hex	**1a**	**2b**	72	95	94	93	98:2
6	$PhCH_2$	**1a**	**2b**	85	90	98	90	99:1
7	(*E*)-EtCH=CH	**1a**	**2b**	78	99	95	97	99:1
8	(*E*)-PhCH=CH	**1a**	**2b**	75	93[h]	85[i]	92[f]	98:2
9	*t*-Bu	**1a**	**2b**	65	78	90	77	97:3
10	Ph	**1b**	**2b**	77	95	98	93	96:4
11	c-Hex	**1b**	**2b**	71	94	97	92	94:6
12	Ph	**1a**	**2c**	75	97	98	94	98:2
13	c-Hex	**1a**	**2c**	78	96	96	94	98:2
14	c-Hex	**1b**	**2c**	70	94	97	94	95:5
15	Ph	**1b**	**2c**	68	93	92	92	94:6

[a] $Li(c\text{-}Hex)_2$. Ate complex formation, decomposition (2.5 equiv of $BF_3{\cdot}OEt_2$) and aldehyde addition at −95 °C (for solvent details see Experimental Section). [b] Obtained by cyclization of chlorohydrins with K_2CO_3/MeOH, unless noted. If oxiranes are insensitive to base (except entries 3, 6 and 7), they can be obtained by oxidation of intermediates **14** or **15** ($NaOH/H_2O_2$), without isolation of chlorohydrin. [c] Isolated yields. [d] Ee's determined by GC (Cyclodex B, 30 m × 0.25 mm i.d. column, carrier gas He at 15 psi, temperature between 100 °C and 200 °C, isothermal), unless noted. The racemic compounds prepared using 9-methoxy-9-BBN instead of Ipc_2BOMe. [e] Determined by ^1H NMR and capillary GC analysis. These ratios were same as *syn*/*anti* ratios of chlorohydrins (determined by capillary GC analyses). [f] ee determined by ^1H NMR analysis (400 MHz) using $Eu(hfc)_3$. [g] Reaction conducted in THF. [h] Determined by ^1H NMR analysis of MTPA ester. [i] Cyclized using KO-*t*-Bu/THF.

Scheme 6



Scheme 7



***syn*-(3*R*,4*R*)-4-Chloro-2,2-dimethyl-5-hexen-3-ol (16h).** IR (film) ν 3396, 1670, 1640, 1101, 968, 927 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.05 (ddd, J = 16.9, 10.2, 1 Hz, 1H), 5.31 (ddd, J = 16.9, 1, 1 Hz, 1H), 5.17 (ddd, J = 10.2, 1, 1 Hz, 1H), 4.64 (dd, J = 4.8, 3.6 Hz, 1H), 3.36 (dd, J = 7.8, 3.6 Hz, 1H), 2.24 (d, J = 7.8 Hz, 1H), 1.00 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 137.61, 117.06, 80.34, 66.32, 35.73, 26.77. CIMS *m*/*z* (isobutane, rel intensity) 163 [$M^+ + 1$ (13.1)], 145 (83.8), 127 (100), 109 (62.1). $[\alpha]^{23}_D$ +38.60 (*c* = 3.50, $CHCl_3$). Anal. Calcd for $C_8H_{15}ClO$: C, 59.07; H, 9.30. Found: C, 59.29; H, 9.20.

Table 4. Effect of Proportion of $BF_3{\cdot}OEt_2$ on the EE of Chlorohydrins[a]

entry	R in $LiNR_2$	$BF_3{\cdot}OEt_2$ (equiv)	R′ in R′CHO	*syn*-α-chlorohydrin **16**, ee %[b]
1	c-Hex	2.5	c-Hex	95
2	i-Pr	2.5	c-Hex	93.5
3	c-Hex	2.5	Ph	98
4	i-Pr	2.5	Ph	84
5	i-Pr	1.33	Ph	95
6	c-Hex	2.5	*t*-Bu	78
7	i-Pr	1.33	*t*-Bu	77
8	c-Hex	2.5	*n*-C_8H_{17}	94
9	i-Pr	2.5	*n*-C_8H_{17}	93
10	i-Pr	1.33	*n*-C_8H_{17}	92

[a] Ate complex formation, decomposition and aldehyde addition at −95 °C. [d] Ipc_2BOMe was used. [b] ee's determined by GC (Cyclodex B, 30 m × 0.25 mm i.d. column using conditions given in Table 3).

