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Tuning of Vinylborane Dienophilicity. Optimization of Reactivity, Regioselectivity, *endo*-Stereoselectivity, and Reagent Stability

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Abstract: Simple syntheses of some vinylboranes are reported, and their properties in Diels-Alder reactions are compared. Vinyl-3,6-dimethylborepane was the most stable simple vinylborane examined, and appears to be indefinitely stable at 25 °C. Surprisingly, trivinylborane is the most reactive, and reacts about 18 times faster than the vinyldialkylboranes with cyclopentadiene. Vinyl-9-BBN is the most regioselective dienophile, in keeping with principally steric control of regioselectivity in Diels-Alder reactions of vinylboranes. All the dienophiles display high *endo*-stereoselectivity with piperylene, but vinyl-3,6-dimethylborepane displays significantly improved stereoselectivity with cyclopentadiene. In general, by choice of alkyl-substituents on boron, the reactivity, regioselectivity, endo-stereoselectivity, and stability of vinylboranes can be optimized.

9-Vinyl-9-borabicyclo[3.3.1]nonane (vinyl-9-BBN) is an exceptional dienophile. The high reactivity of vinyl-9-BBN with electron-rich, electron-poor, and unactivated dienes recently led us to describe it as an *omniphilic* dienophile.[1,2] Vinyl-9-BBN also displays excellent *endo*-stereoselectivity with acyclic dienes, and high and sometimes unusual regioselectivity with 1- and 2-alkyl substituted dienes.[3] Most recently, an easy one-pot procedure for the utilization of vinylboranes starting from commercially available materials has been developed.[4] Coupling of these features with the great synthetic versatility of boranes should allow the simple synthesis of a wide variety of structures not otherwise available directly from Diels-Alder reactions.

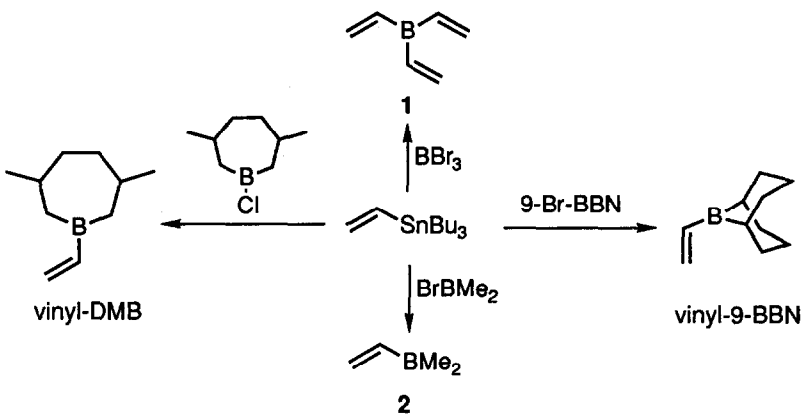
A special feature of using vinylboranes as dienophiles is the potential for control of their properties based on variation of the alkyl groups on the boron. We hoped that new vinylboranes would display even greater reactivity than vinyl-9-BBN, better *endo*-stereoselectivity with cyclic dienes, and improved stability. We report here on the often surprising alkyl-substitution effects on the reactions of vinyldialkylboranes, and how these effects allow the tuning of vinylboranes for useful features.

RESULTS AND DISCUSSION

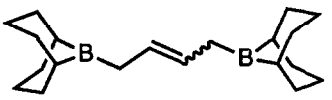
Synthesis and Stability of Vinylboranes

We communicated that vinyl-9-BBN can be made conveniently by reaction of *B*-bromo-9-BBN with vinyltributyltin.[3] Similar procedures are useful for the synthesis of other vinylboranes. 1-Vinyl-3,6-dimethylborepane (vinyl-DMB) was obtained in 59% yield from the reaction of *B*-chloro-3,6-dimethylborepane[5] with vinyltributyltin at 25 °C. Trivinylborane (**1**) has previously been synthesized in 32% yield by condensing BBr_3 with tetravinyltin at -196 °C, or by a three-step procedure via fluorodivinylborane, each followed by a tedious separation on a low-temperature column.[6] In contrast, we have found that direct reaction of BBr_3 with excess vinyltributyltin at 0-25 °C followed by vacuum transfer affords trivinylborane cleanly in 88% yield. Trivinylborane is stable in solution at 25 °C. Neat samples can be stored at -78 °C but tend to polymerize at 25 °C, especially when not kept perfectly airless.

