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Improved Synthetic Route to *n*-$B_{18}H_{22}$

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Simple iodine oxidation of the $B_9H_{12}^-$ anion in toluene at room temperature reliably gives excellent yields (~80%) of *n*-$B_{18}H_{22}$ (*anti*-$B_{18}H_{22}$) and thus provides a convenient, large-scale, safe route to this important polyborane cluster.

Octadecaborane has been isolated in two isomeric forms, *n*-$B_{18}H_{22}$ (also known as *anti*-$B_{18}H_{22}$) and *i*-$B_{18}H_{22}$ (*sym*-$B_{18}H_{22}$). Crystallographic determinations[1] have shown that both compounds have fused-cage structures in which two 10-vertex frameworks share a common edge. The *n*-$B_{18}H_{22}$ isomer has a structure (Figure 1) containing a center of symmetry, while *i*-$B_{18}H_{22}$ has the two fragments related by C_2 symmetry. Their high boron content and air stability make these compounds particularly attractive for many potential medicinal[2,3] and materials[2,4] applications.

The *n*-$B_{18}H_{22}$ isomer was originally prepared by degradation of the $B_{20}H_{18}^{2-}$ anion,[5] but better yield syntheses have been developed starting with 4-L-*arachno*-B_9H_{13} (L = Lewis base) adducts. As shown in eq 1, pyrolysis of 4-Me_2S-*arachno*-B_9H_{13} either in vacuo or in xylene solution produced *n*-$B_{18}H_{22}$ in ~20−28% yields along with a mixture of other polyboranes,[6] while pyrolysis of in situ generated 4-Bu_2O-*arachno*-B_9H_{13} (eq 2) was reported to give a 34% yield.[7]

$$Me_2SB_9H_{13} \xrightarrow{\Delta} n\text{-}B_{18}H_{22} + B_{10}H_{14} + B_{16}H_{20} + B_5H_9 + MeSBH_3 + H_2 \quad (1)$$

$$K^+[B_9H_{14}^-] + HCl + Bu_2O \xrightarrow{H_2,\ KCl} Bu_2OB_9H_{13} \xrightarrow{\Delta} n\text{-}B_{18}H_{22} + Bu_2O + H_2 \quad (2)$$

More recently, we have found[8] (eq 3) that when the 4-Me_2S-*arachno*-B_9H_{13} pyrolysis is carried out in the presence of the inert ionic liquid solvent 1-butyl-3-methylimidazolium chloride (BmimCl) under biphasic conditions, the yield of *n*-$B_{18}H_{22}$ increased to ~50%.

$$Me_2SB_9H_{13} \xrightarrow[120\ °C]{BmimCl/toluene} n\text{-}B_{18}H_{22} + B_{10}H_{14} + H_2 \quad (3)$$

The best previously reported route[9] to *n*-$B_{18}H_{22}$ has been via oxidation of the $B_9H_{12}^-$ anion with mercuric ion, which gave a 68% yield according to eq 4.

$$3HgBr_2 + 4[Me_4N^+][B_9H_{12}^-] \rightarrow 2n\text{-}B_{18}H_{22} + Hg + Hg_2Br_2 + 4Me_4NBr + 2H_2 \quad (4)$$

Although this method has proven useful for laboratory-scale syntheses of *n*-$B_{18}H_{22}$, the cost, safety concerns, and waste disposal problems associated with the use of the $HgBr_2$ oxidant limit the usefulness of this route for the large-scale production of *n*-$B_{18}H_{22}$.

The oxidation of polyborane anions with iodine has been previously employed in a number of reactions to effect arachno to nido or nido to closo polyhedral conversions. Examples include the synthesis of *nido*-SB_9H_{11} from *arachno*-$SB_9H_{12}^-$ [10] and the synthesis of [*closo*-1-$CB_8H_9^-$] from *nido*-1-CB_8H_{12} (in the presence of Et_3N).[11] In other cases, such as in the formation of $B_3H_8^-$ from BH_4^-,[12] iodine oxidation

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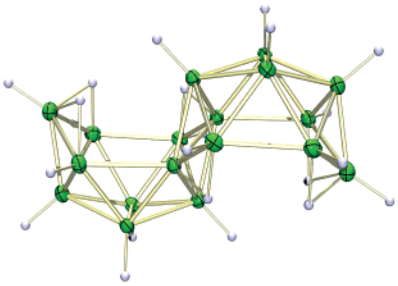

Figure 1. Structure of n-$B_{18}H_{22}$.

