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Directive effects in the hydroboration of 1-alkenyl derivatives of *o*-carborane with representative hydroborating agents [1]

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Abstract

A series of 1-alkenyl-*o*-carboranes was hydroborated using representative hydroborating agents with different steric requirements. The steric and electronic effects of the carboranyl group were evaluated by examining the distribution of the isomeric alcohols obtained after oxidation of the intermediate carboranyl-substituted organoboranes. © 1997 Elsevier Science S.A.

Keywords: Hydroboration; Alkenylcarboranes; *o*-Carborane; Borane–THF; Boron

1. Introduction

The regioselectivity of the hydroboration reaction is markedly influenced by the steric and electronic effects of the hydroborating agent as well as those exerted by the substituents on the alkene [1]. In the hydroboration of simple vinyl derivatives by borane (BH_3), the distribution of boron in the product is dependent upon the electronic nature of the substituent [2,3]. Thus, during the hydroboration of *p*-methoxystyrene only 7% of the boron becomes attached to the internal carbon of the original double bond; whereas in the hydroboration of *p*-chlorostyrene this percentage increases to 27%. Similarly, in allyl derivatives the percentage addition of boron to the internal carbon of the original double bond is dependent on the electronegativity of the substitutent: allyl borate, 18%; allyl benzoate, 25%; allyl acetate, 35%; allyl chloride, 40%; allyl tosylate, 45% [4]. Alkyl substitution on the terminal carbon of the allyl system greatly increases the percentage of boron at the position nearest to the electronegative substituent: crotyl chloride, 100%; crotyl acetate, 95%; crotyl benzyl ether, 91%; crotyl alcohol, 90%; crotyl ethyl ether, 84% [5]. In the hydroboration of homoallyl derivatives, substituents exhibit a diminished but still noticeable directive effect [6]. When the double bond is positioned further than three CH_2 units from the substituent, the hydroboration reaction proceeds in a normal fashion such that 94% of the boron becomes attached to the terminal carbon [7]. The use of more sterically demanding hydroborating agents such as dicyclohexylborane (Chx_2BH) and 9-borabicyclo[3.3.1]nonane (9-BBN) generates similar product distributions, except that the percentage of boron attached to the more open carbon of the original double bond is increased [8–10].

The hydroboration of 1-alkenyl-*o*-carboranes is of particular interest, both with respect to reactivity and regioselectivity. The carborane cage should deactivate the double bond towards hydroboration due to both its electronic (−I effect) and its steric bulk [11–18]. In addition, the steric factor should direct boron to the terminal carbon of the vinyl group, whereas the electronic factor should favor internal boron addition. Thus, the hydroboration reactions of several 1-alkenyl-*o*-carboranes were examined using representative hydroborating agents of different steric requirements; these include borane–THF ($BH_3 \cdot THF$), borane–methyl sulfide (BMS), Chx_2BH and 9-BBN [19], Scheme 1.

2. Results

The following alkenyl-*o*-carboranes were selected for study: 1-ethenyl-*o*-carborane (**1a**), 1-(1-methylethenyl)-

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[1] Dedicated to the memory of Professor Yuri Struchkov.

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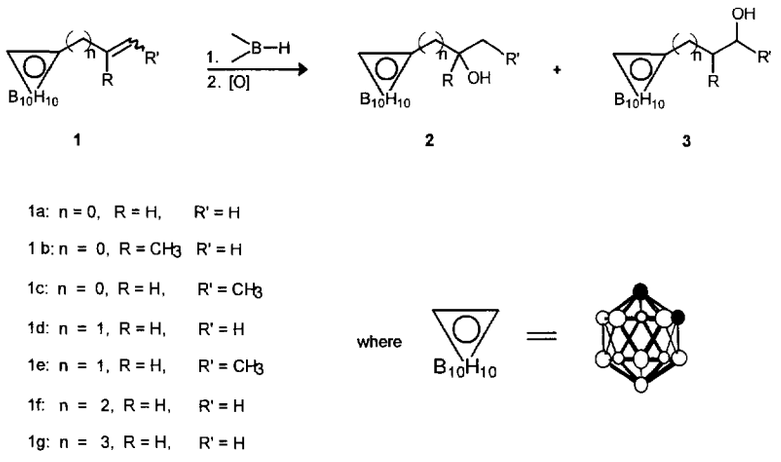


Scheme 1.

o-carborane (**1b**), 1-(*trans*-1-propenyl)-*o*-carborane (**1c**), 1-(2-propenyl)-*o*-carborane (**1d**), 1-(2-butenyl)-*o*-carborane (**1e**), 1-(3-butenyl)-*o*-carborane (**1f**), 1-(4-pentenyl)-*o*-carborane (**1g**), Table 1.

The hydroboration of 1-ethenyl-*o*-carborane (**1a**) with BMS (3:1 molar ratio) in THF at 25 °C proceeded slowly. Monitoring the reaction by ^{1}H NMR indicated that approximately 70% of the alkene had been hydroborated after 24 h. The data suggest that the hydroboration reaction proceeds primarily to the dialkylborane stage, which is typical of hindered alkenes. Oxidation of the organoborane intermediates with alkaline hydrogen peroxide and sodium perborate afforded the product alcohols in 44% and 65% yields respectively. The major by-product in the reaction was 1-ethyl-*o*-carborane. It has been reported [20] that organoboranes of the benzylic type undergo facile hydrolysis of the α-boron derivatives under oxidative conditions. In a separate experiment, deuterated methanol was added to the hydroboration reaction mixture prior to oxidation. ^{13}C NMR analysis indicated that 1-(1-deuterioethyl)-*o*-carborane was formed, as evidenced by a resonance at δ 31.70 which was split into a triplet (J_{DC} = 20.6 Hz) due to deuterium incorporation. Thus, in establishing the boron distribution between the α- and β-positions during the hydroboration of **1a** the percentage yield of 1-ethyl-*o*-carborane was added to that of the 1-(1-hydroxyethyl)-*o*-carborane (**2a**). The results indicate a boron distribution ratio between the internal and terminal positions (leading to **2a** and **3a**) of approximately 52:48. A trace (≤ 3%) of an adduct of carborane with THF was also detected in these reactions.

When the hydroboration reaction mixture (containing the dialkylborane intermediate generated from **1a**) was added to 1-hexene, the final reaction yielded the expected 1- and 2-hexanols in a ratio of 97:3 respectively after oxidation, confirming the presence of a dialkylborane reaction intermediate. The increased regioselectivity resulting from the use of disubstituted boranes has been well documented [21].

The hydroboration of 1-ethenyl-*o*-carborane (**1a**) with dicyclohexylborane Chx_2BH in THF (1:1 molar ratio) at 25 °C was 88% complete in 20 h. Oxidation of the hydroboration mixture with sodium perborate yielded

Table 1
Hydroboration of *o*-carboranylalkenes followed by oxidation [a]

Compound	*n*	BH_3		9-BBN		Chx_2BH	
		2:3	(2 + 3)%	2:3 [a]	(2 + 3)%	2:3	(2 + 3)%
1a	0	52:48 [b]	69 [b]	4:96	84	6:94	78
1b	0	< 1: > 99	68 [c]	—	—	—	—
1c	0	92:8 [b]	62 [b,c]	—	—	—	—
1d	1	34:66	88	< 1: > 99	91	< 1: > 99	96
1e	1	91:9	92 [c]	93:7	87 [c]	—	—
1f	2	7:93	72	—	—	< 1: > 99	91
1g	3	6:94	92	< 1: > 99	87 [c]	—	—

[a] Oxidation achieved using sodium perborate unless indicated otherwise.
[b] The percentage of isomer **2** was increased by a percentage equal to the quantity of 1-alkylcarborane formed by protonolysis.
[c] Hydrogen peroxide used as oxidant.

the expected primary and secondary carborane alcohols (**3a** and **2a**) in a 94:6 ratio respectively in an overall yield of 78% assuming the 2% of 1-ethylcarborane present in the mixture was generated from the boronated precursor of **2a**. Additional products in the reaction were adducts of both cyclohexyl and furanyl groups with carborane (7%). The hydroboration of **1a** with 9-BBN in hexanes (1:1 molar ratio) proceeded very slowly at 25 °C. Ultrasound irradiation at 30–35 °C enhanced the reaction rate such that the reaction was 92% complete in 12 h [22]. Oxidation of the reaction intermediates with sodium perborate produced a 84% yield of the primary and secondary alcohols (**3a** and **2a**) in a ratio of 96:4 respectively, assuming the 3% 1-ethyl-*o*-carborane arose from the precursor to **2a**.