The synthesis of vinyldimethylborane (**2**)[7] can be accomplished by reaction of bromodimethylborane with vinyltributyltin in a similar fashion, but the manipulations of purified samples of this pyrophoric, highly volatile material proved too dangerous for use in routine synthetic reactions. The reactions of vinyldimethylborane are best accomplished by our recently reported *in situ* procedure.[4]



A problem in using vinyl-9-BBN is that it undergoes an interesting slow ($k=1\times10^{-6}$ $M^{-1}s^{-1}$) dimerization at 25 °C to form **3** as a ≈60:40 mixture of trans and cis isomers. The mechanism of this dimerization is unclear, but clean second-order kinetics were observed. The dimerization is not a problem in reactions of most dienes, but can compete with the Diels-Alder reactions of relatively unreactive dienes and limit yields. Because the dimerization is second order in vinyl-9-BBN, it can be avoided by diluting the vinyl-9-BBN in excess diene, but this is not practical with complex dienes. The formation of **3** is also slowed but not stopped in the presence of triethylamine.



3

Fortunately, vinyl-DMB is much more stable than the other vinylboranes and should prove superior for reactions with unreactive dienes. In contrast to vinyl-9-BBN, vinyl-DMB appears indefinitely stable at 25 °C and may be heated to 65 °C for days with the only apparent reaction being equilibration of the mixture of cis and trans isomers. No dimerization products analogous to **3** could be observed even after prolonged heating.

Reactivity

As was true of vinyl-9-BBN and vinyldimethylborane, vinyl-DMB and trivinylborane react with 2-substituted butadienes and cyclopentadiene at temperatures ranging from 25 to 65 °C, though trivinylborane is noticeably more reactive than the others. The cycloadditions appear clean and quantitative by NMR before workup, but the isolated yields (unoptimized) of cyclohexenols after oxidative workup were variable (Table 1). The reactions were performed either with neat purified vinylboranes or vinylboranes formed *in situ* from the corresponding haloboranes and vinyltributyltin. Identical regioselectivity was observed in the two procedures. Only bromodialkylboranes were used in previous work with the *in situ* procedure;[4] the current examples show that trihaloboranes and chlorodialkylboranes work as well. The tin-boron exchange is much slower with 1-chloro-3,6-dimethylborepane than with bromoboranes and requires three days at rt to go to completion.

In kinetic studies (Table 2), trivinylborane is about 18 times more reactive than vinyl-9-BBN with cyclopentadiene. The reaction of trivinylborane with excess cyclopentadiene utilizes two of the vinyl groups, and a best fit of experimental data is obtained if the second vinyl group is ≈12 times less reactive than the first. In this complex system, the reliability of the calculated rate constant is diminished, but clearly trivinylborane is far more reactive than the other vinylboranes.

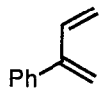
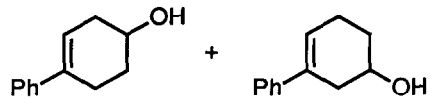
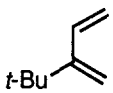
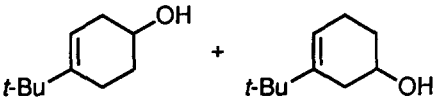
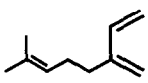
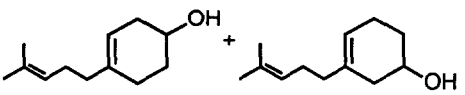
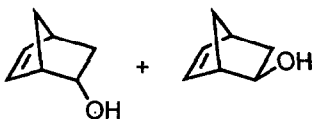
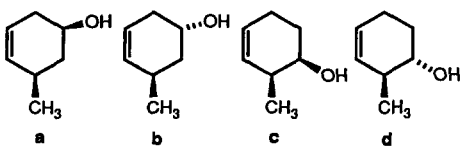
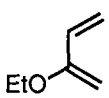
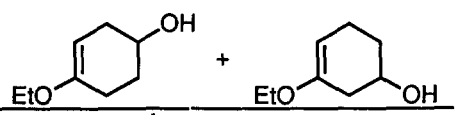
The elevated reactivity of trivinylborane is quite surprising. If it is assumed that the high reactivity of

Table 2. Rate Constants for the Reaction of Cyclopentadiene with Vinylboranes at 25 °C

vinyl-9-BBN[a]	vinyldimethylborane[b]	vinyl-DMB	trivinylborane
6.5×10^{-5} $M^{-1}s^{-1}$	$\approx6\times10^{-5}$ $M^{-1}s^{-1}$	2×10^{-5} $M^{-1}s^{-1}$	1.2×10^{-3} $M^{-1}s^{-1}$ (±20%)

[a]Taken from ref 3. [b]Taken from ref 4.

