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Hydroboration of (1*R*)-(+)-α-pinene and (1*S*)-(−)-β-pinene with $B_{10}H_{12}(SMe_2)_2$: a straightforward approach to the preparation of optically active 6-(alkyl)-*nido*-$B_{10}H_{13}$ derivatives

Mitchel D. Millan [†] and James H. Davis Jr. [‡,*]

Department of Chemistry, Brandeis University, Waltham, Massachusetts, MA 02254, USA

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Abstract

In separate three-step, one-pot procedures, the known polyhedral boron hydride *arachno*-6,9-$(Me_2S)_2B_{10}H_{12}$ is combined with α- or β-pinene to produce the optically active boranes (−)-6-(α-pinanyl)–$B_{10}H_{13}$ (**1**) and (−)-6-(β-pinanyl)–$B_{10}H_{13}$ (**2**), respectively, as crystalline solids in good yields.

Decaborane(14) and B-substituted variants are the starting materials of choice for the preparation of a variety of boron-based polyhedral clusters, including many carboranes. Of the known B-substituted polyhedral clusters, few have been isolated in an optically-active form, and none have been prepared in a stereospecific fashion.[1] We now wish to report that we have prepared two optically active 6-*R*-$B_{10}H_{13}$ clusters by means of the regio- and stereospecific addition of the B_{10} skeleton to the bulky, optically active olefins α- and β-pinene.

The reaction sequence (Equations 1–3) used to prepare the 6-*R*-$B_{10}H_{13}$ species is one which relies upon the long-known capacity of the decaborane(14)-derivative $B_{10}H_{10}(SMe_2)_2$ to hydroborate carbon–carbon multiple bonds.[2] This approach, which has recently been elaborated by Gaines into one which accomplishes the net exchange of a B(6/9) hydride for an alkyl group, places the new group onto a boron vertex located on a molecular mirror plane.[3] We reasoned that this might be used to our advantage in the synthesis of optically active decaboranes if a chiral auxiliary could be grafted onto the cage in a stereospecific fashion. Notably, the steric bulk of *arachno*-6,9-$B_{10}H_{10}(SMe_2)_2$ is greater even than that of 9-BBN, which is known to add to bulky olefins regio- and stereospecifically.[4]

Equations:

(1) 6,9-$(Me_2S)_2$–$B_{10}H_{12}$ + (α or β)-pinene → 6-(α or β)-pinanyl-8(10)-Me_2S–$B_{10}H_{11}$ + Me_2S

* Corresponding author. E-mail: jdavis@jaguar1.usouthal.edu

† Current Address: Department of Chemistry, University of Manila, Manila, Philippines.

‡ Current Address: Department of Chemistry, University of South Alabama, Mobile, AL 36688, USA.

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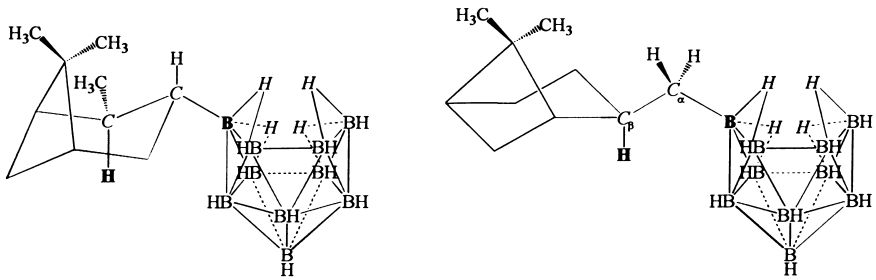

1 **2**

Fig. 1. BH=skeletal boron bearing a terminal hydride; **B**, **H**=boron and hydrogen atoms added to olefinic bonds; *C*=carbon atoms of original olefin; *H*=B–B edge-bridging hydride

(2) 6-(α or β)-pinanyl-8(10)-Me_2S–$B_{10}H_{11}$ + $Li^+HBEt_3^-$ → Li^+[6-(α or β)-pinanyl–$B_{10}H_{12}^-$] + Me_2S + BEt_3

(3) Li^+[6-(α or β)-pinanyl–$B_{10}H_{12}^-$] + HCl/Et_2O → 6-(α or β)-pinanyl–$B_{10}H_{13}$ + LiCl

By incorporating into the reaction sequence *(above)* the olefins (1*R*)-(+)-α-pinene [Aldrich; 99+%, (97% ee/GLC)] and (1*S*)-(−)-β-pinene [Aldrich; 99+%, (97% ee/GLC)], we have prepared and isolated the optically active decaboranes 6-(α-pinanyl)-$B_{10}H_{13}$ (**1**) [α^{20}_D=−55.9 ($CHCl_3$, c=0.5)] and 6-(β-pinanyl)–$B_{10}H_{13}$ (**2**) [α^{20}_D=−26.7 ($CHCl_3$, c=0.5)], as air-sensitive, crystalline solids (Fig. 1).