The hydroboration of 1-(1-methylethenyl)-*o*-carborane (**1b**) with $BH_3 \cdot THF$ (3:1 molar ratio) in THF proceeded slowly, being nearly 73% complete in 16 h. As in the 1-ethenyl-*o*-carborane reactions, the reaction apparently proceeds to the dialkylborane stage. Oxidation of the products with sodium perborate revealed the exclusive formation of 1-(2-hydroxy-1-methylethyl)-*o*-carborane (**3b**). Further reactions with 9-BBN and dicyclohexylborane were not attempted due to the exclusive formation of **3b**. Interestingly, in a reaction in which alkaline hydrogen peroxide was utilized as an oxidant, 68% **3b** was obtained along with 5% 1-(1 methylethyl)-*o*-carborane, *o*-carborane (3%) and unreacted 1-(1-methylethenyl)-*o*-carborane (21%). *o*-Carborane presumably arises via an elimination reaction involving β-boron-substituted intermediates under the strongly alkaline conditions in the H_2O_2/OH^- oxidation.

The hydroboration of 1-(*trans*-1-propenyl)-*o*-carborane (**1c**) with $BH_3 \cdot THF$ (3:1 molar ratio) proceeded rapidly to the monoalkylborane stage and then very slowly to the dialkylborane stage. One-third of the starting alkene disappeared in 0.5 h and only 62% was hydroborated in 31 h. Examination of the ^1H NMR spectrum revealed that the major product was one in which the boron atom had become attached to the carbon adjacent to the carborane. Thus, the spectrum contained a singlet at 4.11 ppm due to a cage C–H proton, two overlapping multiplets at 1.49 ppm due to –CHB and $-CH_2$ groups, and a triplet at 0.85 ppm due to the terminal CH_3 group. The ^{13}C NMR spectrum supported these assignments. Oxidation of the hydroboration mixture using a simultaneous addition of sodium hydroxide and hydrogen peroxide afforded 45% 1-(1-hydroxypropyl)-*o*-carborane (**2c**), 5% 1-(2-hydroxypropyl)-*o*-carborane (**3c**), 1-propyl-*o*-carborane (12%), *o*-carborane (2%) and 1-(*trans*-1-propenyl)-*o*-carborane (33%). Thus the boron distribution was 92:8, favoring attachment of the boron to the carbon adjacent to the carborane.

The hydroboration of 1-(2-propenyl)-*o*-carborane (**1d**) with $BH_3 \cdot THF$ (3:1 molar ratio) in THF was complete in 60 min. In benzene, the reaction required 180 min. Oxidation of the reaction products afforded the primary and secondary alcohols in a ratio of 66:34 respectively in 88% yield. ^{11}B NMR analysis indicated the formation of around 3% of a cage degradation product using H_2O_2/OH^- as an oxidant, but only a trace (< 1%) when $NaBO_3$ was utilized. The degradation was evidenced by resonances at δ −15.84, −17.01, −20.82, −32.03 and −35.85, which are typical of *nido* carboranes [23]. Interestingly, the formation of 1-propyl-*o*-carborane (9%) was also noted. The ratio of isomeric alcohols could not be readily corrected due to uncertainty regarding the source of this hydrolysis product, and thus the uncorrected, observed values are reported. Hydroboration of **1d** with 9-BBN in hexanes (1:1 molar ratio) using ultrasound at 25 °C proceeded smoothly to the trialkylborane stage. ^{11}B NMR spectroscopy revealed the appearance of a resonance at 87.40 ppm due to the trialkylborane intermediate, and indicated that the reaction was complete in 3.5 h. Oxidation of the reaction intermediates with sodium perborate resulted in the formation of 1-(3-hydroxypropyl)-*o*-carborane (**3d**) in 91% yield. Similarly, the hydroboration of **1d** with Chx_2BH, followed by oxidation, afforded a 96% yield of **3d** and **2d** in a ratio greater than 99:1.

The hydroboration of a 15:85 *cis*:*trans* mixture of 1-(2-butenyl)-*o*-carborane (**1e**) with $BH_3 \cdot THF$ at 25 °C (3:1 molar ratio) was complete in 12 h. The *cis* olefin hydroborated much faster than the *trans* olefin. The hydroboration being complete within 2 h. Oxidation of the reaction products by alkaline hydrogen peroxide afforded a 92% yield of the product alcohols in a 91:9 ratio with the major product being the 1-(2-hydroxy-1-butyl)-*o*-carborane (**2e**) and the minor product being **3e**. Examination of the ^{11}B NMR spectrum of the crude products indicated the presence of 3% cage degradation products. The hydroboration of **1e** with 9-BBN in hexanes (1:1 molar ratio) using ultrasound irradiation proceeded slowly to the B-R-9-BBN intermediate. Oxidation of the reaction mixture with alkaline hydrogen peroxide produced an 87% yield of the isomeric alcohols in a 93:7 ratio for **2e**:**3e**.

Hydroboration of the 1-(3-butenyl)-*o*-carborane (**1f**) with $BH_3 \cdot THF$ proceeded smoothly. Oxidation of the reaction mixture with alkaline hydrogen peroxide afforded carborane products in 96% yield. The yield of the expected product alcohols, however, was only 72%. Large amounts of 1-butyl-*o*-carborane (9%) and of coupling products between THF and a butyl-*o*-carborane (15%) were also detected. The ratio of primary to secondary alcohols (**3f** to **2f**) was 93:7. Hydroboration of **1f** with dicyclohexylborane increased the ratio to greater than 99:1, as anticipated.

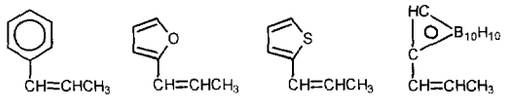
The hydroboration of 1-(4-pentenyl)-*o*-carborane (**1g**) with $BH_3 \cdot THF$ proceeded rapidly to the trialkylborane

stage. The reaction was complete in 3 h. Oxidation of the reaction products with sodium perborate afforded a 92% yield of primary and secondary alcohols (**3g** and **2g**) in a ratio of 94:6. Trace amounts of 1-pentyl-*o*-carborane (2%) and cage degradation products (3%) were also detected by ^{1}H and ^{11}B NMR. The hydroboration of **1g** with 9-BBN in hexanes, under ultrasound irradiation, was complete within 2 h as evidenced by ^{11}B NMR. Oxidation with alkaline hydrogen peroxide afforded **3g** in 87% yield along with 1-pentyl-*o*-carborane in 9% yield. A trace amount of cage degradation products was also detected by ^{11}B NMR.

3. Discussion

The hydroboration of 1-ethenyl-*o*-carborane (**1a**) with borane proceeds to place 45% of the boron at the terminal carbon and 55% at the internal position. The large percentage of boron attached to the carbon adjacent to the carborane nucleus is an indication of the powerful electron-withdrawing characteristics of the *o*-carboranyl group. This effect is exerted mostly by an inductive mechanism but a resonance contribution involving conjugation of the p orbital of the vinyl group and the p-type orbital of the cage cannot be excluded [24–26]. The terminal boron intermediate was found to be stable towards elimination even under alkaline conditions. The boron intermediate in which the boron was attached to the carbon adjacent to the carborane was found to be susceptible to protonolysis owing to the strong electron-withdrawing properties of the carborane cage. The formation of these alkyl-*o*-carborane by-products could be minimized by employing sodium perborate as the oxidizing agent. Thus, a remarkable decrease in the yield of ethyl-*o*-carborane was made possible by utilizing the more mild $NaBO_3$ (4%) instead of H_2O_2/OH^- (22%) as the oxidizing agent. Hydroboration with Chx_2BH and 9-BBN resulted, as anticipated, in the predominant addition of boron to the terminal carbon atom. The role of the electronic effect of the cage is largely overcome by the large steric effects of these reagents.