Table 5. Effect of Lithium Dialkylamide Base Structure on Stereoselectivity of Chlorohydrin Formation[a]

			α-chlorohydrin, **16**	
entry	lithium dialkylamide used	R′CHO R′ =	ee (%)[b]	ds[c] *syn vs anti*
1	LDA	c-Hex	94	97:3
2	LDA	Ph	82	95:5
3	LiTMP	c-Hex	94	>99:1
4	Li(*i*-Pr)c-Hex	c-Hex	93	97:3
5	$LiN(c\text{-}Hex)_2$	c-Hex	96	>99:1
6	$LiN(c\text{-}Hex)_2$	Ph	98	99:1

[a] Reactions at −95 °C using [d] Ipc_2BOMe and 2.5 equiv of $BF_3{\cdot}OEt_2$. [b] ee's determined by GC (Cyclodex B, 30 m × 0.25 mm ID column, using conditions in Table 3). [c] de's determined by ^1H NMR and capillary GC analysis.

***syn*-(1*R*,2*R*)-2-Bromo-1-cyclohexyl-3-buten-1-ol (16i).** IR (film) ν 3378, 1494, 1278, 1087 cm^{-1}. ^1H NMR ($CDCl_3$) δ 6.11 (ddd, J = 16.9, 10, 10 Hz, 1H), 5.31 (ddd, J = 16.9, 1, 1 Hz, 1H), 5.15 (ddd, J = 10, 1, 1 Hz, 1H), 4.70 (dd, J = 17.6, 5.4 Hz, 1H), 3.26 (dd, J = 12, 5.6 Hz, 1H), 1.96 (d, J = 6.6 Hz, 1H), 1.84−1.14 (m, 11H). ^{13}C NMR ($CDCl_3$) δ 136.49, 118.04, 78.09, 62.26, 41.56, 29.79, 26.84, 26.49, 26.22, 25.91. CIMS *m*/*z* (isobutane rel intensity) 217 [($M^+ + 2$) − 18 + 1 (13.4)], 215 [($M^+ - 18$) + 1, (13.4)], 153 (81.4), 135 (63.5), 111 (100). $[\alpha]^{23}_D$ +25.52 (*c* = 3.02, Et_2O). Anal. Calcd for $C_{10}H_{17}BrO$: C, 51.71; H, 7.38. Found: C, 51.90; H, 7.35.

***syn*-(1*R*,2*R*)-2-Bromo-1-phenyl-3-buten-1-ol (16j).** IR (film) ν 3445, 1640, 1489, 1425, 1048, 989, 926 cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.18−7.43 (m, 5H), 5.94 (ddd, J = 17.6, 10.2, 8 Hz, 1H), 5.13 (ddd, J = 17.6, 1, 1 Hz, 1H), 5.03 (ddd, J = 10, 1, 1 Hz, 1H), 4.74 (dd, J = 7.2, 4.1 Hz, 1H), 4.43 (dd, J = 4.1, 3.6 Hz, 1H), 2.81 (d, J = 3.6 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 135.27, 129.79, 129.04, 128.62, 126.55, 119.19, 77.04, 63.35. CIMS *m*/*z* (isobutane, rel intensity) 211 [($M^+ + 2$) − 18 (44.3)], 209 [($M^+ - 18$ (44.3)], 147 (35.9), 129 (59.7), 107 (100). $[\alpha]^{23}_D$ +36.78 (*c* = 2.31, $CHCl_3$). Anal. Calcd for $C_{10}H_{11}OBr$: C, 53.10; H, 4.91. Found: C, 53.08; H, 4.98.

***syn*-(1*S*,2*S*)-2-Bromo-1-cyclohexyl-3-buten-1-ol (17a).** $[\alpha]^{23}_D$ −25.27 (*c* = 2.91, Et_2O).

***syn*-(1*S*,2*S*)-2-Bromo-1-phenyl-3-buten-1-ol (17b).** $[\alpha]^{23}_D$ −34.68 (*c* = 2.13, $CHCl_3$).

***syn*-(1*S*,2*S*)-2-Chloro-1-cyclohexyl-3-buten-1-ol (17c).** $[\alpha]^{23}_D$ −52.57 (*c* = 2.21, $CHCl_3$).

***syn*-(1*S*,2*S*)-2-Chloro-1-phenyl-3-buten-1-ol (17d).** $[\alpha]^{23}_D$ −18.50 (*c* = 2.0, $CHCl_3$).

Synthesis of *cis*-Vinylepoxides 18/19. (i) General Procedure for Oxidation of Boron Intermediates 14/15. The residue obtained (see experimental procedure for preparation of **16a**) was dissolved in THF (20 mL) with stirring and cooled to 0 °C. Then, 3 M NaOH (12 mL) and 30% H_2O_2 (12 mL) were sequentially added. The reaction mixture was allowed

to warm to rt (14 h). Standard workup followed by flash chromatography yielded a colorless liquid, **18a** (1.29 g, 74% yield).