Table 1. Diels-Alder Reactions of Vinyl-DMB and Trivinylborane

Diene	Vinylborane Source and Rxn Conditions	Yield (Ratio)[a]	Product(s)
	1-chloro-3,6-dimethylborepane,[b] CH_2=CHSnBu$_3$, 55 °C, 48 h	68% (97:3)[c]	
	BBr_3, CH_2=CHSnBu$_3$ 25 °C, 22 h	79% (88:12)	
	trivinylborane, 25 °C, 24 h	70% (90:10)	
	vinyl-DMB 55 °C, 33 h	82% (90:10)	
	1-chloro-3,6-dimethylborepane,[b] CH_2=CHSnBu$_3$, 55 °C, 33 h	83% (90:10)	
	BBr_3, CH_2=CHSnBu$_3$ 25 °C, 26 h	56% (92:8)	
	1-chloro-3,6-dimethylborepane,[b] CH_2=CHSnBu$_3$, 65 °C, 19 h	71% (70:30)	
	BBr_3, CH_2=CHSnBu$_3$ 55 °C, 48 h	57% (62:38)	
	vinyl-DMB 25 °C, 48 h	69% (87:13)	
	trivinylborane 25 °C, 18 h	83% (78:22)	
	vinyl-DMB 55 °C, 4 d	48% of **a**+**b** (94:6) (**a**+**b**:**c**+**d** = 65:35)[d]	
	vinyl-DMB 55 °C, 4 d	65% (54:46)	

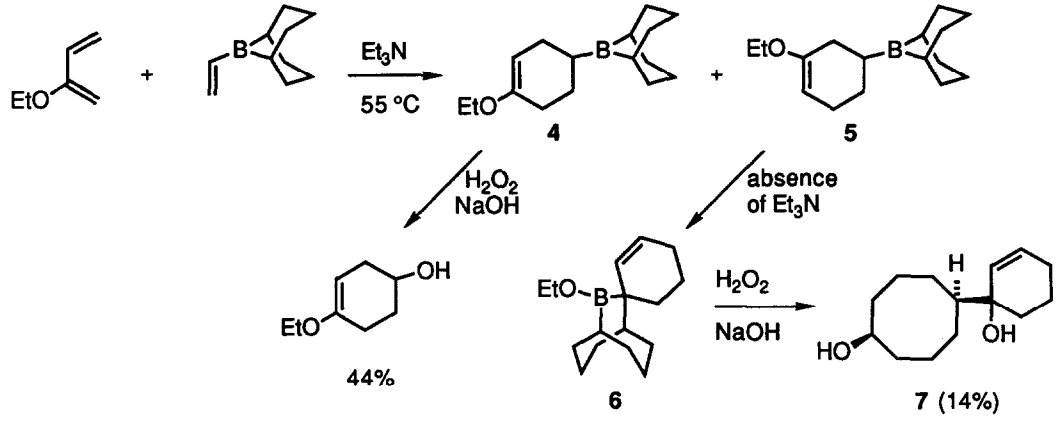
[a] Determined from NMR integration of the vinylic or carbinyl methine protons. [b] Ref 5. [c] The actual ratio of isomers formed was 84:16, but a large part of the minor product was not isolated in pure form due to an inseparable impurity. [d] Isomers **c** and **d** could not be isolated in pure form.

vinylboranes is in some way due to π-electron withdrawal by the boron, the donation by vinyl groups should deactivate the dienophile, but the opposite result is observed. Although recent results have indicated that vinylboranes do not react like electron-deficient dienophiles,[1] it is difficult to understand how donation to the boron could *accelerate* the reactions. In fact, we had ascribed the very low reactivity of vinylboronic esters to π donation to the boron by oxygen. An alternative is to attribute the reactivity of trivinylborane to σ-electron withdrawal by the vinyl groups, but the low reactivity of vinylboronic esters is also contrary to this idea.

The high stability of vinyl-DMB is paralleled to an extent by lower reactivity with dienes. Vinyl-DMB is less reactive than vinyl-9-BBN with cyclopentadiene by a factor of 3 and noticeably less reactive with other dienes. However, the reactions of vinyl-DMB with the relatively unreactive dienes piperylene and 2-ethoxybutadiene[1] appear significantly cleaner than the corresponding reactions of vinyl-9-BBN due to the

absence of dimerization and afford slightly better overall yields of cyclohexenols.

Besides dimerization, the reaction of 2-ethoxybutadiene with vinyl-9-BBN is complicated by an intriguing rearrangement. Under normal reaction conditions, the minor product regioisomer **5** rearranges to afford an intermediate for which the ^{1}H NMR suggested the presence of a 1,2-disubstituted alkene and an $EtOBR_2$ group. This intermediate was assigned as **6** after oxidation afforded **7**, whose structure was confirmed by X-ray analysis. The mechanism of formation of **6** is unclear, but it is apparently an acid-catalyzed process because the presence of 1 mol % of triethylamine completely inhibits the rearrangement.



Regioselectivity

Based on the observation of decreasing selectivity with decreasing size of the substituent in 2-substituted butadienes, we previously speculated that the regioselectivity with vinyl-9-BBN is controlled by steric interactions with the large BBN group. This idea is confirmed by observations of the regioselectivity with different vinylboranes (Table 3). The most regioselective vinylborane in each case was vinyl-9-BBN. A decrease in the steric bulk of alkyl groups on boron is accompanied by a marked decrease in the regioselectivity. With minimal steric effects, as in the reaction of trivinylborane with myrcene, vinylboranes display very low selectivity.