Despite the large electron-withdrawing effect of the carboranyl group, introduction of the methyl group on the alkenyl carbon adjacent to the carboranyl cage in 1-(1-methylethenyl)-*o*-carborane (**1b**) was sufficient to bring about the reversal of the direction of boron addition; thus placement of the boron in the product was primarily at the terminal carbon atom. This can be attributed to steric effects. Similar results were previously obtained in the hydroboration of α-methylstyrene and 1,1-diphenylethylene [27]. In the case of the 1-(1-propenyl)-*o*-carborane (**1c**), boron distribution is a consequence of the −I effect of the carboranyl cage. Comparing the boron distribution in the hydroboration of several aromatic propenyl derivatives (see below) with **1c**, it appears that the *o*-carboranyl moiety exhibits a directive effect similar to that of furan or thiophene.



	%	%	%	%	%	%	%	%
BH_3-THF	85	15	91	9	89	11	91	9
9-BBN	97	3	96	4	94	6	93	7

During oxidation of the borane products obtained from both **1b** and **1c** with H_2O_2/OH^-, a base-catalyzed elimination generating 2–3% of *o*-carborane was observed; presumably this side reaction is proceeding via a *beta* elimination reaction. However, when the oxidation was carried out using $NaBO_3$, the production of *o*-carborane was minimized.

In the reaction of $BH_3 \cdot THF$ with 1-(2-propenyl)-*o*-carborane (**1d**), 66% of the boron added to the terminal carbon and 34% to the internal carbon. The considerable degree of boron addition to the internal carbon of the double bond is presumably a result of the strong electronic effects exerted by the carboranyl group. In the reaction of borane with allylbenzene, 10% of the boron adds to the internal carbon, whereas with allyl chloride and allyl acetate this percentage increases to 60% and 65% respectively. The use of Chx_2BH and 9-BBN as hydroborating agents resulted in the expected reversal of regioselectivity, boron once again adding to the terminal carbon.

In the crotyl derivative **1e**, there was a marked enhancement in the addition of the boron to the alkene carbon closest to the carborane. Thus, the reaction with $BH_3 \cdot THF$ with **1e** resulted in 91% of the boron attached to the carbon nearest to the carborane nucleus. In the crotyl system, the directive effect of the carborane cage appears to be similar to the directive effect of either a hydroxy or benzyl ether group.

The carboranyl group in 1-(3-butenyl)-*o*-carborane (**1f**) exhibits a diminished directive effect during the hydroboration. The average distribution of the boron, as evidenced by ^{1}H NMR and GC analyses, was 92% terminal addition and 8% internal. When the carboranyl group is more remote from the double bond, the directive effect diminishes. Thus, in 1-(4-pentenyl)-*o*-carborane (**1g**) hydroboration affords the anticipated 94:6 boron distribution (terminal versus internal respectively). Formation of the internal boron derivatives was minimized through the use of 9-BBN and Chx_2BH as hydroborating agents. Greater than 99% selectivity for the terminal carbon was obtained in all cases.

4. Experimental section

The *o*-carborane and 1-ethenyl-*o*-carborane were purchased from Dexsil Corp. Compounds **1d**, **1e**, **1f** and **1g** were prepared as previously reported by Hawthorne and coworkers [28], compound **1c** was prepared by isomerizing 1-(2-propenyl)-*o*-carborane (**1d**) as previously reported by Hermanek and coworkers [29] and compound **1b** was prepared as reported by Zakharkin et al. [30].

Reaction flasks and other glassware were stored overnight in a drying oven at 150 °C and assembled in a stream of dry nitrogen gas. Syringes were assembled, fitted with needles while hot and then cooled in a stream of dry nitrogen gas. The handling of air-sensitive materials was carried out in a dry-box or a glove-bag under argon or nitrogen. In this study, all hydroborations with $BH_3 \cdot THF$ or BMS were carried out using a 1:1 molar ratio of hydride to alkene at 25 °C. The hydroborations with 9-BBN were performed using ultrasound at 35–40 °C while those using Chx_2BH were performed under standard conditions in which the reaction temperature was allowed to rise from 0 to 25 °C. In all cases the progress of the reaction was followed by ^1H NMR unless otherwise indicated. The yields of the reactions were calculated by ^1H NMR using dibromobenzene as internal standard. The ratio of the isomeric alcohols was established by ^1H NMR and GC/MS following treatment of the crude products with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The agreement between the two techniques was generally good (±1%).

Proton (^1H NMR), carbon (^{13}C NMR) and boron (^{11}B NMR) spectra were recorded on a Bruker AMX 400 spectrometer at 400.13, 100.62 and 128.38 MHz respectively. Chemical shifts for ^1H NMR and ^{13}C NMR spectra were referenced to $SiMe_4$ (0.00 ppm) and measured with respect to residual protons in the deuterated solvent. Chemical shift values for ^{11}B spectra were referenced relative to $BF_3 \cdot OEt_2$ (0.00 ppm). Coupling constants *J* are given in hertz. Resonances observed upfield of the references were assigned negative chemical shift values in all cases. Mass spectra were recorded on GC/MS (Hewlett-Packard 5890 gas chromatograph and 5970 series mass selective detector equipped with a cross-bonded 100% dimethylpolysiloxane column). Melting points were determined on a Thomas-Hoover capillary melting point apparatus. The melting points are uncorrected.

The gas chromatographic analyses were performed on either a Varian Associates Model 3700 or a Hewlett-Packard Model 5750 gas chromatograph. The following columns were used: 5% SE-30 on Chromosorb W (10 ft × 0.25 in), 10% SE-30 on Chromosorb W (10 ft × 0.25 in), or 10% Carbowax 20 M on Chromosorb W (10 ft × 0.25 in). Products were isolated by HPLC on a Varian Associate Model 5000 HPLC fitted with programmable gradient elution capability and utilizing a reverse-phase ODC-3 column.

4.1. 1-Ethenyl-o-carborane (1a)

The 1-ethenyl-*o*-carborane was purified by vacuum sublimation. Purity was checked by mass spectrometry, ^1H NMR, ^{13}C NMR and ^{11}B NMR. The purified material was a waxy solid at room temperature with a sharp melting point at 79 °C [31]. ^1H NMR (THF-d_8) δ 6.09 (dd, 1H, J = 16.92, 10.56 Hz), 5.60 (d, 1H, J = 16.92 Hz), 5.36 (d, 1H, J = 10.56 Hz), 4.57 (s, 1H). ^{13}C NMR (THF-d_8) δ 133.2, 122.4, 74.8, 61.6. ^{11}B NMR (THF-d_8) δ −2.28 (d, 1B), −4.86 (d, 1B), −9.05 (d, 2B), −11.21 (d, 4B), −12.78 (d, 2B). ^{11}B NMR ($CDCl_3$) δ −3.16 (d, 1B), −5.72 (d, 1B), −9.87 (d, 2B), −11.93 (d, 4B), −13.51 (d, 2B).

