Inorganica Chimica Acta, 53 (1981) L139–L140
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Studies on the Lithiation of 1,2-Dicarba-closo-Decaborane(10)

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Received September 29, 1980

Metallation of the slightly acidic protons on polyhedral carboranes has been one of the most versatile ways of functionalizing these boron clusters at their carbon vertices [1]. The lithiation of all three isomers of the icosahedral dicarba-dodecaborane(12) $C_2B_{10}H_{12}$ has been thoroughly investigated. Of the three isomers of the smaller dicarbadecaborane(10) $C_2B_8H_{10}$ (Fig. 1), lithiation and derivatization has been successfully carried out first by Hawthorne and coworkers on the 1,6- and 1,10-isomers [1–3]. The least stable of the three isomers, 1,2-$C_2B_8H_{10}$, has been prepared by both Hermanek and Schaeffer [4, 5]. No reports of the metallation of this carborane has yet appeared in the literature. Of special interest is the presence of two distinct sites for lithiation; the apical five-coordinate C(1), and the equatorial six-coordinate C(2). We now report our results on the lithiation of this carborane.

Results and Discussion

The dilithiation of 1,2-$C_2B_8H_{10}$ can be carried out in diethyl ether at −20 °C using stoichiometric amounts of n-butyllithium. The white precipitate of dilithiated carborane was reacted with methyl iodide to give the previously reported 1,2-dimethyl-1,2-$C_2B_8H_8$ derivative in 35% yield [5].

$$C_2B_8H_{10} \xrightarrow{2\ \mathrm{BuLi}} Li_2C_2B_8H_8 \xrightarrow{2\ \mathrm{MeI}} Me_2C_2B_8H_8$$

The identity of this product was confirmed by its ^{11}B, ^{1}H NMR, IR, and mass spectrum (Table I).

Addition of one equivalent of n–BuLi under these conditions resulted in decreased yields of sublimable neutral products after quenching with methyl iodide. Both the ^{11}B and ^{1}H nmr indicated the presence of dimethylated carborane in about 20–30% of the isolated product. Of the monomethylated product, methylation at the equatorial C(2) was found to be predominant. This is supported by the IR spectrum which clearly indicated the almost complete disappearance of the C(2)–H band at 3070 cm^{-1} compared to the C(1)–H band at 3118 cm^{-1} [4]. Furthermore, the ^{1}H NMR exhibited a broad singlet at 5.2 ppm assignable to C(1)'s proton and a sharp singlet at 1.6 ppm assigned to the C(2)-methyl protons [6]. A small singlet was also observed at 3.0 ppm due to small amounts of the C(1)-methylated product.

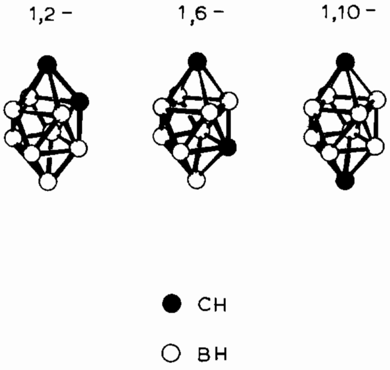

Fig. 1. The three isomers of dicarba-closo-decaborane(10).

We therefore conclude that lithiation under these conditions resulted in a preference for the equatorial site at C(2) by about 20 to 1. Lipscomb and

TABLE I. ^{11}B NMR Data for 1,2-$C_2B_8H_{10}$ and its Methyl-Derivatives.

Proton-Decoupled ^{11}B NMR (28.70 MHz) Data

Compound	Chemical Shifts (ppm)	Relative Intensities
1,2-$C_2B_8H_{10}$	36.2, −9.2, −20.2, −26.2	1:1:2:4
1,2-Me_2-1,2-$C_2B_8H_8$	29.9, −6.6, −15.5, −21.7, −24.6	1:1:2:2:2
Me-1,2-$C_2B_8H_9$[a]	35.0, −9.3, −17.2, −23.3 (bd)	1:1:2:4

[a] Mixture of two isomers.

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coworkers have recently reported theoretical calculations on the 1,6-$C_2B_8H_{10}$ and predicted the apical C(1)-proton to be slightly more acidic than the equatorial C(6)-proton [7]. Indeed this was the observed behavior as Hawthorne has previously reported the formation of the C(1) lithiated product to be favored by a factor of two [2]. Our results would indicate a reversal in this selectivity for the 1,2-dicarbadecaborane with the equatorial proton being significantly more acidic. This warrants further theoretical work on this isomer of $C_2B_8H_{10}$. Furthermore, our successful metallation of this carborane should facilitate functionalization of it.

Experimental

All reactions were carried out under inert atmospheric conditions. Diethyl ether was distilled from sodium-benzophenone. 1,2-dicarbadecaborane-(10) was prepared by literature methods [4].

Proton-decoupled ^{11}B NMR spectra wre obtained using the JEOL FX90Q FT spectrometer. $CDCl_3$ was used as the solvent and all shifts are relative to external $BF_3 \cdot Et_2O$.

Reaction of 1,2-$C_2B_8H_{10}$ with 2 n-BuLi

Freshly sublimed 1,2-$C_2B_8H_{10}$ (106 mg, 0.87 mmol) was dissolved in 10 ml of ether and chilled to –20 °C. Two equivalents of BuLi was added via syringe and the solution allowed to warm slowly to 10 °C whereupon a white precipitate formed. After cooling again to –20 °C, excess methyl iodide was added and the solution warmed to room temperature. Removal of solvent and sublimation of the residue at 80–90 °C using a mechanical pump vacuum gave 45 mg, 0.3 mmol of white crystalline 1,2-Me_2C_2-B_8H_8.

Reaction of 1,2-$C_2B_8H_{10}$ with n-BuLi

A similar procedure was used to produce the monolithiated product and methyl iodide used to give the methylated products. The mono- and dimethylated carboranes can be separated by GLC. The composition of the products was analyzed by spectral means.

Acknowledgement

We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Research Corporation for financial support.

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Erratum to Volume 44

Inorganica Chimica Acta, 44 (1980) L291–L294

Spin Spin Interactions in Polymeric Copper(II) Complexes: Cu(II)(Piperidylcarbamate)$_2$(Cu(I)X)$_4$ (X = Cl, Br)

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Page L292, Figures 2(a) and 2(b) should be interchanged but the legends should remain as they are.