These results highlight the failure of FMO theory[8] to adequately explain many aspects of Diels-Alder reactions of vinylboranes. We originally attributed the special reactivity and selectivity of vinyl-9-BBN as being due to its having a low energy LUMO (relating to reactivity) with a large difference in vinylic LUMO coefficients (relating to regioselectivity) and a large coefficient on boron (relating to endo stereoselectivity).[3] This analysis was obviously flawed. The omniphilicity of vinylboranes demonstrates that their reactivity is not in keeping with the FMO model, and the low regioselectivity observed in the absence of steric effects clearly demonstrates the irrelevance of FMO in understanding the regioselectivity of vinylboranes.

Table 3. Regioselectivity of Diels-Alder Reactions with Vinylboranes[a]

diene	vinyl-9-BBN	vinyldimethylborane	vinyl-DMB	trivinylborane
myrcene	96:4[d]	61:39[d]	70:30	62:38
2-phenylbutadiene	>98:2[b]	84:16[d]	84:16	90:10
2-*t*-butylbutadiene	>98:2[b]	90:10[d]	90:10	>98:2
piperylene	>98:2[c]	50:50	65:35	49:51

[a] The ratios given are for "para":"meta" (1,4:1,3) products for myrcene, 2-phenylbutadiene, and 2-*t*-butylbutadiene, and are for "meta":"ortho" (1,5:1,2) products for piperylene. [b] Taken from ref 1. [c] Taken from ref 3. [d] Taken from ref 4.

The reaction of piperylene with vinyl-9-BBN was notable for producing the "meta" (1,5) product disfavored in most Diels-Alder reactions. In contrast, the reaction of piperylene with trivinylborane displays a slight preference for formation of the "ortho" (1,2) product. Although the selectivity in this case is very low,

the ability to change the preferred regioisomer by choice of vinylborane demonstrates unprecedented prospects for control of the regiochemical course of these reactions.

endo-*Stereoselectivity*

The reactions of vinyl-9-BBN with acyclic dienes were highly *endo*-stereoselective, and same was observed to be true for other vinylboranes (Table 4). However, the endo-stereoselectivity with cyclopentadiene was disappointing, and we hoped that other vinylboranes would be more selective. We were pleased to find that this is indeed the case. The less bulky vinylboranes all display greater endo stereoselectivity in reactions with cyclopentadiene, with the greatest being observed with vinyl-DMB. The change in stereoselectivity is probably of steric origin, but examination of models provides no obvious details of this steric effect. It is possible that more bulky boranes will afford greater amounts of the exo product.

Table 4. *Endo*-stereoselectivity of Diels-Alder Reactions with Vinylboranes

Diene	Vinyl-9-BBN	Vinyldimethylborane	vinyl-DMB	Trivinylborane
cyclopentadiene	67:33	84:16	87:13	78:22
piperylene	92:8	>90% endo for each regioisomer	94:6	>90% endo for each regioisomer

CONCLUSION

The ability to vary the properties of vinylboranes by variation in their structure provides chemists with unique power. This variability not only provides control over practical properties such as stability, but also allows tuning of the fundamental reactivity and selectivity properties of vinylboranes in Diels-Alder reactions. We are continuing to study the synthetic utility and properties of these intriguing dienophiles.

EXPERIMENTAL SECTION

All reactions were carried out in dry glassware under a nitrogen atmosphere using solvents dried by standard techniques. All of the vinylboranes herein are air sensitive and pyrophoric. Schlenck techniques were used in the manipulation and distillation of the vinylboranes, and standard syringe and septa techniques[9] were used to transfer the vinylboranes. Flash chromatography was performed using 230-400 Mesh Kieselgel 60 silica gel from Merck. ^{1}H and ^{13}C NMR spectra were observed at 200 and 50 MHz, respectively. The spectra of boranes were taken as neat liquids in glass capillaries within NMR tubes and referenced approximately using the external $CDCl_3$. Other NMR spectra were taken in $CDCl_3$ solution unless otherwise noted. All of the major 3-cyclohexenol products have been previously reported.[10]

In a "standard extraction," the reaction mixture was extracted with 3 10-50 mL portions of the solvent to be named, and the combined organic layers were rinsed with 10-20 mL of a saturated aqueous KF (only for those reactions that used vinyltributyltin) and 10 mL of brine, dried (Na_2SO_4), and the solvent was removed on a rotary evaporator.