(ii) General Procedure for Cyclization of *syn*-α-Chlorohydrins. To a solution of α-chlorohydrin **16d** (0.95 g, 5 mmol) in MeOH (40 mL) was added K_2CO_3 (1.20 g, 10.0 mmol). This mixture was stirred for 6 h after which time most MeOH was removed *in vacuo*. The resulting slurry was then diluted with water (20 mL), and the mixture was extracted with Et_2O (3 × 40 mL). Standard workup followed by flash chromatography (hexane:Et_2O, 99:1) gave *cis*-vinyloxirane **18d** (0.74 g, 98% yield).

***cis*-(1*R*,2*S*)-1-Cyclohexyl-1,2-epoxy-3-butene (18a).** IR (film) ν 1449, 1256, 1182, 985, 922, 823, 789 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.72 (ddd, J = 17.2, 10, 7.4, 1H), 5.47 (ddd, J = 17.2, 1, 1 Hz, 1H), 5.33 (ddd, J = 10, 1, 1 Hz, 1H), 3.39 (dd, J = 7.5, 4.4 Hz, 1H), 2.77 (q, J = 4.4 Hz, 1H), 1.77−1.13 (m, 11H). ^{13}C NMR ($CDCl_3$) δ 133.57, 120.15, 63.45, 57.78, 36.13, 31.67, 28.95, 26.24, 25.78, 25.09. CIMS m/z (isobutane, rel intensity) 153 [M^+ + 1 (100)], 135 (68.5), 125 (8.7). $[\alpha]^{23}_D$ +35.18 (c = 2.08, EtOH). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.15; H, 10.73.

***cis*-(1*R*,2*S*)-1,2-Epoxy-1-phenyl-3-butene (18b).** IR (film) ν 1496, 1442, 1388, 1250, 1181, 986, 927, 821, 787 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.36−7.25 (m, 5H), 5.57−5.53 (m, 1H), 5.43−5.34 (m, 1H), 5.29−5.26 (m, 1H), 4.25 (d, J = 4.1 Hz, 1H), 3.67 (q, J = 4.1 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 135.19, 132.15, 128.54, 128.13, 127.73, 126.48, 125.53, 121.84, 59.78, 58.85. CIMS m/z (rel intensity) 147 [M^+ + 1 (100)], 146 [M^+ (12.5)], 129 (54.7), 119 (11.7), 117 (14.4), 105 (23.0). $[\alpha]^{23}_D$ +97.36 (c = 2.65, EtOH). Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 82.23; H, 6.99.

***cis*-(3*R*,4*R*)-3,4-Epoxy-1-dodecene (18c).** IR (film) ν 1639, 1465, 1256, 984, 922, 815 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.71 (ddd, J = 17.2, 10.4, 7.2 Hz, 1H), 5.46 (ddd, J = 17.2, 1, 1 Hz, 1H), 5.34 (ddd, J = 10.2, 1, 1 Hz, 1H), 3.39 (dd, J = 7.2, 4.3 Hz, 1H), 3.06 (m, 1H), 1.58−0.85 (m, 17H). ^{13}C NMR ($CDCl_3$) δ 132.79, 120.04, 58.74, 57.12, 31.80, 29.39, 29.15, 27.73, 26.26, 22.60, 13.98. CIMS m/z (isobutane, rel intensity) 183 [M^+ + 1 (27)], 165 [(M^+ − 18) + 1 (12.5)], 141 (100). $[\alpha]^{23}_D$ +15.7 (c = 1.56, EtOH). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.01; H, 12.20.