4.2. 1-(1-Methylethenyl)-o-carborane (1b)

The potassium salt of 1-(1-methylethenyl)-*o*-carboranecarboxylic acid (11.3 mmol, 3.02 g) was refluxed with H_2O (50 ml) for 15 min [32]. After cooling to 25 °C, the mixture was transferred to a separatory funnel and diluted with diethyl ether (50 ml). The layers were separated and the aqueous layer was extracted with additional Et_2O (2 × 20 ml). The combined ether extracts were then dried over anhydrous $MgSO_4$ and concentrated in vacuo. HPLC separation on an ODC-3 column (CH_3OH:H_2O 80:20) afforded a 62% yield (7.13 mmol, 1.33 g) of a white fine solid; m.p. 43–45 °C [31]. ^1H NMR ($CDCl_3$) δ 5.24 (bs, 1H), 5.12 (bs, 1H), 3.77 (s, 1H), 1.89 (bs, 3H). ^{13}C NMR ($CDCl_3$) δ 137.9, 118.5, 77.1, 59.5, 23.1. ^{11}B NMR ($CDCl_3$) δ −3.06 (d, 1B), −4.93 (d, 1B), −9.40 (d, 2B), −11.51 (d, 2B), −12.06 (d, 2B), −13.58 (d, 2B). MS (EI): *m/z* Found 186.2193; $C_5H_{16}B_{10}$ Calc. 186.2183.

4.3. 1-(trans-1-Propenyl)-o-carborane (1c)

A solution of 1-(2-propenyl)-*o*-carborane **1d** (15.4 mmol, 2.83 g), benzene (20 ml) and potassium *tert*-butoxide (24.3 mmol, 2.73 g) was heated for 3 h at 40–45 °C. The mixture was neutralized with dilute HCl and washed with water (30 ml). The layers were separated and the aqueous layer was extracted with Et_20 (3 × 30 ml). The combined extracts were dried over anhydrous $MgSO_4$ and concentrated in vacuo to give **1c** as a white solid which was further purified by HPLC using an ODC-3 column [H_2O (15%): MeOH (85%)] to afford a 45% yield (6.90 mmol, 1.27 g) of a white solid; m.p. 78–79 °C [29]. ^1H NMR ($CDCl_3$) δ 6.05 (dd, 1H, J = 15.2, 6.4 Hz), 5.66 (dd, 1H, J = 15.2, 1.8 Hz), 1.71 (dd, 3H, J = 6.4, 1.8 Hz). ^{13}C NMR ($CDCl_3$) δ 135.3, 125.4, 74.2, 60.9, 17.6. ^{11}B NMR ($CDCl_3$) δ −3.15 (d,

1B), −6.48 (d, 1B), −10.49 (d, 2B), −12.14 (d, 2B), −12.87 (d, 2B), −14.06 (d, 2B). MS (EI): *m/z* Found 186.2194; $C_5H_{16}B_{10}$ Calc. 186.2183.

4.4. 1-(2-Propenyl)-o-carborane (1d)

The general procedure involves sequential silylation–alkylation–desilylation starting with *o*-carborane and was utilized to prepare **1e**, **1f** and **1g**.

(a) 1-^{t}Butyldimethylsilyl-*o*-carborane (**4**). To a solution of *o*-carborane (99.8 mmol, 14.4 g) in a dry benzene–diethyl ether (2:1) mixture (85 ml) at 0 °C was added ^{n}BuLi in hexane (105 mmol, 42.0 ml of a 2.50 M solution) dropwise with stirring. The mixture was allowed to stir for 30 min while warming to ambient temperature. The solution was then cooled to 0 °C and *tert*-butyldimethysilyl chloride (110 mmol, 16.5 g) in a benzene–diethyl ether (2:1) mixture (25 ml) was rapidly added dropwise. The solution was refluxed overnight, cooled, quenched with water (40 ml), transferred to a separatory funnel and diluted with diethyl ether (85 ml). The layers were separated and the aqueous layer was extracted with additional Et_2O (2 × 300 ml). The combined extracts were then dried over anhydrous $MgSO_4$ and concentrated in vacuo. Heating the mixture to 80 °C (0.001 mmHg) removed unreacted *o*-carborane by sublimation. The product **4** was distilled at 120 °C to yield 90% of the desired product (89.8 mmol, 23.2 g); m.p. 54–56 °C. ^{1}H NMR ($CDCl_3$) δ 3.28 (s, 1H), 1.05 (s, 9H), 0.30 (s, 6H). ^{11}B NMR ($CDCl_3$) δ 0.05 (d, 1B), −2.02 (d, 1B), −7.25 (d, 2B), −10.97 (d, 2B), −12.52 (d, 2B), −13.49 (d, 2B).

(b) 1-^{t}Butyldimethylsilyl-2-(2-propenyl)-*o*-carborane (**4d**). To a solution of **4** (17.5 mmol, 4.52 g) in a dry benzene–diethyl ether mixture (50 ml) at 0 °C was added ^{n}BuLi in hexane (17.8 mmol, 7.11 ml of a 2.50 M solution) dropwise with stirring. The mixture was allowed to stir for 30 min while warming to ambient temperature. After cooling to 0 °C, allyl bromide (17.9 mmol, 1.55 ml) was added dropwise with stirring. After refluxing overnight, the solution was quenched with water (30 ml), transferred to a separatory funnel, and diluted with diethyl ether (60 ml). The layers were separated and the aqueous layer was extracted with Et_2O (2 × 50 ml). The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated in vacuo to give a 73% yield (12.8 mmol, 3.82 g) of crude **4d** which was used in the next reaction sequence.

(c) 1-(2-propenyl)-*o*-carborane. A solution of **4d** (12.0 mmol, 3.58 g) in dry THF (35 ml) was cooled to −76 °C and tetrabutylammonium fluoride in THF (13.2 mmol, 13.2 ml of a 1.00 M solution) was added dropwise with stirring. The mixture was allowed to stir for 30 min while warming to room temperature and then water (15 ml) was added. The solution was diluted with diethyl ether (20 ml) and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted into Et_2O (2 × 25 ml). The combined extracts were dried over anhydrous $MgSO_4$ and concentrated in vacuo to give **1d** as a viscous liquid in 72% yield (8.57 mmol, 1.58 g). Spectroscopic data were in agreement with literature values [28]. ^{1}H NMR ($CDCl_3$) δ 5.67 (1H, m), 5.20 (d, 1H, J = 10.0 Hz), 5.13 (m, 1H), 3.58 (s, 1H), 2.94 (d, 2H, J = 7.2 Hz). ^{13}C NMR ($CDCl_3$) δ 131.2. 120.1, 73.7, 59.6, 41.8. ^{13}C NMR (C_6D_6) δ 131.7. 120.4, 73.9, 60.2, 41.4. ^{11}B NMR (acetone) δ −2.27 (d, 1B), −5.44 (d, 1B), −8.95 (d, 2B), −10.82 (d, 2B), −11.73 (d, 2B), −12.37 (d, 2B). ^{11}B NMR ($CDCl_3$) δ −2.62 (d, 1B), −5.96 (d, 1B), −9.38 (d, 2B), −11.26 (d, 2B), −13.16 (d, 4B). MS (EI): *m/z* Found 186.2174; $C_5H_{16}B_{10}$ Calc. 186.2183.

4.5. 1-(2-Butenyl)-o-carborane (1e)

The reagent was prepared via the silylation–alkylation–desilylation procedure outlined for **1d**.

(a) 1-^{t}Butyldimethylsilyl-1-(2-butenyl)-*o*-carborane (**4e**). **4** (19.8 mmol, 5.11 g) vida supra was treated with ^{n}BuLi in hexane (20.3 mmol, 8.10 ml of a 2.50 M solution) and 1-bromo-2-butene (85:15 *trans*:*cis* mixture) (20.4 mmol, 2.15 ml) to afford a 77% yield (15.2 mmol, 4.75 g) of a *cis*:*trans* mixture of **4e** which was utilized directly in the next step.

