Notes

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Chemistry of Boranes. XIII. Chloromethyldimethylamino Derivatives of $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$

By W. R. Hertler

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In the course of a study of reactions of the polyhedral boron hydride anions $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ with various electrophilic reagents, their reaction with the Vilsmeier reagent,[1] $CHCl{=}N(CH_3)_2Cl$ (I), was examined. A large body of literature exists on reactions of I with various nucleophiles. In general, such reactions lead to products derived from attack of nucleophile on the electron-deficient carbon atom of I. The Vilsmeier reagent (I) reacts with $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ under mild conditions in an unusual manner to give products in which a B–N bond has been formed according to eq. 1 and 2 to give the structural unit $B{-}N^+(CH_3)_2CH_2Cl$.

$$B_{10}H_{10}^{-2} + \underset{\text{I}}{2CHCl{=}N(CH_3)_2Cl} \longrightarrow \underset{\text{II}}{2,7(8)\text{-}B_{10}H_8[N(CH_3)_2CH_2Cl]_2} \quad (1)$$

$$\begin{array}{c} B_{12}H_{12}^{-2} + CHCl{=}N(CH_3)_2Cl \longrightarrow \underset{\text{III}}{B_{12}H_{11}N(CH_3)_2CH_2Cl^-} \\ \Big\downarrow \text{I} \qquad (2) \\ \underset{\text{IV}}{B_{12}H_{10}[N(CH_3)_2CH_2Cl]_2} \end{array}$$

The structural assignments of compounds II–IV are confirmed by the H^1 n.m.r. spectra which are discussed in the Experimental section.

Although no attempt has been made to differentiate among the several possible mechanisms for this reaction, the favorable energetics of B–N bond formation relative to B–C bond formation may be of significance in determining the final product. The generally greater reactivity of derivatives of $B_{10}H_{10}^{-2}$ than the corresponding derivatives of $B_{12}H_{12}^{-2}$ toward electrophilic reagents is reflected in the ready formation of the disubstituted derivative II, whereas preparation of the disubstituted derivative of $B_{12}H_{12}^{-2}$ (IV) requires a longer reaction time.

The chlorine atoms in compounds II–IV are quite inert toward nucleophilic displacement as would be expected in such a neopentyl-like system in which there is a proximate cationic nitrogen atom. The chlorine atoms are, however, reactive toward alkali metal. Reduction of II with sodium in alcohol gives $2,7(8)\text{-}B_{10}H_8[N(CH_3)_3]_2$ (V) according to eq. 3. Comparison of the B^{11} n.m.r. spectra of II and V indicates that no change in geometry has occurred during the reduction.

$$2,7(8)\text{-}B_{10}H_8[N(CH_3)_2CH_2Cl]_2 \xrightarrow[\text{ROH}]{\text{Na}} 2,7(8)\text{-}B_{10}H_8[N(CH_3)_3]_2 \quad (3)$$

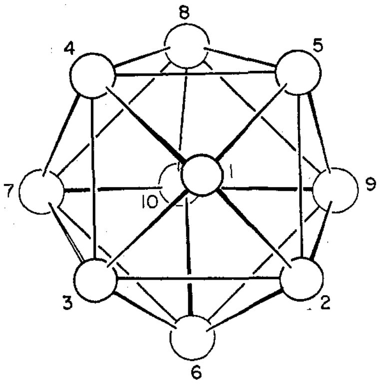

Fig. 1.—$B_{10}H_{10}^{-2}$.

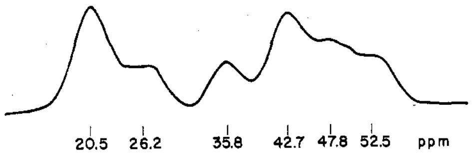

Fig. 2.—B^{11} n.m.r. spectrum of $2,7(8)\text{-}B_{10}H_8[N(CH_3)_3]_2$ in acetonitrile at 19.25 Mc., δ relative to external methyl borate.

Stereochemistry.—Three of the seven possible isomers of $B_{10}H_8[N(CH_3)_3]_2$ have recently been reported[2]—1,10-, 2,4-, and $2,3\text{-}B_{10}H_8[N(CH_3)_3]_2$ (see Fig. 1 for numbering system of $B_{10}H_{10}^{-2}$)[3]—but V differs from these isomers with respect to infrared spectrum, X-ray powder pattern, and B^{11} n.m.r. spectrum. The B^{11} n.m.r. spectrum of V (Fig. 2) is in accord with 2,7(8) geometry (see Experimental section for details). The 2,7(8) assignment for V must also apply to II as evidenced by the similarity of the B^{11} n.m.r. spectra of the two compounds. Thus, the formation of $2,7(8)\text{-}B_{10}H_8[N(CH_3)_2CH_2Cl]_2$ from the reaction of I with $B_{10}H_{10}^{-2}$ is another example[2,4] of equatorial electrophilic substitution on $B_{10}H_{10}^{-2}$. However, in view of the low yield of isolated product, it is possible that other isomers were formed in the reaction but were selectively lost during isolation and purification. The stereochemistry of IV has not been established.