The formation of the initial 6-pinanyl-8(10)-Me_2S–$B_{10}H_{11}$ adducts (Equation 1; monitored by ^{11}B-NMR) was slow, taking five days with β-pinene and ten days with α-pinene to reach completion. These results are consistent with the large steric bulk of both the borohydride reagent and substrates. When the hydroboration reactions reached completion, the intermediate decaborane–dimethylsulfide adducts were used in the subsequent reaction steps (Equations 2 and 3) without purification or further characterization.

These new compounds have been thoroughly characterized by ^{1}H-, ^{11}B- and ^{13}C-NMR as well as by elemental analysis.[5] The structures and absolute configurations of the products are assigned by analogy to the parent borane and olefins and the presumption of an anti-Markovnikov, *endo* addition of the borane B–H across each olefinic bond.[6] Furthermore, each crystalline product gives only one peak when subjected to HPLC on a chiral column (Pirkle phenylglycine; i-propanol–hexane eluent), an observation consistent with products of good chemical and optical purity.

Our formulation of **1** and **2** as *arachno*-6-*R*-$B_{10}H_{13}$ derivatives is unambiguously supported by the ^{11}B-NMR spectra of the two complexes.[5] Present in the spectrum of each compound is a singlet of intensity one, at 25.4 and 29.0 ppm (rel. Et_2OBF_3), respectively. These values closely parallel those reported for 6-CH_3–$B_{10}H_{13}$ and 6-(thexyl)–$B_{10}H_{13}$, which exhibit singlets at 25.5 and 28.8 ppm in the ^{11}B-NMR.[3] Interestingly, the presence of a secondary carbon bonded to boron in the cases of 6-(thexyl)–$B_{10}H_{13}$ and **1** versus a primary carbon in **2** and 6-CH_3–$B_{10}H_{13}$ results in a downfield shift for the B(6) resonance of roughly 3 ppm. In **1** and **2** the remaining resonances of relative intensities 1:2:1:2:2:1 are virtually isochronous with those of the 6-alkyldecaboranes reported by Gaines.[3] Interestingly, no perceptible anisochronism between the boron atoms located on either side of the plane bisecting B(6), B(2), B(4) and B(9) is observed.

The assigned structures of the alkyl substituents in **1** and **2** are verified by a comparison of the ^{1}H- and ^{13}C-NMR spectra of the products to those of the parent olefins. In both cases the appearance and chemical shift of many of the resonances from the pinanyl substituent are substantially unchanged from those of the parent olefins. However, in the ^{1}H-NMR of complex **2**, the two protons of the new CH_2 group arising from anti-Markovnikov addition of the B(6)–H bond to the olefin gives rise to two new and diagnostic

resonances at 1.56 and 1.60 ppm (rel. TMS). These resonances, each of integrated intensity one, are broad, ill-defined multiplets by virtue of coupling to the geminal proton as well as the single proton on C_β and to the quadrupolar B(6) nucleus. Both the chemical shift and broadening of the latter resonances are consistent with those of boron-bound methylene groups in other alkyl-substituted polyhedral boranes. A resonance which is similarly diagnostic of the proposed mode of addition of the borane cage to α-pinene is observed as a doublet at 1.08 ppm in the ^{1}H-NMR spectrum of **1**. This resonance arises from the C_β methyl group, which is now coupled to a single proton on C_β. The resonance for this methyl group appears as a singlet in the spectrum of the parent olefin.

The ^{13}C spectrum of each compound exhibits ten resonances, consistent with the proposed formulations.[5] Unlike the parent alkenes, neither spectrum exhibits any resonances in the olefinic range, an observation consistent with reduction of the pinanyl double bonds. The regiospecificity of the addition is also apparent from the ^{13}C spectra of the complexes. The spectrum of **1** exhibits four doublets, an increase of one over the parent molecule. Had the addition taken place in a Markovnikov fashion, only two doublets would be observed. Similarly, the spectrum of **2** exhibits three doublets, an increase of one over the olefin and also consistent only with Markovnikov B–H addition. Finally, **1** and **2** respectively exhibit broad resonances at 26.6 and 25.2 ppm which are consistent with an sp^3-carbon atom bonded to boron.

Preliminary investigations of the reaction chemistry of **1** and **2** suggest that each reacts with isonitriles or cyanide in a fashion typical of *nido*-B_{10} clusters, to give chiral, *nido*-carbaundecaboranes. Further investigation of the utilization of **1** and **2** to prepare optically-active ligands for transition metal complexation is anticipated.