(b) 1-(2-Butenyl)-*o*-carborane. A solution of **4e** (13.8 mmol, 4.32 g) was treated with tetrabutylammonium fluoride in THF (15.0 mmol, 15.0 ml of a 1.00 M solution) as described earlier to produce **1e** as a *cis*:*trans* mixture in 76% yield (10.5 mmol, 2.08 g). *Trans* isomer: ^{1}H NMR (C_6D_6) δ 5.55 (m, 1H), 5.33 (m, 1H), 3.56 (s, 1H), 2.93 (d, 2H, J = 8 Hz), 1.71 (d, 3H, J = 8 Hz). ^{13}C NMR (C_6D_6) 131.9, 124.2, 74.9, 60.07, 40.70, 17.70. *Cis* isomer: ^{1}H NMR (C_6D_6) δ 5.73 (m, 1H), 5.35 (m, 1H), 3.56 (s, 1H), 2.99 (d, 2H, J = 8 Hz), 1.62 (d, 3H, J = 8 Hz). ^{13}C NMR (C_6D_6) δ 129.8, 123.2, 74.8, 60.3, 34.4, 13.6. ^{11}B NMR (C_6D_6) *cis*/*trans* mixture δ −2.83 (d, 1B), −6.13 (d, 1B), −9.49 (d, 2B), −11.28 (d, 2B), −13.25 (d, 4B). Purification (HPLC) also afforded the [1,2-$B_9C_2H_{11}(C_4H_9)$][$(C_4H_7)_4N$] salt: ^{11}B NMR ($CDCl_3$) δ −11.31 (2B, d), −14.21 (1B, d), −18.24 (3B, d), −22.49 (1B, d), −33.73 (1B, dd, J = 123.1 and 41.2 Hz), −37.47 (1B, d). MS (EI): *m/z* Found 200.00; $C_6H_{18}B_{10}$ Calc. 200.23.

4.6. 1-(3-Butenyl)-o-carborane (1f)

The reagent was prepared via a silylation–alkylation–desilylation procedure as described earlier.

(a) 1-^{t}Butyldimethylsilyl-2-(3-butenyl)-*o*-carborane (**4f**). **4** (17.8 mmol, 4.59 g) vida supra was reacted with ^{n}BuLi in hexane (18.8 mmol, 7.51 ml of a 2.50 M solution) and 4-bromo-1-butene (19.4 mmol, 2.00 ml) to af-

ford a 75% yield (13.4 mmol, 4.18 g) of **4f** which was used in the next step without further purification.

(b) 1-(3-Buten-1-yl)-*o*-carborane (**1f**). A solution of **4f** (12.4 mmol, 3.98 g) in dry THF (35 ml) was treated with tetrabutylammonium fluoride (14.2 mmol, 14.2 ml of a 1.00 M solution) as described earlier. HPLC purification on an ODC-3 column (80:20 MeOH:H_2O) afforded 57% yield (7.21 mmol, 1.43 g) of **1f**; m.p. 45–46 °C [33]. ^{1}H NMR ($CDCl_3$) δ 5.75 (m, 1H), 5.04 (m, 2H), 4.57 (s, 1H), 2.42 (m, 2H), 2.27 (m, 2H). ^{13}C NMR (acetone-d_6) δ 136.4, 116.5, 76.3, 63.1, 37.3, 33.7. ^{11}B NMR (acetone) δ −2.40 (d, 1B), −5.50 (d, 1B), −9.08 (d, 2B), −10.96 (d, 4B), −12.51 (d, 2B). ^{11}B NMR (THF-d_8) δ −1.09 (d, 1B), −4.28 (d, 1B), −7.86 (d, 2B), −9.76 (d, 4B), −11.28 (d, 2B). MS (EI): m/z Found 200.2342; $C_6H_{18}B_{10}$ Calc. 200.2339.

4.7. 1-(4-Pentenyl)-o-carborane (1g)

The reagent was prepared via a silylation–alkylation–desilylation procedure as described for **1d**.

(a) 1-^{t}Butyldimethylsilyl-2-(4-pentenyl)-*o*-carborane (**4g**). **4** (23.6 mmol, 6.10 g) vide supra was treated with ^{n}BuLi in hexane (25.0 mmol, 10.0 ml of a 2.50 M solution) and then 5-bromo-1-pentene (26.7 mmol, 3.10 ml) to yield 71% (16.7 mmol, 5.44 g) of the desired product which was used without further purification.

(b) 1-(4-Pentenyl)-*o*-carborane (**1g**). A solution of **4g** (16.4 mmol, 5.36 g) was treated with tetrabutylammonium fluoride (17.0 mmol, 17.0 ml of a 1.00 M solution) to afford **1g** as a viscous liquid in 78% yield (12.8 mmol, 2.71 g). ^{1}H NMR (C_6D_6) δ 5.51 (m, 1H), 4.88 (m, 2H), 3.06 (s, 1H), 1.80 (m, 2H), 1.72 (m, 2H), 1.23 (m, 2H). ^{1}H NMR ($CDCl_3$) δ 5.71 (m, 1H), 5.03 (m, 2H), 3.56 (s, 1H), 2.19 (m, 2H), 2.04 (m, 2H), 1.56 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 136.7, 116.1, 75.4, 61.2, 37.3, 32.7, 28.3. ^{11}B NMR ($CDCl_3$) δ −3.02 (d, 1B), −6.28 (d, 1B), −9.63 (d, 2B), −11.78 (d, 2B), −12.43 (d, 2B), −13.43 (d, 2B). MS (EI): m/z Found 214.2527; $C_7H_{20}B_{10}$ Calc. 214.2496. The purification process (HPLC) also afforded the [1,2-$B_9C_2H_{11}(C_5H_9)$][$(C_4H_9)_4N$] salt (15%). ^{11}B NMR ($CDCl_3$) δ −11.74 (2B, d), −14.39 (1B, d), −18.39 (3B, d), −22.62 (1B, d), −33.88 (1B, d), −37.76 (1B, d). ^{13}C NMR ($CDCl_3$) δ 136.6, 113.5, 60.0, 47.5, 38.4, 33.4, 30.00; $(C_4H_7)N$ 58.41, 23.41, 19.12, 13.10. ^{1}H NMR ($CDCl_3$) δ 5.777 (1H, m), 4.936 (2H, m), 1.99 (2H, m), 1.77 (2H, m), 1.52 (2H, m); $(C_4H_7)_4N$ 3.19 (2H, m), 1.79 (2H, m), 1.53 (2H, m), 1.01 (3H, t, J = 7.04 Hz).

4.8. Hydroboration

4.8.1. General procedure

The hydroborations were carried out using published procedures [3,4]. The alkene was added to a dry, argon-flushed, 25 ml three-necked flask, equipped with an argon inlet tube, a gas outlet tube connected to a mercury bubbler, a thermometer and a magnetic stirring bar while maintaining a positive pressure of argon. The flask was cooled to 0 °C, and hydroboration was initiated by the dropwise addition of borane. The mixture was stirred at room temperature for variable amounts of time.

4.8.2. Hydroboration of 1-ethenyl-o-carborane (1a) with BMS

1a (3.11 mmol, 530 mg) in THF (2.5 ml) was cooled to 0 °C and BMS (1.05 mmol, 0.590 ml of a 1.78 M solution in THF) was added dropwise via a syringe. The reaction was allowed to stir at 25 °C for 24 h. The solution was analyzed for residual hydride by addition of H_2O (1 ml) and the hydrogen evolved indicated a maximum of 70% hydroboration of the 1-ethenyl-*o*-carborane in the reaction. The reaction mixture was oxidized, at 0 °C, by addition of THF (10 ml), H_2O (10 ml) and sodium perborate (4.66 mmol, 717 mg). The mixture was stirred vigorously overnight at 25 °C. The aqueous phase was saturated with NaCl, the phases separated and the aqueous layer extracted with ether (5 × 10 ml). The combined organic phase was dried over anhydrous $MgSO_4$ and the product analyzed by GLC using a 6 ft column packed with 5% SE-30 on Chromosorb W with tetradecane (0.253 mmol, 50.2 mg) as internal standard. The analysis indicated that the following products were formed: 1-(2-hydroxyethyl)-*o*-carborane (33%) (**3a**), 1-(1-hydroxyethyl)-*o*-carborane (32%) (**2a**), 1-ethyl-*o*-carborane (4%), a 1-ethyl-*o*-carborane · THF adduct (2%) and unreacted starting material (23%).