9-Vinyl-9-borobicyclo[3.3.1]nonane (Vinyl-9-BBN). A mixture of 14.6 mL (15.8 g, 50 mmol) of vinyltributyltin and 50.0 mL (50 mmol) of 1.0 M *B*-bromo-9-BBN in CH_2Cl_2 (Aldrich) was stirred for 11 h at rt. The solvent was then carefully removed under vacuum at rt and the residue was distilled through a 15 cm Vigreaux column to afford 5.48 g (74%) of a clear colorless liquid: bp 28-30 °C (0.25-0.30 mm); ^{1}H NMR δ 6.66 (dd, 1 H) 6.26 (dd, 1 H) 6.12 (dd, 1 H), 2.21 (m, 12 H), 1.50 (m, 2 H); ^{13}C NMR (CD_2Cl_2 at -40 °C) δ 140.65 (C), 136.90 (CH_2), 32.66 (CH_2), 29.00 (CH), 22.52 (CH_2); exact mass m/e 148.14146 (calcd for $C_{10}H_{17}B$, 148.14233).

Sealed samples of vinyl-9-BBN stored at rt slowly reacted to form **3** as a ≈60:40 mixture of isomers. The major isomer had spectral properties: ^{1}H NMR δ 5.64 (br t, 2 H), 2.44 (br s, 4 H), 2.2-1.8 (m, 24 H), 1.41 (m, 4 H); ^{13}C NMR δ 125.90 (CH), 33.44 (CH_2), 23.55 (CH_2); exact mass m/e 296.28496 (calcd for $C_{20}H_{34}B_2$, 296.28466). The minor isomer displayed characteristic spectral properties: ^{1}H NMR δ 5.65 (br t); ^{13}C NMR δ 124.56.

1-Vinyl-3,6-dimethylborepane (Vinyl-DMB). A mixture of 4.90 g (30.9 mmol) of *B*-chloro-3,6-

dimethylborepane[5] and 12.74 g (40.2 mmol) of vinyltributyltin was stirred at rt for 76 h. The mixture was then vacuum distilled through a 15 cm Vigreaux column to afford 2.74 g (59%) of the clear, colorless liquid vinyl-DMB as a 85:15 mixture of diastereomers: bp 25-30 °C (0.15 mm); ^{1}H NMR δ 6.88 (dd, 1 H), 6.45 (dd, 1 H), 6.32 (dd, 1 H), 2.90 (m, 2 H), 2.2-1.7 (m, 8 H), 1.34 (d, 6 H); ^{13}C NMR δ 134.05 (CH_2), 36.82 (CH_2), 30.76 (CH), 25.48 (CH_3); exact mass m/e 150.15648 (calcd for $C_{10}H_{19}B$, 150.15798). (Peaks for carbons bonded to boron were not observed). The minor isomer had observable spectral properties as follows: ^{1}H NMR δ 1.41 (d); ^{13}C NMR 134.38 (CH_2), 41.12 (CH_2), 32.07 (CH), 28.14 (CH_3).

Trivinylborane (1). A solution was prepared by treating dropwise under nitrogen atmosphere 47.6 g (150 mmol) of vinyltributyltin at 0 °C with 10.6 g (42.0 mmol) of BBr_3. The resulting mixture was then allowed to reach rt, stirred for 11 h, and vacuum transferred at 25 °C and 1 mm Hg to afford 3.44 g (88%) of the extremely pyrophoric trivinylborane[6]: ^{1}H NMR δ 6.81 (dd, 1 H), 6.20 (m, 2 H). ^{13}C NMR δ 139.30.

4-Phenyl-3-cyclohexen-1-ol, Method A. A mixture of 624.8 mg (3.94 mmol) of *B*-chloro-3,6-dimethylborepane and 1.58 g (4.98 mmol) of vinyltributyltin was heated to 55 °C for 3 d. To this mixture 193.5 mg (1.49 mmol) of 2-phenyl-1,3-butadiene was added and the solution was heated at 55 °C for 2 d. The reaction mixture was then cooled to rt, treated with 3.0 mL of THF, 3.0 mL of 3 N NaOH, 5.25 mL of 30% H_2O_2, and 2.0 mL of ethanol, and stirred at rt for 2 h. A standard extraction with ether and chromatography on a 15" x 5/8" silica gel column using 20% EtOAc/30-60° petroleum ether (pet ether) as eluent afforded247 mg of a 84:16 mixture of 1,4 and 1,3 regioisomers contaminated by tin-containing impurities. A second identical chromatography afforded 176.0 mg (68%) of a 97:3 mixture of isomers as a white solid. The major isomer had spectral properties matching those previously reported[10a] and those of the single regioisomer produced using vinyl-9-BBN[1]: mp 79-82 °C (lit[10a] 79-81 °C) ^{1}H NMR δ 7.30 (m, 5 H), 6.00 (m, 1 H), 4.05 (m, 1 H), 2.65 - 2.35 (m, 3 H), 2.22 - 1.70 (m, 4 H); ^{13}C NMR δ 141.80 (C), 136.20 (C), 128.23 (CH), 126.86 (CH), 125.04 (CH), 121.36 (CH), 66.58 (CH), 34.88 (CH_2), 31.16 (CH_2), 25.52 (CH_2). The minor product was not obtained in pure form but displayed a characteristic peak at δ 6.12 in the ^{1}H NMR.