***cis*-(2*R*,3*S*)-2,3-Epoxy-1-phenyl-4-pentene (18d).** IR (film) ν 3086, 1639, 1496, 1250, 985, 928, 871, 778 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.35−7.23 (m, 5H), 5.90 (ddd, J = 17.2, 10.4, 6.9 Hz, 1H), 5.57 (ddd, J = 17.2, 1, 1 Hz, 1H), 5.46 (ddd, J = 10.4, 1, 1 Hz, 1H), 3.52 (dd, J = 6.9, 4.2 Hz, 1H), 3.33 (ddd, J = 6.1, 6.1, 4.2 Hz, 1H), 2.96 (dd, J = 14.8, 6.0 Hz, 1H), 2.82 (dd, J = 14.8, 6.7 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 137.68, 132.47, 128.90, 128.64, 126.64, 120.56, 58.96, 57.24, 34.17. EIMS m/z (rel intensity) 160 [M^+ (9.7)], 142 (43.3), 131 (17.5), 117 (14.3), 104 (87.5), 103 (47.3), 91 (100), 78 (53.2), 69 (52.8), 51 (18.9), 41 (11.2). $[\alpha]^{23}_D$ +15.48 (c = 3.08, EtOH). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.30; H, 7.56.

***cis*-(3*R*,4*S*)-3,4-Epoxy-(5*E*)-1,5-octadiene (18e).** IR (film) ν 3088, 1641, 1244, 984, 927, 840, 792 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 6.01 (dt, J = 15.5, 6.4 Hz, 1H), 5.78 (ddd, J = 17.3, 10.2, 7.1 Hz, 1H), 5.50 (dd, J = 17.3, 1.5 Hz, 1H), 5.37 (dd, J = 10.2, 1.5 Hz, 1H), 5.26−5.33 (m, 1H), 3.54 (m, 2H), 2.10 (m, 2H), 1.00 (t, J = 7.6 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 139.99, 132.71, 122.80, 120.37, 58.84, 58.80, 25.58, 13.18. CIMS m/z (isobutane, rel intensity) 183 [M^+ + 1 (21.3)], 165 (12.1), 141 (100), 123 (3.7). $[\alpha]^{23}_D$ + 30.83 (c = 1.05, EtOH). Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.20; H, 9.90.

***cis*-(3*R*,4*S*)-3,4-Epoxy-1-phenyl-(1*E*)-1,5-hexadiene (18f).** IR (film) ν 1641, 1494, 1451, 984, 927 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.42−7.23 (m, 5H), 6.78 (d, J = 16 Hz, 1H), 6.25 (dd, J = 16, 7.6 Hz, 1H), 5.81 (ddd, J = 17.2, 10.2, 7.2 Hz, 1H), 5.63 (ddd, J = 17.2, 1, 1 Hz, 1H), 5.41 (ddd, J = 10.2, 1, 1 Hz, 1H), 3.74 (ddd, J = 7.6, 4, 1 Hz, 1H), 3.65 (dd, J = 7.2, 4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 136.35, 135.70, 132.51, 128.67, 128.33, 128.15, 126.57, 123.49, 120.70, 59.29, 58.85. EIMS m/z (rel intensity) 172 [M^+ (9.7)], 144 (10.1), 143 (33.9), 129 (17.7), 128 (37), 117 (17.7), 116 (23.5), 115 (100), 65 (10.5), 63 (11.1), 50 (12.7). $[\alpha]^{23}_D$ +102.0 (c = 0.7, EtOH). HRMS Calcd for $C_{12}H_{12}O$: 172.0888. Found: 172.0882.

***cis*-(3*R*,4*S*)-3,4-Epoxy-5-methyl-1-hexene (18g).** IR (film) ν 3034, 1641, 1244, 1197 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 5.75 (ddd, J = 17.2, 10.4, 7.4, 1H), 5.47 (ddd, J = 17.2, 1, 1 Hz, 1H), 5.33 (ddd, J = 10.4, 1, 1 Hz, 1H), 3.44 (dd, J = 7.4, 4.4 Hz, 1H), 2.74 (dd, J = 7.4, 4.4 Hz, 1H), 1.49−1.40 (m, 1H), 1.07 (d, J = 1.3 Hz, 3H), 0.91 (d, J = 1.3 Hz, 3H). ^{13}C NMR ($CDCl_3$) δ 133.78, 120.69, 65.65, 58.78, 28.13, 20.27, 18.38. EIMS m/z 112 [M^+ (11.2)], 97 (26.5), 83 (18.7), 79 (13.4), 69 (68.7), 56 (100), 41 (29.7). $[\alpha]^{23}_D$ −69.60 (c = 1.25, EtOH). HRMS Calcd for $C_7H_{12}O$: 112.0888. Found: 112.0885.

