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New Routes to Monoalkyldecaborane(14) Derivatives

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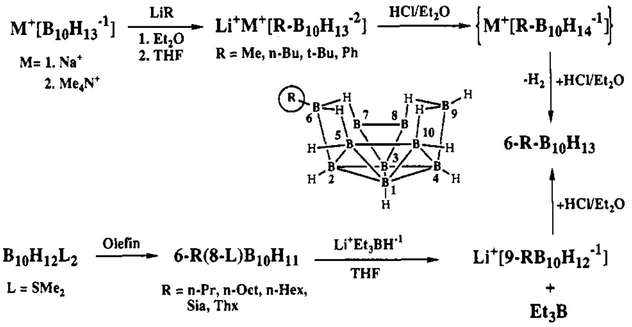
Summary: Specific monoalkylation of decaborane has been achieved through two distinct routes. One proceeds through alkyllithium addition to $B_{10}H_{13}^-$, and the other proceeds via hydroboration of an alkene using the bis-adduct of decaborane, $B_{10}H_{12}{\cdot}2SMe_2$.

Specific alkylation of decaborane, $B_{10}H_{14}$, at the 6-position has been a mixed success,[1–3] depending on the alkyl group, counterions, and other variables. In all cases the $B_{10}H_{14}$ conversion likely proceeds through some anionic alkylated intermediate, though none have been identified. In one instance, ethyllithium was reported to produce 6-Et-$B_{10}H_{13}$ in 90% yield,[4] but most other alkyllithium alkylations produce mixed 5- and 6-isomers in substantially lower yields, contaminated with uncharacterized dialkyl products. Further, identification of 6- versus 5-substitution was often not possible on the basis of the available ^{11}B NMR data. In the course of other investigations it became apparent that the mechanisms of nucleophilic alkylation of $B_{10}H_{14}$ should be explored. The initial results, reported here, are the two high-yield regiospecific routes to 6-alkyldecaborane via rational pathways shown in Scheme I. The identity of the intermediate alkyldecaborane anions is in several cases clearly established on the basis of (1) the ^{11}B NMR spectra obtained during the course of the reactions and (2) the reaction stoichiometries.

The first route involves reaction of alkyllithium with $B_{10}H_{13}^-$ to produce an R-$B_{10}H_{13}^{2-}$ anion, which is sequentially acidified to produce first R-$B_{10}H_{14}^-$ and then the 6-R-$B_{10}H_{13}$ product and hydrogen.[5] Methyl, butyl, *tert*-butyl, and phenyl derivatives have been prepared in this manner. Unlike $B_{10}H_{14}$, which has a number of positive centers for nucleophilic attack as evidenced by the numerous alkylated products, $B_{10}H_{13}^-$ appears to possess only one unique positive site for nucleophilic attack, namely the 6/9-boron vertex. Thus, use of the anion rather than $B_{10}H_{14}$ allows for specific alkyl addition to the cage.

Scheme I



The choice of solvent and cation for the $B_{10}H_{13}^-$ anion is critical. Deprotonation rather than addition can result in systems where the anion is strongly solvated. In systems involving THF (such as *t*-BuLi, which is commercially available in THF), use of the tetramethylammonium salt is warranted. In systems where weakly solvating Et_2O is used, the sodium cation is preferred, primarily because elimination of NaCl is more efficient than elimination of Me_4NCl in the subsequent protonation steps. It is important to note that tetraalkylammonium cations larger than methyl do not appear to eliminate R_4NCl easily in the second protonation step and, in some cases, not at all. For example, $(Et_4N)Li[R\text{-}B_{10}H_{13}]$ derivatives are easily protonated with HCl/Et_2O to give $Et_4N[R\text{-}B_{10}H_{14}]$ and LiCl, but further protonation to give R-$B_{10}H_{13}$, Et_4NCl, and H_2 is sluggish and incomplete, requiring large excesses of HCl/Et_2O and much longer reaction times.