In a separate experiment, **1a** (1.00 mmol, 170 mg) in THF (0.70 ml) was hydroborated at 0 °C by the dropwise addition of BMS (0.35 mmol, 0.20 ml of a 1.75 M solution in THF). The reaction was allowed to stir at 25 °C for 24 h. Treatment with sodium hydroxide (1.98 mmol, 0.66 ml of a 3.0 N solution) and hydrogen peroxide (6.6 mmol, 0.66 ml of a 30% solution) at 0 °C resulted in an exothermic reaction. The mixture was allowed to stir for 3 h at 25 °C and then heated for 1 h at 50 °C. The aqueous phase was saturated with NaCl, extracted with ether (5 × 15 ml) and the combined ether extracts dried over anhydrous $MgSO_4$. Following solvent evaporation, the residue was examined by ^{1}H NMR with the following results: 15% 1-(1-hydroxyethyl)-*o*-carborane (**2a**), 29% 1-(2-hydroxyethyl)-*o*-carborane (**3a**), 1-ethyl-*o*-carborane (21%) and 1-ethenyl-*o*-carborane (29%). A portion of the reaction mixture was treated with BSTFA and the isomeric silyl ethers analyzed by GLC on a 6 ft 5% SE-30 on Chromosorb W. The results indicate an isomer distribution of primary to secondary alcohols of 67:33, which is in line with the NMR data. The mixture was separated by

preparative GLC on a 7% SE-30 column on Chromosorb W.

2a. Oil. ^{1}H NMR (CD_3CN) δ 4.34 (1H, s), 4.26 (1H, q, $J = 6.4$ Hz), 1.30 (3H, d, $J = 6.4$ Hz). ^{13}C NMR ($CDCl_3$) δ 79.5, 68.9, 58.6, 23.6. ^{11}B NMR (32.1 MHz) ($CDCl_3$) δ −3.61 (2B, d), −12.02 (8B, d). MS (EI) m/z Found 190.2134; $C_4H_{16}^{11}B_{10}O$ Calc. 190.2132.

3a. M.p. 51–52 °C [34]. ^{1}H NMR (CD_3CN) δ 4.35 (1H, s), 3.61 (2H, t, $J = 6.4$ Hz), 2.45 (2H, t, $J = 6.4$ Hz). ^{13}C NMR ($CDCl_3$) δ 73.1, 60.6, 60.4, 39.7. ^{11}B NMR ($CDCl_3$) δ −1.72 (1B, d), −4.78 (1B, d), −8.67 (2B, d), −12.9 (6B, d). MS (EI) m/z Found 190.2102; $C_4H_{16}B_{10}O$ Calc. 190.2132.

1-Ethyl-*o*-carborane. M.p. 38–40 °C [35]. ^{1}H NMR (acetone-d_6) δ 4.52 (1H, s), 2.37 (2H, q, $J = 7.5$ Hz), 1.09 (3H, t, $J = 7.5$ Hz). ^{1}H NMR ($CDCl_3$) δ 3.56 (1H, s), 2.29 (2H, q, $J = 7.6$ Hz), 1.09 (3H, t, $J = 7.6$ Hz). ^{13}C NMR ($CDCl_3$) δ 76.4, 60.9, 31.6, 13.5. ^{11}B NMR ($CDCl_3$) δ −2.65 (1B, d), −6.21 (1B, d), −9.58 (2B, d), −11.7 (2B, d), 12.6 (2B, d), −13.4 (2B, d).

*4.8.3. Reaction of 1-ethenyl-o-carborane (**1a**) with BMS and subsequent reaction of the dialkylborane intermediate with hexene*

Into a 5 mm NMR tube (dry-box) were placed, sequentially, **1a** (1.27 mmol, 216 mg), dibromobenzene (0.106 mmol, 25.0 mg) and THF-d_8 (0.5 ml). The NMR tube was then capped with a plastic stopper and an additional rubber septum. The NMR tube was placed in an ice bath and, under argon, BMS (0.42 mmol, 0.22 ml of a 1.92 M solution in THF) was carefully added via a syringe. The NMR tube was withdrawn from the ice, shaken, and monitored by ^{1}H NMR. When 65% of the olefin had been consumed (28 h), a slight excess of hexene (0.51 mmol, 42.6 mg) was added at 25 °C. The reaction was maintained at 25 °C and monitored by ^{11}B NMR and ^{1}H NMR. After 2 h, the contents of the NMR tube were carefully washed (dry-box) with THF (20 ml) into a flask which contained sodium perborate (1.9 mmol, 290 mg) which was sealed with a rubber septum and removed from the dry-box. Water (10 ml) was added via a syringe and the solution was stirred at 25 °C for 8 h. The layers were separated and the aqueous layer was extracted with additional Et_20 (2 × 10 ml). The combined organic phase was dried over anhydrous $MgSO_4$ and most of the solvent was evaporated. Tetradecane (0.215 mmol, 42.6 mg) was added and the yield of alcohols was determined by GLC using a 10% Carbowax 20 M column on Chromosorb W. The yield of hexanol was found to be 70%. The ratio of 1-hexanol to 2-hexanol was 97:3.

*4.8.4. Reaction of 1-ethenyl-o-carborane (**1a**) with dicyclohexylborane*

To a 25 ml two-necked flask containing cyclohexene (2.9 mmol, 0.29 ml) in THF (1 ml), immersed in an ice-bath, was added BMS (1.38 mmol, 0.71 ml of a 1.94 M solution in THF). The reaction was allowed to stir at 0 °C for 3 h. **1a** was added (1.38 mmol, 235 mg in 1 ml of THF) under a blanket of argon and the reaction mixture was allowed to warm to 25 °C and stirred for 20 h. Oxidation was performed by the sequential addition of THF (5 ml), H_2O (5 ml), and sodium perborate (6.2 mmol, 0.96 g). The reaction was allowed to proceed for 12 h with vigorous stirring. The organic layer was separated and the aqueous layer extracted with ether (4 × 10 ml). The combined ether extracts were washed with saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was evaporated to afford a clear liquid which, upon analysis by ^{1}H NMR using hexadecane (0.618 mmol, 140 mg) as internal standard, indicated 84% 1-(2-hydroxyethyl)-*o*-carborane (**3a**), 3% 1-(1-hydroxyethyl)-*o*-carborane (**2a**), 1-ethyl-*o*-carborane (2%) and cyclohexyl and furanyl adducts of ethyl-*o*-carborane (8%). An aliquot of the dried extract was treated with BSTFA and heated for 1 h at 35 °C. The resulting silylated derivatives of the isomeric alcohols were analyzed by GC/MS. The distribution of primary to secondary alcohols was found to be 98:2.

*4.8.5. Reaction of 1-ethenyl-o-carborane (**1a**) with 9-BBN in hexanes*

1a (1.02 mmol, 174 mg) in a 10 mm NMR tube was reacted with (dry-box) 9-BBN (1.07 mmol, 2.14 ml of a 0.50 M solution in hexane) at 25 °C. The NMR tube was placed in a sonicator and the reaction monitored periodically by ^{1}H NMR for remaining olefin. At the end of 24 h, the reaction mixture was oxidized by the sequential addition of H_2O (5 ml), THF (5 ml) and sodium perborate (4.82 mmol, 741 mg). After 14 h at room temperature the contents of the tube were washed with ether (5 × 5 ml) into a separatory funnel, the tube rinsed with an equal volume of water, and the organic phase separated.

Analysis by ^{1}H NMR using dibromobenzene (0.159 mmol, 37.6 mg) as internal standard indicated the following: **3a** (90%), **2a** (1%), 1-ethyl-*o*-carborane (3%). An aliquot of the crude product was treated with 0.4 ml of BSTFA and the mixture was heated for 1 h at 30 °C. Examination of the product mixture by GC/MS confirmed the isomer distribution.