Method B. A mixture of 1500 μL (1.5 mmol) of 1.0 M BBr_3 in hexanes and 1800 μL (1.96 g, 6.18 mmol) of vinyltributyltin was prepared at 0 °C and then stirred at rt for 100 min. There was then added 130.1 mg (1.0 mmol) of 2-phenyl-1,3-butadiene, and the mixture was stirred at rt for 22 h. The reaction was then cooled to 0 °C and treated with 5 mL of ethanol, 4 mL of 3 N NaOH, and 4 mL of 30 % H_2O_2. The resulting mixture was heated to 55 °C for 1 h, and 20 mL of water was added. A standard extraction with 50% diethyl ether/pet ether and chromatography on a 10" x 19 mm silica gel column using 15% EtOAc/pet ether as eluent afforded 138.0 mg (79%, based on 94% pure product) of a 88:12 mixture of 1,4 and 1,3 regioisomers.

Method C. A mixture of 393 mg (4.27 mmol) of **1** and 198 mg (1.52 mmol) of 2-phenylbutadiene was stirred for 24 h at rt. There was then added successively 5 mL of THF, 5 mL of water, and 2.3 g (15 mmol) of $NaBO_3 \cdot (H_2O)_4$ and the resulting mixture was stirred at rt for 1 h. After a standard extraction using CH_2Cl_2, the residue was chromatographed on a 8" x 19 mm silica gel column using 25% EtOAc/pet ether as eluent to afford 184 mg (70%) of a 90:10 mixture of 1,4 and 1,3 regioisomers.

4-*tert*-Butyl-3-cyclohexen-1-ol, Method A. A mixture of 373 mg (2.48 mmol) of vinyl-DMB and 353 mg (3.20 mmol) of 2-t-butyl-1,3-butadiene was heated to 55 °C for 33 h. The reaction mixture was then cooled to 0 °C, treated with 2.0 mL of 3 N NaOH, 2.0 mL of 30% H_2O_2, and 2.0 mL of ethanol, and stirred at rt for 3 h. After a standard extraction with pet ether, the residue was chromatographed on a 14" x 5/8" silica gel column using 12% EtOAc/pet ether as eluent to afford 314 mg (82%) of a white crystalline solid that was a 90:10 mixture of 1,4 and 1,3 regioisomers. The known[10b] major isomer had spectral properties matching the single regioisomer produced using vinyl-9-BBN[1]: mp 80-81 °C (lit[10b] 86-86.5 °C); ^{1}H NMR δ 5.32 (m, 1 H), 3.89 (m, 1 H), 2.37 (m, 1 H), 2.19 (m, 1 H), 2.02 (m, 2 H), 1.84 (m, 1 H), 1.60 (m, 1 H), 1.51 (s, 1 H), 1.00 (s, 9 H); ^{13}C NMR δ 145.37 (C), 114.60 (CH), 67.08 (CH), 35.20 (C), 34.71 (CH_2), 31.65 (CH_2), 29.05 (CH_3), 22.63 (CH_2). The minor isomer displayed characteristic spectral properties as follows: ^{1}H NMR δ 5.41 (m); ^{13}C NMR δ 116.74 (CH), 28.86 (CH_3).

Method B. A mixture of 676 mg (4.26 mmol) of *B*-chloro-3,6-dimethylborepane and 2.70 g (8.53 mmol) of vinyltributyltin was stirred at rt for 72 h, and 316 mg (2.87 mmol) of 2-t-butyl-1,3-butadiene was

added. The mixture was heated to 55 °C for 33 h, then cooled to 0 °C and treated with 10 mL of THF, 2.5 mL of 3 N NaOH, 3.0 mL of 30% H_2O_2, and 2.0 mL of ethanol. The resulting mixture was stirred at rt for 3 h. A standard extraction with pet ether and chromatography on a 14" x 5/8" silica gel column using 12% EtOAc/pet ether as eluent to afford 366 mg (83%) of a white solid that was a 90:10 mixture of isomers.

Method C. A mixture of 1500 μL (1.5 mmol) of 1.0 M BBr_3 in hexanes and 1800 μL (1.96 g, 6.18 mmol) of vinyltributyltin was prepared at 0 °C for 20 min, and stirred at rt for 100 min, and 129.3 mg (1.17 mmol) of 2-*tert*-butyl-1,3-butadiene was added. The mixture was stirred at rt for 26 h. The mixture was cooled to 0 °C and treated with 5 mL of ethanol, 5 mL of 3 N NaOH, and 5 mL of 30 % H_2O_2. The resulting mixture was heated to 55 °C for 1 h. After a standard extraction with 1:1 ether/pet ether, the residue was chromatographed on a 10" x 19 mm silica gel column using 12% EtOAc/pet ether as eluent to afford 101.3 mg (56%) of a 92:8 mixture of isomers.