has been reported to result in oxidative dehydrocondensation to produce fused polyborane fragments. We report here that simple iodine oxidation of the $B_9H_{12}^-$ anion in toluene at room temperature (eq 5) likewise results in an intermolecular dehydrocondensation reaction that reliably gives excellent yields (~80%) of n-$B_{18}H_{22}$. This reaction thus provides a convenient, large-scale, safe route to this important polyborane cluster.

$$2[Me_4N^+][B_9H_{12}^-] + I_2 \xrightarrow{\text{toluene}} n\text{-}B_{18}H_{22} + 2Me_4NI + H_2 \qquad (5)$$

In a typical reaction, a 250-mL two-necked, round-bottomed flask equipped with a stir bar was charged, under an argon atmosphere, with 10.11 g (55.0 mmol) of $[Me_4N^+][B_9H_{12}^-]$[13] and ~60 mL of dry toluene. After the mixture was sonicated to form a slurry, 7.39 g (29.1 mmol) of I_2 and an additional ~85 mL of toluene were added. This mixture was then vigorously stirred at room temperature until (~40 min) the iodine color disappeared and a precipitate had formed. The precipitate was removed from the light-yellow solution by filtration. Rotovaporization of the filtrate solvent gave a yellow solid, which $^{11}B\{^1H\}$ NMR analysis (Figure 2a) showed to be predominantly n-$B_{18}H_{22}$ along with minor amounts of $B_{10}H_{14}$ and another unidentified product. The impurities were then easily removed by pumping the material overnight at room temperature on the high vacuum line to leave behind 4.87 g (22.5 mmol, 81.6% yield) of n-$B_{18}H_{22}$ as a light-yellow solid. Only trace impurities in the final product could be detected by thin-layer chromatography, $^{11}B\{^1H\}$ NMR (Figure 2b), $^1H\{^{11}B\}$ NMR (Figure 3), or mass spectrometry. The spectroscopic data and observed melting point (178−181 °C) of this powdery solid agree with the literature values.[14] If necessary, further purification can be readily achieved by sublimation in vacuo at 115 °C onto a −78 °C coldfinger.

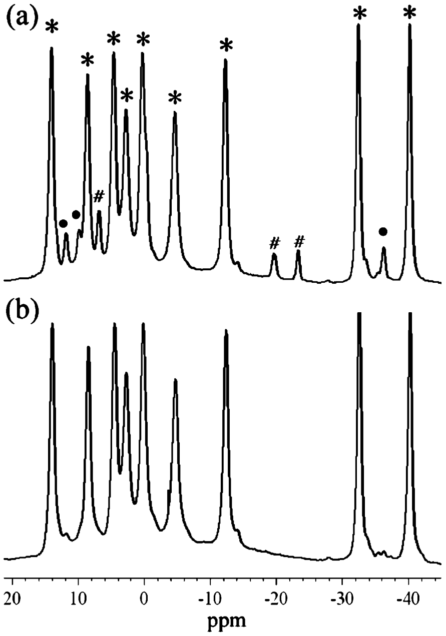

Figure 2. (a) $^{11}B\{^1H\}$ NMR spectrum of the crude reaction product: (*) n-$B_{18}H_{22}$; (●) $B_{10}H_{14}$; (#) unidentified product. (b) $^{11}B\{^1H\}$ NMR spectrum of the final product obtained after pumping in vacuo.

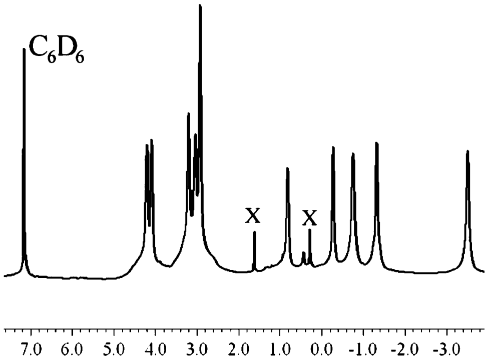

Figure 3. $^1H\{^{11}B\}$ NMR spectrum of the final product obtained after pumping in vacuo.

Because of its combination of mild conditions, high yields, simple workup, innocuous side products, and the use of an economical and safe oxidation reagent (iodine), the method described above has clear advantages over the other reported procedures. This method will now allow the production of n-$B_{18}H_{22}$ on much larger scales than previously possible. These results also suggest that analogous iodine oxidations of other polyborane anions may provide simple routes to other fused-cage polyboranes.

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