1. Experimental

*1.1. Preparation of compound **1***

A 100 mL flask was charged with 6,9-$(Me_2S)_2$–$B_{10}H_{12}$ (3.00g, 14 mmol) and 40 mL of dry CH_2Cl_2 under nitrogen. To this was added 9.0 mL (57 mmol) of (1*R*)-(+)-α-pinene by syringe. The tan-colored solution was stirred at room temperature for 228 h, at which point the reaction was judged to be complete by ^{11}B-NMR. The solvent and excess olefin were then removed under vacuum. After drying, a nitrogen atmosphere was reestablished and the reaction residue redissolved in dry CH_2Cl_2 (40 mL). To the yellow solution was added 14 mmol of 'Super Hydride' (1 M $LiHBEt_3$ in THF), which turned the solution cloudy. After 10 min, 14 mmol of HCl/OEt_2 (1 M) was added by syringe. The yellow solution became colorless and a white solid precipitated. The solution was filtered through Celite to remove the insoluble LiCl, and the filtrate evaporated under vacuum. The crude, oily product (3.24 g, 89.5%, pure by ^{11}B-NMR) was chromatographed on preparative silica tlc plates using hexane as eluent. The major band was isolated by extraction, producing 1.31 g of beige crystals upon removal of the extracting solvent. Mp. 89–91°C. Anal. calcd: C, 46.47; H, 11.70. Found: C, 45.69; H, 11.45 [traces of boric acid present (^{11}B-NMR)].

*1.2. Preparation of compound **2***

A 100 mL flask was charged with 6,9-$(Me_2S)_2$–$B_{10}H_{12}$ (4.80g, 22 mmol) and 50 mL of dry CH_2Cl_2 under nitrogen. To this was added 14.5 mL (91 mmol) of (1*S*)-(−)-β-pinene by syringe. The yellow solution was stirred at room temperature for 116 h, at which point the reaction was judged to be complete

by ^{11}B-NMR. The solvent and excess olefin were then removed under vacuum. After drying, a nitrogen atmosphere was reestablished and the reaction residue redissolved in dry CH_2Cl_2 (50 mL). To the yellow solution was added 22.4 mmol of 'Super Hydride' (1 M $LiHBEt_3$ in THF), which turned the solution cloudy. After 10 min, 22.4 mmol of HCl/OEt_2 (1 M) was added by syringe. The yellow solution became colorless and a white solid precipitated. The solution was filtered through Celite to remove the insoluble LiCl, and the filtrate evaporated under vacuum. The crude, oily product (4.67 g, 80.7%, pure by ^{11}B-NMR) was chromatographed on preparative silica tlc plates using hexane as eluent. The major band was isolated by extraction, producing 1.29 g of off-white crystals upon removal of the extracting solvent. Mp. 72–74°C. Anal. calcd: C, 46.47; H, 11.70. Found: C, 46.05; H, 11.16 [traces of boric acid present (^{11}B-NMR)].

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References

1. (a) Plesek, J.; Gruner, B.; Hermanek, S. *Collect. Czech. Chem. Commun*. **1994**, *59*, 374. (b) Plesek, J.; Gruner, B.; Maoln, P. *J. Chromatogr*. **1992**, *626*, 197. (c) Plesek, J.; Stibr, B.; Hermanek, S. *Pure & Appl. Chem*. **1991**, *63*, 399.
2. Tolpin, E. I.; Mizusawa, E.; Becker, D. S.; Venzel, J. *Inorg. Chem*. **1980**, *19*, 1182.
3. Gaines, D. F.; Bridges, A. N. *Organometallics* **1993**, *12*, 2015.
4. Brown, H. C.; Liotta, R.; Brener, L. *J. Am. Chem. Soc*. **1977**, *99*, 3427.
5. ^{11}B-NMR [δ ($CDCl_3$), rel. Et_2OBF_3] (**1**): +29.0 s (1B), +9.9 d (2B), +8.8 d (1B), +0.9 d (2B), −3.7 d (2B), −34.3 d (1B), −38.9 d (1B); (**2**): +25.5 s (1B), +10.2 d (2B), +8.4 d (1B), +0.9 d (2B), −2.8 d (2B), −33.9 d (1B), −38.9 d (1B). ^{1}H-NMR [δ ($CDCl_3$), rel. TMS] (**1**): 0.85 d (1H), 1.08 s (3H), 1.08 d (3H), 1.21 s (3H), 1.82 m (2H), 1.95 m (2H), 2.25 m (2H), 2.35 m (1H); (**2**): 0.88 d (1H), 1.05 s (3H), 1.19 s (3H), 1.48 m (1H), 1.56 br (1H), 1.60 br (1H), 1.88 m (2H), 2.00 m (2H), 2.30 m (3H). ^{13}C-NMR [δ ($CDCl_3$), rel. TMS] (**1**): 22.37 q, 22.78 q, 26.6 br, 28.30 q, 34.39 t, 34.52 t, 38.72 s, 41.62 d, 42.72 d, 48.13 d; (**2**): 23.21 q, 24.38 t, 25.2 br, 26.46 t, 28.20 q, 33.73 t, 38.82 s, 40.48 d, 41.15 d, 48.36 d.
6. Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *J. Org. Chem*. **1982**, *47*, 5074.