Although the reaction sequence can be accomplished in two separate protonation steps, one-step diprotonation is desirable because the intermediate, R-$B_{10}H_{14}^-$, is thought to be a nonstatic system. Several of the reactions produced small amounts of 5-R-$B_{10}H_{13}$. We believe this results from a conformational change of the 6-R-$B_{10}H_{14}^-$ anion to 5-R-$B_{10}H_{14}^-$ when the former is allowed to stand for a period of time. When THF/Et_2O solutions of isolated 6-R-$B_{10}H_{14}^-$ are allowed to stand for hours, a new compound starts to appear in the ^{11}B NMR. Therefore, it is advisable not to allow the sequence to linger at the R-$B_{10}H_{14}^-$ stage. Reactions conducted with this in mind show no evidence of 5-R-$B_{10}H_{13}$.

The second route begins with hydroboration of an alkene using the bis(dimethyl sulfide) adduct of decaborane, $B_{10}H_{12}{\cdot}2SMe_2$.[8] The hydroboration product, 6-R-8-SMe_2-

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(5) In a typical reaction 7.40 mL of MeLi (1.4 M in Et_2O) is injected dropwise with stirring into a 175-mL Et_2O solution of 1.230 g (8.54 mmol) of $Na[B_{10}H_{13}]$, which is characteristically yellow, at −78 °C under N_2. The solution quickly becomes colorless, and small amounts of a precipitate form. The system is brought to ambient temperature over a period of 20–25 min. The room-temperature ^{11}B NMR spectrum of the reaction mixture consists of six peaks at δ +0.3 d (1B), −4.8 d (1B), −17.6 d (2B), −21.1 d (1B), −22.2 d (2B), −38.6 d (2B), and −40.8 t (1B), consistent with the formation of Me-$B_{10}H_{13}^{2-}$, a derivative of $B_{10}H_{14}^{2-}$. Upon addition of *1* equiv of 1 M HCl/Et_2O to Me-$B_{10}H_{13}^{2-}$, an intermediate species is formed that we propose is the Me-$B_{10}H_{14}^-$ anion, as $B_{10}H_{15}^-$ is prepared via protonation of the $B_{10}H_{14}^{2-}$ dianion.[6] The ^{11}B NMR spectrum of the proposed Me-$B_{10}H_{14}^-$ anion is characteristically compressed between δ −11 and −24, as is the spectrum of the parent $B_{10}H_{15}^-$ anion.[7] Addition of excess 1 M HCl/Et_2O to the Me-$B_{10}H_{14}^-$ anion results in slow evolution of hydrogen and formation of the neutral 6-Me-$B_{10}H_{13}$ in high yield. In some experiments traces of 5-(alkyl)-$B_{10}H_{13}$ are also observed. The mixture is stirred for 1.5 h to ensure complete conversion. Analysis via ^{11}B NMR shows 6-Me-$B_{10}H_{13}$ almost exclusively with resonances at δ +25.5 s (1B), +10.1 d (1B), +9.0 d (2B), −0.8 d (2B), −3.7 d (2B), −32.4 d (1B), and −37.8 d (1B). The solvent and excess acid are removed at reduced pressure. The residue is extracted several times with hexanes, the extracts are combined and filtered to remove NaCl and LiCl, and the solvent is evaporated, leaving 1.145 g of a yellow oil (98.6%). ^{11}B analysis shows the presence of 6-Me-$B_{10}H_{13}$ (88.6%), $B_{10}H_{14}$ (3.1%), and an unidentified product (8.3%). The overall yield of 6-Me-$B_{10}H_{13}$ is 87.3%. The product can be further purified by column chromatography using hexanes as eluant.