*4.8.6. Reaction of 1-(1-methylethenyl)-o-carborane (**1b**) with BMS and $BH_3 \cdot THF$*

1b (1.54 mmol, 283 mg) was hydroborated as described earlier using BMS (0.52 mmol, 0.29 ml of a 1.8 M solution in THF). After 8 h, sodium perborate (1.625 mmol, 250.0 mg) was added as oxidant and ^{1}H NMR analysis of the product mixture using hexadecane (0.356 mmol, 80.5 mg) as internal standard indicated the presence of 1-(2-hydroxy-1-methylethyl)-*o*-carborane (**3b**) (40%) and unreacted starting material (54%). In a

separate experiment, **1b** (1.20 mmol, 221 mg) was treated with $BH_3 \cdot THF$ (0.41 mmol, 0.41 ml of a 1.0 M solution). After 20 h, the reaction mixture was oxidized by the simultaneous addition of sodium hydroxide (0.60 mmol, 0.20 ml of a 3.0 N solution) and hydrogen peroxide (2.0 mmol, 0.20 ml of a 30% solution) at 25 °C for 6 h. Analysis by ^{1}H NMR revealed the following products: 68% **3b**, 1-(1-methylethyl)-*o*-carborane (5%), *o*-carborane (3%) and **1b** (21%). An aliquot of the crude product was treated with BSTFA to afford only the silylated ether of **3b**. No silyl derivative of the 1-(1-hydroxy-1-methylethyl)-*o*-carborane was detected. The 1-(2-hydroxy-1-methylethyl)-*o*-carborane was purified by recrystallization from hexanes: ^{1}H NMR (acetone-d_6) δ 4.77 (1H, s), 3.60 (1H, dd, $J = 6.4$ Hz), 3.53 (1H, dd, $J = 6.4$ Hz), 2.55 (1H, m), 1.15 (3H, d, $J = 7.2$ Hz). ^{13}C(^{1}H) COSY NMR (acetone-d_6) δ 79.5, 65.1 (3.60, 3.53), 61.1 (4.77), 41.3 (2.55), 17.3 (1.15). ^{11}B NMR (acetone-d_6) δ −2.12 (1B, d), −3.79 (1B, d), −8.61 (2B, d), 10.32 (4B, d), −12.04 (2B, d). MS (EI) *m/z* (m−CH_4) Found 259.230; $C_7H_{22}B_{10}OSi$ Calc. 259.273.

*4.8.7. The reaction of 1-(1-propenyl)-o-carborane (**1c**) with $BH_3 \cdot THF$*

1c (0.493 mmol, 90.9 mg) in THF (0.5 ml) contained in a 5 mm tube was treated with $BH_3 \cdot THF$ (0.17 mmol, 0.17 ml of a 1.0 M solution) and the reaction was monitored by ^{1}H NMR and ^{11}B NMR. After 31 h, the reaction mixture was oxidized at 0 °C with sodium hydroxide (0.30 mmol, 0.10 ml of a 3.0 N solution) and hydrogen peroxide (1.0 mmol, 0.10 ml of a 30% solution) for 6 h. Analysis by ^{1}H NMR using dibromobenzene (0.0744 mmol, 18.9 mg) as an internal standard indicated the following: 45% 1-(1-hydroxypropyl)-*o*-carborane (**2c**), 5% 1-(2-hydroxypropyl)-*o*-carborane (**3c**), 1-propyl-*o*-carborane (12%), *o*-carborane (2%) and **1c** (33%).

2c. ^{1}H NMR (acetone-d_6) δ 4.70 (1H, s), 4.03 (1H, m), 1.28 (2H, m), 0.89 (3H, t, $J = 7.2$ Hz). ^{13}C(^{1}H) COSY NMR (acetone-d_6) δ 79.9, 73.7 (4.03), 58.6 (4.70), 30.2 (1.28), 10.9 (0.87). MS (EI) *m/z* (m−H) Found 203.229; $C_5H_{17}B_{10}O$ Calc. 203.233.

*4.8.8. Hydroboration of 1-(2-propenyl)-o-carborane (**1d**) with $BH_3 \cdot THF$*

1d (1.53 mmol, 282 mg) in THF (2 ml) was treated with $BH_3 \cdot THF$ (0.56 mmol, 0.56 ml of a 1.0 M solution) at room temperature for 5 h. The resultant organoborane was oxidized by addition of H_2O (5 ml), an equal volume of THF and sodium perborate (2.52 mmol, 387 mg) at room temperature for 12 h. After work up in the usual manner, analysis by ^{1}H NMR using dibromobenzene (0.071 mmol, 16.8 mg) as internal standard indicated the following: 58% 1-(3-hydroxypropyl)-*o*-carborane (**3d**), 30% 1-(2-hydroxypropyl)-*o*-carborane (**2d**) and 1-propyl-*o*-carborane (9%). An aliquot of the dried extract was treated with BSTFA and the silylated derivatives analyzed by GC/MS to reveal a 65:35 ratio of primary to secondary alcohols.

3d. M.p. 53–57 °C [35]. ^{1}H NMR ($CDCl_3$) δ 3.64 (2H, t, $J = 6.0$ Hz), 3.59 (1H, s), 2.35 (2H, m), 1.72 (2H, m). ^{13}C NMR ($CDCl_3$) δ 75.14, 61.24, 61.50, 34.86, 32.03. ^{11}B NMR (acetone-d_6) δ −1.78 (1B, d), −5.02 (1B, d), −8.51 (2B, d), −10.34 (4B, d), −11.83 (2B, d). MS (EI) *m/z* Found 204.227; $C_5H_{18}B_{10}O$ Calc. 204.229.

2d. M.p. 75–76 °C [34]. ^{1}H NMR ($CDCl_3$) δ 4.03 (1H, m), 3.63 (1H, s), 2.35 (2H, m), 1.20 (3H, d, $J = 6.1$ Hz). ^{13}C NMR ($CDCl_3$) δ 73.0, 66.6, 59.8, 45.6, 24.2.

1-Propyl-*o*-carborane. M.p. 64 °C [31]. ^{1}H NMR (CD_3CN) δ 4.03 (1H, s), 2.20 (2H, m), 1.46 (2H, m), 0.87 (3H, t, $J = 7.1$ Hz). ^{13}C NMR (CD_3CN) δ 76.5, 62.3, 39.7, 22.9, 13.2.

*4.8.9. Hydroboration of 1-(2-propenyl)-o-carborane (**1d**) with dicyclohexylborane*

To a dicyclohexylborane solution generated by addition of BMS (2.26 mmol, 1.20 ml of a 1.88 M solution in THF) and cyclohexene (4.74 mmol, 0.48 ml) in THF (3 ml) was added at 0 °C **1d** (1.05 mmol, 193 mg) in THF (2 ml). The reaction was allowed to proceed for 12 h at 25 °C with stirring. The organoborane was diluted with THF (5 ml), H_2O (5 ml) and sodium perborate (10.0 mmol, 1.54 g) was added. After 12 h at 25 °C the reaction was worked up in the usual way and analyzed by ^{1}H NMR to reveal a 95% yield of **3d** along with 1% **2d**. An aliquot of the crude product was treated with BSTFA and the resulting silylated derivatives analyzed by GC/MS to reveal a 99:1 ratio of primary to secondary alcohols.

*4.8.10. Hydroboration of 1-(2-propenyl)-o-carborane (**1d**) with 9-BBN*

In a 10 mm NMR tube, **1d** (1.37 mmol, 253 mg) in THF (1.5 ml) was hydroborated with 9-BBN (1.44 mmol, 2.87 ml of a 0.50 M solution in hexane) at 25 °C under sonication. The progress of the reaction was monitored by ^{11}B NMR. The resultant organoborane was oxidized with sodium perborate (6.48 mmol, 997 mg) for 12 h at 35 °C. The reaction was worked up in the normal fashion and analyzed by ^{1}H NMR using dibromobenzene (0.172 mmol, 40.6 mg) as internal standard which indicated the exclusive formation of **3d** in a 91% yield. 1-Propyl-*o*-carborane was also detected (5%).