***cis*-(3*R*,4*S*)-3,4-Epoxy-2,2-dimethyl-5-hexene (18h).** ^{1}H NMR ($CDCl_3$) δ 5.94 (ddd, J = 17.8, 10.4, 8 Hz, 1H), 5.47 (dd, J = 17.8, 1 Hz, 1H), 5.27 (dd, J = 10.2, 1 Hz, 1H), 3.47 (dd, J = 8.0, 4.5 Hz, 1H), 2.82 (d, J = 4.5 Hz, 1H), 1.00 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 134.08, 119.44, 67.19, 59.07, 33.63, 27.60. CIMS m/z (isobutane, rel intensity) 143 [(M^+ − 18) + 1 (100)], 125 (29.8), 107 (57.5). $[\alpha]^{23}_D$ +15.89 (c = 1.45, EtOH). Anal. Calcd for $C_8H_{14}O$: C, 76.13; H, 11.19. Found: C, 76.04; H, 11.24.

***cis*-(1*S*,2*R*)-1-Cyclohexyl-1,2-epoxy-3-butene (19a).** $[\alpha]^{23}_D$ −38.58 (c = 2.68, EtOH).

***cis*-(1*S*,2*R*)-1,2-Epoxy-1-phenyl-3-butene (19b).** $[\alpha]^{23}_D$ −90.16 (c = 2.05, EtOH).

General Procedure for Chloroallylboration of Aldehydes Using 9-MeO-9-BBN. To a stirred and cooled (−78 °C) mixture of MeO-9-BBN (11.5 mmol) and allyl chloride (15 mmol) in anhyd ether (50 mL) was added a solution of LiN(c-Hex)$_2$ (15 mmol) in THF (25 mL). After stirring for 0.5 h, BF_3·OEt_2 (30 mmol) was added followed by cyclohexanecarboxaldehyde (11.5 mmol). The reaction mixture was stirred for 3 h at −78 °C, then the cold bath was removed and the flask allowed to warm to rt. All solvents were removed *in vacuo*, and the residue was triturated with *n*-pentane (40 mL) and allowed to settle (12 h). The supernatant was transferred to another predried flask through a cannula. The residue was further treated with pentane (2 × 30 mL), and the pentane extracts were combined. Removal of pentane *in vacuo* furnished a semisolid. This was dissolved in ether and treated with ethanolamine following the reported procedure.[19] Standard workup followed by flash chromatography (hexane:ether, 95:5) yielded a mixture of **6a, 7a**, and **8a**.

Preparation of (±) *cis*-vinylepoxide **9b** by oxidation of boron intermediate employed a procedure analogous to that described for the synthesis of **18a**.

***(Z)*-4-Chloro-1-phenyl-3-buten-1-ol (6a).** ^{1}H NMR and ^{13}C NMR spectra of **6a** are in agreement with those reported.[29] CIMS m/z (isobutane, rel intensity) 165 [(M^+ − 18) + 1 (100)], 147 (29.8), 129 (100).

***(Z)*-4-Chloro-1-cyclohexyl-3-buten-1-ol (6b).** ^{1}H NMR ($CDCl_3$) δ 6.13 (dd, J = 7.1, 1.0 Hz, 1H), 5.90 (dd, J = 9.4, 7.1 Hz, 1H), 3.44−3.49 (m, 1H), 2.60 (s, 1H), 2.32−2.49 (m, 2H), 1.88−1.66 (m, 6H), 1.02−1.39 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 128.6, 119.8, 75.2, 43.5, 32.2, 29.2, 28.0, 26.5, 26.3. CIMS m/z (isobutane, rel intensity) 173 [(M^+ − 18) + 2 + 1 (8.4)], 171 [(M^+ − 8) + 1 (28)], 135 (100). Anal. Calcd for $C_{10}H_{17}ClO$: C, 63.65; H, 9.08. Found: C, 63.50; H, 9.12.

***(Z)*-4-Bromo-1-phenyl-3-buten-1-ol (6c).** ^{1}H NMR and ^{13}C NMR spectra of **6c** are in agreement with those reported.[29] CIMS m/z (isobutane, rel intensity) 211 [(M^+ + 2) − 18 (13.4)], 209 [(M^+ − 18) (13.4)], 153 (21.4), 135 (100).