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$B_{10}H_{11}$ is then treated with "Super-Hydride" (Li[Et_3BH]/THF), to produce the 6-R-$B_{10}H_{12}^-$ anion, which is then acidified to produce 6-R-$B_{10}H_{13}$ in high yield.[9] Similar experiments show that mono-, tri-, and tetrasubstituted alkenes react to completion with $B_{10}H_{12}\cdot 2SMe_2$ within 3 days to produce essentially quantitative yields of 6-R-8-SMe_2-$B_{10}H_{11}$. Two factors important for complete, efficient hydroboration are a large (3-fold or greater) excess of alkene and a dynamic nitrogen atmosphere to facilitate the initial dissociation step of $B_{10}H_{12}\cdot 2SMe_2$.[10] The hydroboration reactions proceed exclusively via anti-Markovnikov addition. As an example, propene reacts with $B_{10}H_{12}\cdot 2SMe_2$ to produce 6-*n*-propyl-8-SMe_2-$B_{10}H_{11}$ as the sole product. In addition, *n*-hexyl, *n*-octyl, 3-methyl-2-butyl (Sia), and 2,3-dimethyl-2-butyl (Thx) derivatives have been prepared similarly thus far.

Super-Hydride was chosen as a hydride source over a number of other hydrides that were too basic or too hydridic or suffered from solubility problems. In addition, the byproducts of the hydride reacting further with the boron cage were also a concern. Lithium triethylborohydride is soluble in THF and appears to have the right hydridic properties for a monoreduction. The byproduct, triethylborane, is inert to the system and is conveniently monitored by ^{11}B NMR. Sodium triethylborohydride in toluene was too strong a reducing agent, producing only the double-reduction product R-$B_{10}H_{13}^{2-}$.

With the exception of the thexyl derivative, the decaboranes reported here are viscous, clear liquids that can be distilled at elevated temperatures under vacuum. All derivatives display very similar ^{11}B NMR spectral patterns that are completely consistent with reports of other 6-substituted decaborane derivatives.[11,12] Two-dimensional ^{11}B–^{11}B COSY NMR analyses provide unambiguous assignments of all resonances.

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Supplementary Material Available: A figure giving the ^{11}B NMR spectrum of 6-Thx-$B_{10}H_{13}$ (1 page). Ordering information is given on any current masthead page.

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(9) In a typical reaction 36.85 mmol of 2,3-dimethyl-2-butene is injected into a stirred solution of 2.247 g (9.21 mmol) of $B_{10}H_{12}\cdot 2SMe_2$ in dry CH_2Cl_2 under N_2. The solution is vented to a nitrogen bubbler to allow for the evolution of dimethyl sulfide. ^{11}B NMR analysis shows quantitative formation of the asymmetric product 6-Thx-8-Me_2S-$B_{10}H_{11}$, with resonances at δ +19.3 d (1B), +11.8 s (1B), +4.43 d (1B), −0.42 br (2B), −4.48 d (1B), −5.91 d (1B), −13.56 d (1B), −31.39 d (1B), and −40.99 d (1B). ^{13}C and ^{1}H NMR confirm the presence of both the thexyl and dimethyl sulfide group. The solvent and excess alkene are evaporated, and the mixture is redissolved in CH_2Cl_2. Upon addition of 1 molar equiv of "Super-Hydride" (1 M $LiEt_3BH$ in THF) the colorless solution turns yellow. ^{11}B NMR shows Et_3B and one other product with resonances at δ +18.0 s (1B), +9.5 d (1B), +0.4 br (1B), −4.1 d (3B), −8.5 d (2B), and −35.8 d (2B), consistent with the formation of Thx-$B_{10}H_{12}^-$. The addition of 1 molar equiv of HCl/Et_2O produces a colorless solution, and a white solid precipitates. ^{11}B NMR analysis shows 6-Thx-$B_{10}H_{13}$ as the exclusive, soluble product with resonances at δ +28.8 s (1B), +10.3 d (2B), +9.0 d (1B), +0.8 d (2B), −2.9 d (2B), −34.2 d (1B), and −38.3 d (1B). ^{13}C and ^{1}H NMR confirm the identity of the alkyl group. The mixture is filtered through Celite to remove LiCl. 6-Thx-$B_{10}H_{13}$ is purified by vacuum distillation at 100–120 °C at ca. 10^{-4} Torr or by rotary chromatography using hexanes as the eluant. 6-Thx-$B_{10}H_{13}$ (1.605 g, 84%) is a clear liquid that crystallizes upon standing.

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