4-(4-Methyl-3-pentenyl)-3-cyclohexen-1-ol and 3-(4-Methyl-3-pentenyl)-3-cyclohexen-1-ol, Method A. A mixture of 246 mg (1.64 mmol) of vinyl-DMB and 435 mg (2.97 mmol, based on 93% purity) of tech grade myrcene was heated to 65 °C for 19 h. The mixture was then cooled to 0 °C, treated with 10 mL of THF, 1.2 mL of 3 N NaOH, 1.0 mL of 30% H_2O_2, and 2.0 mL of ethanol, and stirred at rt for 2 h. A standard extraction with pet ether and chromatography on a 10" x 3/4" silica gel column using 12% EtOAc/pet ether as eluent afforded 210 mg (71%) of a 70:30 mixture of the title compounds as a colorless oil. The known[10c] major isomer had spectral properties matching that of the 96:4 mixture produced using vinyl-9-BBN[4]: ^{1}H NMR δ 5.25 (m, 1 H), 5.05 (m, 1 H), 3.90 (m, 1 H), 2.40 - 2.22 (m, 1 H), 2.10 - 1.55 (m, 16 H); ^{13}C NMR δ 137.72 (C), 131.65 (C), 124.31 (CH), 117.73 (CH), 66.98 (CH), 37.18 (CH_2), 34.25 (CH_2), 30.94 (CH_2), 26.26 (CH_2), 26.26 (CH_2), 25.50 (CH_3), 17.46 (CH_3). The minor isomer had observable spectral properties as follows: ^{1}H NMR δ 5.35 (m, 1 H); ^{13}C NMR δ 135.14 (C), 124.25 (CH), 120.27 (CH), 67.40 (CH), 37.45 (CH_2), 37.40 (CH_2), 30.54 (CH_2), 26.15 (CH_2), 25.50 (CH_3), 23.03 (CH_2), 17.46 (CH_3).

Method B. A mixture of 1500 μL (1.5 mmol) of 1.0 M BBr_3 in hexanes and 1800 μL (1.96 g, 6.18 mmol) of vinyltributyltin was prepared at 0 °C, allowed to warm to rt for 100 min, and 100.4 mg (0.737 mmol, based on 93% purity) of tech grade myrcene was added. The reaction was heated to 55 °C for 48 h. The mixture was then cooled to 0 °C, treated with 5 mL of ethanol, 5 mL of 3 N NaOH, and 5 mL of 30 % H_2O_2, and then heated to 55 °C for 1 h. After a standard extraction with 1:1 ether/pet ether, the residue was chromatographed on a 10" x 19 mm silica gel column using 12% EtOAc/pet ether as eluent to afford 75.2 mg (57%) of a 62:38 mixture of isomers.

***endo*-5-Norbornen-2-ol and *exo*-5-Norbornen-2-ol, Method A.** A mixture of 400 mg (2.66 mmol) of vinyl-DMB and 633 mg (9.58 mmol) of freshly cracked cyclopentadiene was stirred at rt for 43 h. The reaction mixture was then cooled to 0 °C, treated with 2.0 mL of 3 N NaOH, 2.0 mL of 30% H_2O_2, and 2.0 mL of methanol, and then heated to 55 °C for 1 h. A standard extraction with ether and chromatography on a 15" x 5/8" silica gel column using 12% EtOAc/hexanes as eluent afforded 202 mg (69%) of an 87:13 mixture of *endo* and *exo* alcohols with NMR spectra identical to the commercial material.

Method B. A mixture of 423 mg (4.60 mmol) of **1** and 1850 mg (28.0 mmol) of cyclopentadiene was allowed to react at rt for 18 h. There was then added successively 5 mL of THF, 5 mL of water, and 2.3 g (15 mmol) of $NaBO_3$•$(H_2O)_4$ and the resulting mixture was stirred at rt for 1 h. After a standard extraction using CH_2Cl_2, the residue was chromatographed on a 8" x 20 mm silica gel column using 10-20% EtOAc/pet ether as eluent to afford 850 mg (83%) of a 78:22 mixture of the *endo*- and *exo*-norbornenols.