***(Z)*-4-Bromo-1-cyclohexyl-3-buten-1-ol (6d).** ^{1}H NMR ($CDCl_3$) δ 6.27 (m, 2H), 3.48 (ddd, J = 12.0, 5.6, 4 Hz, 1H), 2.41 (dd, J = 4.8, 4 Hz, 1H), 2.34 (m, 1H), 2.15 (s, 1H), 1.87−0.99 (m, 11H). ^{13}C NMR ($CDCl_3$) δ 131.9, 109.5, 75.1, 43.5, 34.8, 29.2, 28.0, 26.5, 26.3, 26.1. CIMS m/z (isobutane, rel intensity) 217 [(M^+ + 2) − 18 + 1 (7.4)], 215 [(M^+ − 18) + 1 (6.9)], 135 (78), 111 (100). Anal. Calcd for $C_{10}H_{17}BrO$: C, 51.52; H, 7.35. Found: C, 51.65; H, 7.50.

***anti*-2-Chloro-1-phenyl-3-buten-1-ol (8a).** ^{1}H NMR and ^{13}C NMR spectra of **8a** are in agreement with those reported.[17b]

***anti*-2-Chloro-1-cyclohexyl-3-buten-1-ol (8b).** ^{1}H NMR and ^{13}C NMR spectra of **8b** are in agreement with those reported.[17b]

(29) (a) Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 1039. (b) Hoffmann, R. W.; Landmann, B. *Chem. Ber.* **1986**, *119*, 2013.

***anti*-2-Bromo-1-phenyl-3-buten-1-ol (8c).** ^{1}H NMR ($CDCl_3$) δ 7.28−7.36 (m, 5H), 6.06 (dt, J = 17.0, 10.2 Hz, 1H), 5.17 (d, J = 17.6 Hz, 1H), 5.13 (d, J = 10.2 Hz, 1H), 4.98 (d, J = 4.4 Hz, 1H), 4.73 (q, J = 4.4 Hz, 1H), 2.79 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 139.53, 134.09, 128.74, 128.45, 126.89, 119.80, 77.21, 60.45. CIMS m/z (isobutane, rel intensity) 211 [(M^+ + 2) − 18 (42.3)], 209 [(M^+ − 18) (44.6)], 147 (35.9), 129 (59.7), 107 (100). Anal. Calcd for $C_{10}H_{11}BrO$: C, 52.89; H, 4.88. Found: C, 53.01; H, 4.95.

***anti*-2-Bromo-1-cyclohexyl-3-buten-1-ol (8d).** ^{1}H NMR ($CDCl_3$) δ 6.12 (ddd, J = 17.0, 10.8, 10 Hz, 1H), 5.30 (ddd, J = 17.0, 1, 1 Hz, 1H), 5.19 (ddd, J = 10.8, 1, 1 Hz, 1H), 4.74 (dd, J = 10, 3.6 Hz, 1H), 3.55 (dd, J = 8, 3.6 Hz, 1H), 2.20 (s, 1H), 2.00 (m, 1H), 1.74−0.97 (m, 10H). ^{13}C NMR ($CDCl_3$) δ 134.57, 119.08, 78.50, 59.73, 40.47, 29.05, 28.72, 26.30, 25.96, 25.80. CIMS m/z (isobutane, rel intensity) 217 [(M^+ + 2) − 18 + 1 (13.4)], 215 [(M^+ − 18) + 1 (12.6)], 153 (39.4), 135 (100). Anal. Calcd for $C_{10}H_{17}BrO$: C, 51.52; H, 7.35. Found: C, 51.60; H, 7.45.

***trans*-1,2-Epoxy-1-phenyl-3-butene (9c).** ^{1}H NMR and ^{13}C NMR spectra of **9c** are in agreement with those reported.[17b] EIMS m/z (rel intensity) 147 [M^+ + 1 (100)], 146 [M^+ (12.5)], 129 (61.7), 119 (15.7), 117 (12.3), 105 (28.5).

***trans*-1-Cyclohexyl-1,2-epoxy-3-butene (9d).** ^{1}H NMR and ^{13}C NMR spectra of **9d** are in agreement with those reported.[17b] CIMS m/z (isobutane, rel intensity) 153 [(M^+ + 1) (100)], 135 (78.5), 125 (15.7).

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **18f** and **18g** (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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