Experimental[5]

$2,7(8)\text{-}B_{10}H_8[N(CH_3)_2CH_2Cl]_2$ (II).—To the stirred slurry resulting from the addition of 4 ml. of oxalyl chloride to 50 ml. of

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[1] H. Eilingsfeld, M. Seefelder, and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960).

[2] W. R. Hertler and M. S. Raasch, *J. Am. Chem. Soc.*, in press.

[3] The numbering system used herein for $B_{10}H_{10}^{-2}$ is the proposed revision by the Boron Nomenclature Subcommittee of the American Chemical Society, 1963, which has been described by R. Adams, *Inorg. Chem.*, **2**, 1087 (1963). It should be noted that a numbering system for $B_{10}H_{10}^{-2}$ and $B_{12}H_{12}^{-2}$ which is slightly at variance with this system has recently appeared from this laboratory (W. H. Knoth, J. C. Sauer, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 115 (1964), and W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia, and E. L. Muetterties, *Inorg. Chem.*, **3**, 159 (1964)) and for reasons of uniformity should be discarded in favor of the Nomenclature Subcommittee's proposed revision.

[4] W. H. Knoth, J. C. Sauer, D. C. England, W. R. Hertler, and E. L. Muetterties, *J. Am. Chem. Soc.*, in press.

[5] All melting points are corrected. H^1 nuclear magnetic resonance spectra were determined with a Varian Model A60 n.m.r. spectrometer.

dimethylformamide and 150 ml. of acetonitrile was added 7.68 g. (0.02 mole) of $Cs_2B_{10}H_{10}$ while cooling in an ice bath. The resulting mixture was stirred at 0° for 30 min. and then at room temperature for 15 min. The mixture was filtered into dilute aqueous sodium acetate and evaporated under reduced pressure to a small volume. The residue was treated with water, and the resulting precipitate was purified by treatment with decolorizing charcoal in refluxing carbon tetrachloride. The resulting solution was evaporated, and the residue was recrystallized from aqueous ethanol to give 645 mg. (11%) of white crystals of II, m.p. 177–186°. Recrystallization from carbon tetrachloride–pentane raised the m.p. to 183–186°. *Anal.* Calcd. for $B_{10}H_{24}C_6N_2Cl_2$: C, 23.8; H, 7.97; B, 35.7; N, 9.25; Cl, 23.4. Found: C, 24.1; H, 7.75; B, 36.3; N, 9.41; Cl, 22.9.

The H^1 n.m.r. spectrum of the product in carbon tetrachloride solution shows two single peaks at τ 5.22 and 7.20 (external $(CH_3)_4Si$) in the ratio 1:3 which can be assigned to the four methylene hydrogens and the twelve methyl hydrogens, respectively.

$(CH_3)_4NB_{12}H_{11}N(CH_3)_2CH_2Cl$ (III).—A solution of 46 g. (0.22 mole) of phosphorus pentachloride in 500 ml. of dry acetonitrile and 36 ml. of dimethylformamide was stirred at room temperature for 15 min. under a nitrogen atmosphere. Then 29 g. (0.1 mole) of $[(CH_3)_4N]_2B_{12}H_{12}$ was added, the resulting mixture was stirred for 4 hr. and filtered into 100 ml. of 1 *M* aqueous sodium acetate, and the resulting solution was evaporated under reduced pressure to a small volume. The residue was treated with water and extracted with 1:1 methylene chloride–benzene. The extract was evaporated, and the residue was recrystallized from ethyl acetate to give 3.71 g. (12%) of white crystals, m.p. 285°. Recrystallization from water, from acetone–water, and finally from water gave crystals of $(CH_3)_4NB_{12}H_{11}N(CH_3)_2CH_2Cl$, m.p. 283–284°. *Anal.* Calcd. for $B_{12}H_{31}C_7N_2Cl$: C, 27.2; H, 10.1; B, 42.1; N, 9.02; Cl, 11.5; 0.5 mol. wt., 154.3. Found: C, 27.4; H, 9.90; B, 41.4; N, 9.17; Cl, 12.9; mol. wt., 161. The infrared spectrum of the product shows no absorption characteristic of N—H or C=N. The H^1 n.m.r. spectrum of the product in trifluoroacetic acid solution shows three single peaks at τ 5.35, 7.05, and 7.3 (external $(CH_3)_4Si$) with relative intensities 1:6:3 which can be assigned to the two hydrogens adjacent to chlorine, the twelve hydrogens of $(CH_3)_4N^-$, and the six hydrogens of the $N(CH_3)_2$ group, respectively.