5-Methyl-3-cyclohexen-1-ol and 2-Methyl-3-cyclohexen-1-ol. A mixture of 642 mg (4.28 mmol) of vinyl-DMB and 1.12 g (10.5 mmol, based on 64% trans-piperylene) of technical grade piperylene was stirred at 55 °C for 4 d. The mixture was then cooled to 0 °C, treated with 10 mL of THF, 2.0 mL of 3 N NaOH, 2.5 mL of 30% H_2O_2, and 2.0 mL of ethanol, and stirred at rt for 2 h. A standard extraction with pentane afforded a crude residue containing a 65:35 mixture of 5-methyl-3-cyclohexen-1-ol and 2-methyl-3-cyclohexen-1-ol isomers. The residue was chromatographed on a 14" x 5/8" silica gel column using 35% ether/pentane as eluent to afford 228.6 mg (48%) of a 94:6 mixture of cis and trans isomers of 5-methyl-3-cyclohexen-1-ol.[10d] The spectral properties of the cis isomer were as follows: ^{1}H NMR δ 5.45 (m, 2 H), 3.85 (d of d of d of d, J = 11.5, 9.7, 5.6, and 3.5 Hz, 1 H), 2.30 (m, 2 H), 1.90 (m, 3 H), 1.02 (q, J = 11.5 Hz), 0.95 (d, J = 7.0 Hz, 3 H); ^{13}C NMR δ 133.31 (CH), 125.36 (CH), 67.88 (CH), 41.18 (CH_2), 34.55 (CH_2), 31.19(CH), 21.28 (CH_3). The minor trans isomer had observable properties as follows: ^{1}H NMR δ 4.03 (m, 1 H), 0.99 (d, 3 H). The 2-

methyl-3-cyclohexen-1-ol[10e] was not isolated in pure form.

4-Ethoxy-3-cyclohexenol and 1-(5-Hydroxycyclooctyl)-2-cyclohexen-1-ol (7). A mixture of 642 mg (4.34 mmol) of vinyl-9-BBN and 686 mg (6.99 mmol) of 2-ethoxy-1,3-butadiene was heated to 50 °C for 77 h. The excess diene was removed in vacuo, and the residue was cooled to 0 °C and treated with 13 mL of THF, 1.8 mL of 3 N NaOH, and 1.8 mL of 30% H_2O_2. The solution was stirred at rt for 2 h and then was extracted with 100 mL of pet ether and 50 mL of ethyl ether. The combined extracts were washed with 50 mL of brine, basified by addition of 10 drops of Et_3N, dried (Na_2SO_4), and the solvent was removed on a rotary evaporator. The residue was chromatographed on a 12" x 5/8" silica gel column using 17% EtOAc/ 1% Et_3N /hexanes as eluent to afford 270.1 mg (44%) of 4-ethoxy-3-cyclohexenol[1] as a slightly yellowish liquid: ^1H NMR δ 4.42 (br t, 1 H), 3.93 (m, 1H), 3.65 (d of q, 2 H), 2.35 (m, 1 H), 2.18 (m, 2 H), 2.05 (m, 1 H), 1.84 (m, 1 H), 1.70 (m, 3 H), 1.25 (t, 3 H), ^{13}C NMR δ 153.74 (C), 89.96 (CH), 66.74 (CH), 61.95 (CH_2), 32.46 (CH2), 30.68 (CH_2), 25.48 (CH_2), 14.64 (CH_3), exact mass m/e 142.09958 (calcd for $C_8H_{14}O_2$, 142.09938).

Continued elution of the column with EtOAc, followed by recrystallization of the material obtained from 10% EtOAc/pet ether, afforded 139 mg (14%) of **7** as a white crystalline solid: ^1H NMR δ 5.80 (m, 1 H), 5.48 (br d, 1 H), 3.90 (m, 1 H), 1.00-2.10 (m, 21 H); ^{13}C NMR δ 132.21 (CH), 130.97 (CH), 72.80 (C), 72.01 (CH), 47.19 (CH), 35.98 (CH_2), 35.44 (CH_2), 30.73 (CH_2), 29.16 (CH_2), 28.08 (CH_2), 25.21 (CH_2), 24.16 (CH_2), 23.72 (CH_2), 18.37 (CH_2); exact mass m/e 206.16661 (calcd for $C_{14}H_{22}O$ (m - H_2O) 206.16707). The structure of **7** was confirmed by X-ray crystallographic analysis.

4-Ethoxy-3-cyclohexen-1-ol and 3-Ethoxy-3-cyclohexen-1-ol.. A mixture of 259.2 mg (1.73 mmol) of vinyl-DMB, 410 mg (4.18 mmol) of 2-ethoxybutadiene, and 35 mg (0.35 mmol) of Et_3N was heated to 55 °C for 4 d. The mixture was then cooled to 0 °C, treated with 10 mL of THF, 1.2 mL of 3 N NaOH, 1.0 mL of 30% H_2O_2, and 2.0 mL of ethanol, and stirred at rt for 2 h. A standard extraction with ether and chromatography on a 12" x 3/4" silica gel column using 54% ether/1% Et_3N/pentane as eluent afforded 158.3 mg (65%) of a colorless oil that was a 54:46 mixture of the title compounds. The minor isomer[1] had observable properties as follows: 151.63 (C), 92.85 (CH), 67.01 (CH), 61.89 (CH_2), 36.80 (CH_2), 20.36 (CH_2), 14.62 (CH_3).

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