*4.8.11. Hydroboration of 1-(2-butenyl)-o-carborane (**1e**) with $BH_3 \cdot THF$*

1e (1.14 mmol, 226 mg) in a THF–C_6D_6 mixture (2:1, 1 ml) was hydroborated with $BH_3 \cdot THF$ (0.38 mmol, 0.38 ml of a 1.0 M solution) at 25 °C in a dry-box. After 18 h, sodium hydroxide (0.60 mmol,

0.20 ml of a 3.0 M solution) and hydrogen peroxide (2.0 mmol, 0.2 ml of a 30% solution) were added. The reaction was worked up in the usual fashion and ^{1}H NMR analysis indicated the following: 84% 1-(2-hydroxybutyl)-*o*-carborane (**2e**) and 8% 1-(3-hydroxybutyl)-*o*-carborane (**3e**). Analysis by ^{11}B NMR indicated about 3% cage degradation. An aliquot of the reaction mixture was treated with BSTFA and the resulting silylated derivatives analyzed by GC/MS to confirm a 91:9 ratio of isomeric alcohols.

*4.8.12. Hydroboration of 1-(2-butenyl)-o-carborane (**1e**) with 9-BBN in hexanes*

1e (1.18 mmol, 234.0 mg) was hydroborated with 9-BBN (1.29 mmol, 2.57 ml of a 0.5 M solution in hexanes) at 30 °C under sonication. The reaction mixture was monitored by ^{11}B NMR. After 20 h, 9-BBN (28 ppm) completely disappeared. The reaction was cooled to 0 °C and oxidized by the simultaneous addition of sodium hydroxide (2.58 mmol, 0.86 ml of a 3.0 N solution) and hydrogen peroxide (9.0 mmol, 0.90 ml of a 30% solution). The flask was warmed to room temperature and allowed to stir for 4 h. The reaction was worked up in the usual fashion and ^{1}H NMR analysis indicated the following: **2e** (81%) and **3e** (6%), an isomer ratio of 93:7. 1-Butyl-*o*-carborane (10%) was also detected. An aliquot of the reaction mixture was treated with BSTFA and analyzed by GC/MS to reveal an 89:11 ratio of the isomeric products.

2e. ^{1}H NMR (acetone-d_6) δ 4.68 (1H, s), 3.64 (1H, m), 2.38 (2H, m), 1.41 (2H, m), 0.84 (3H, t, $J = 7.6$ Hz). ^{13}C NMR (acetone-d_6) δ 76.5, 71.9, 63.4, 44.5, 31.3, 9.9. ^{11}B NMR (acetone-d_6) δ −1.05 (1B, d), −4.06 (1B, d), 8.27 (6B, d), −11.14 (2B, d). MS (EI) *m/z* (m–H) Found 217.238; $C_6H_{19}B_{10}O$ Calc. 217.244 [36].

3e. ^{1}H NMR (acetone-d_6) δ 4.62 (1H, s), 3.64 (1H, m), 2.36 (2H, m), 1.38 (2H, m), 1.09 (3H, d, $J =$ 6.4 Hz).

*4.8.13. Hydroboration of 1-(3-butenyl)-o-carborane (**1f**) with $BH_3 \cdot THF$*

1f (1.86 mmol, 368 mg) was hydroborated with $BH_3 \cdot$ THF (0.63 mmol, 0.63 ml of a 1.0 M solution) at 25 °C. After 3 h, the reaction mixture was oxidized with sodium perborate (2.75 mmol, 423 mg). The reaction was worked up in the usual manner and ^{1}H NMR analysis revealed a 93:7 ratio of the primary to secondary alcohol with an overall product distribution: 67% 1-(4-hydroxybutyl)-*o*-carborane (**3f**), 5% 1-(3-hydroxybutyl)-*o*-carborane (**2f**), 1-butyl-*o*-carborane (9%), and a butyl-*o*-carborane · THF adduct (15%). [GLC analysis of the silyl ethers of the isomeric product alcohols indicated a ratio of 91:9.]

3f. M.p. 42–45 °C [35]. ^{1}H NMR (acetone-d_6) δ 4.63 (1H, s), 3.50 (2H, t, $J = 6.1$ Hz), 2.35 (2H, m), 1.55 (2H, m), 1.47 (2H, m). ^{13}C NMR (acetone-d_6) δ 75.7, 61.7, 60.6, 37.0, 31.34, 25.4. ^{11}B (acetone-d_6) δ −0.97 (1B, d), −4.23 (1B, d), −7.73 (2B, d), −9.52 (2B, d), −9.84 (2B, d), −11.12 (2B, d). MS (EI) *m/z* (m–H) Found 217.237; $C_6H_{19}B_{10}O$ Calc. 217.244 [36].

*4.8.14. Hydroboration of 1-(3-butenyl)-o-carborane (**1f**) with dicyclohexylborane*

Dicyclohexylborane was prepared as previously described using BMS (1.33 mmol, 0.680 ml of a 1.95 M solution in THF) and cyclohexene (2.70 mmol, 0.280 ml). **1f** (1.31 mmol, 260 mg) was added and the reaction was permitted to proceed for 12 h at 25 °C. The organoborane was oxidized with sodium perborate (5.71 mmol, 878 mg) and the reaction worked up in the normal fashion. ^{1}H NMR analysis indicated the formation of isomeric alcohols in a 91% total yield in the ratio 99:1 of primary to secondary alcohols (**3f**:**2f**) respectively.

*4.8.15. Hydroboration of 1-(4-pentenyl)-o-carborane (**1g**) with $BH_3 \cdot THF$*

1g (1.48 mmol, 315 mg) was hydroborated with $BH_3 \cdot$ THF (0.51 mmol, 0.53 ml of a 0.96 M solution) and oxidized with sodium perborate (2.29 mmol, 351 mg). The reaction was worked up in the usual fashion and analysis by ^{1}H NMR indicated a 94:6 ratio of the primary to secondary alcohols: 86% 1-(5-hydroxypentyl)-*o*-carborane (**3g**), 6% 1-(4-hydroxypentyl)-*o*-carborane (**2g**) and 1-pentyl-*o*-carborane (2%). ^{11}B NMR analysis indicated cage degradation products (3%). [GLC analysis of the silyl ethers of the isomeric alcohols indicated a ratio of 95:5.]

3g. ^{1}H NMR ($CDCl_3$) δ 3.61 (2H, t, $J = 6.4$ Hz), 3.54 (1H, s), 2.19 (2H, m), 1.52 (4H, m), 1.33 (2H, m). ^{13}C NMR ($CDCl_3$) δ 75.4, 62.01, 61.10. 37.77, 31.84, 28.86, 24.98. ^{11}B NMR (acetone) δ −1.82 (1B, d), −5.05 (1B, d), −8.54 (2B, d), −10.42 (4B, d), −11.90 (2B, d). Low resolution MS (EI) *m/z* Found 232.22; $C_7H_{22}B_{10}O$ Calc. 232.25.

*4.8.16. Hydroboration of 1-(4-pentenyl)-o-carborane (**1g**) with 9-BBN in hexanes*

1g (1.51 mmol, 321 mg) was hydroborated with 9-BBN (1.58 mmol, 3.16 ml, 0.5 M in hexanes) under sonication at 40 °C for 3 h. The reaction mixture was oxidized with sodium hydroxide (4.50 mmol, 1.5 ml of a 3.0 N solution) and hydrogen peroxide (15 mmol, 1.5 ml of a 30% solution). The reaction was worked up in the usual fashion and analysis by ^{1}H NMR revealed: **3g** (87%) and 1-(pentyl)-*o*-carborane (9%). ^{11}B NMR analysis indicated cage degradation products (4%).

Acknowledgements

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