$B_{12}H_{10}[N(CH_3)_2CH_2Cl]_2$ (IV).—To a solution of 31.25 g. (0.15 mole) of phosphorus pentachloride in 150 ml. of dimethylformamide and 500 ml. of acetonitrile was added 14.5 g. (0.05 mole) of $[(CH_3)_4N]_2B_{12}H_{12}$. The resulting mixture was stirred at room temperature under nitrogen for 22 hr. and then filtered into aqueous sodium acetate and evaporated under reduced pressure. The residue was treated with water and extracted with 1:1 methylene chloride–benzene, and the extracts were evaporated. The oily residue was recrystallized from aqueous acetone to give 950 mg. (6%) of off-white crystals of IV, m.p. 198–226°. Two additional recrystallizations raised the m.p. to 245–248°. *Anal.* Calcd. for $B_{12}H_{26}C_6N_2Cl_2$: C, 22.0; H, 8.01; B, 39.7; N, 8.57; Cl, 21.4. Found: C, 22.4; H, 7.94; B, 39.5; N, 8.58; Cl, 21.5.

The H^1 n.m.r. spectrum of the product in methylene chloride solution shows two single peaks at τ 4.9 and 6.9 (external $(CH_3)_4Si$) with an intensity ratio of 1:3 which can be assigned to the four methylene hydrogens and the twelve methyl hydrogens, respectively.

2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$ (V).—A mixture of 50 ml. of *t*-butyl alcohol, 5 ml. of ethyl alcohol, 587 mg. (1.94 mmoles) of II, and several small pieces of sodium was refluxed for 3 hr. during which time additional sodium was added so that there was undissolved sodium present at all times. The mixture was cooled and treated with 30 ml. of water, and the organic solvents were removed under reduced pressure. Filtration of the resulting slurry gave 405 mg. (90%) of V as a white solid. Recrystallization from aqueous ethanol and then from acetone–ethanol gave crystals of 2,7(8)-$B_{10}H_8[N(CH_3)_3]_2$, m.p. 298–300°. *Anal.* Calcd. for $B_{10}H_{26}C_6N_2$: C, 30.4; H, 11.2; B, 46.1; N, 12.0; mol. wt., 234. Found: C, 30.1; H, 10.7; B, 46.1; N, 11.8; mol. wt., 236 (X-ray).

The H^1 n.m.r. spectrum of the product in chloroform-*d* shows a single peak at τ 7.12 ($N-CH_3$). The B^{11} n.m.r. spectrum of the product (Fig. 2) is consistent with 2,7(8) geometry. The unsymmetrical low-field doublet can be assigned to two substituted equatorial boron atoms (peak at +20.5 p.p.m.) and two unsubstituted apical boron atoms (doublet with high-field half at +26.2 p.p.m. and a low-field half beneath the 20.5 p.p.m. peak, $J \sim$ 110 c.p.s.). The +35.8, +42.7, +47.8, and +52.5 p.p.m. peaks can be assigned to the remaining six unsubstituted equatorial boron atoms. On irradiation at 60 Mc., the unsymmetrical low-field doublet can be decoupled to a single, somewhat broad peak centered at +22.4 p.p.m., and the remainder of the peaks can be decoupled more or less independently. The observed intensity ratio of the +22.4 p.p.m. peak to the sum of the +35.8, +42.7, +47.8, and +52.2 p.p.m. peaks of 2:3 is in agreement with theory. The absence of resonance in the vicinity of 0 p.p.m. precludes any apical substitution,[2] and the presence of only a single resonance for both apical boron atoms suggests that their environment is similar and, hence, that each is adjacent to one substituted equatorial boron atom, *i.e.*, the $N(CH_3)_3$ groups are on different equatorial belts. Entirely different results were reported for the B^{11} n.m.r. spectrum of 2,4- and 2,3-$B_{10}H_8[N(CH_3)_3]_2$ in which both substituents are on the same equatorial belt.[2] To the extent which interpretation of the B^{11} n.m.r. spectrum of V has been carried it is not possible to distinguish between 2,7(8) and 2,6(9) substitution, but the latter assignment (substituents on adjacent boron atoms) seems unlikely from steric and electronic considerations.

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Chemistry of Boranes. XVI.[1] A New Heterocyclic Boron Compound

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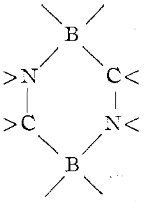
A number of heterocyclic boron compounds have been prepared and characterized in recent years.[2] One of the simpler ring systems yet to be described is the six-membered ring with a repeating BCN sequence, **1**. We have prepared the N-tetramethyl derivative,



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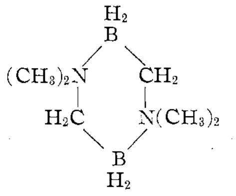

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2, in low yield from sodium hydride and $H_2B[N(CH_3)_3]_2Cl$.[3] The stability of **2** is fair. The compound is stable to long exposure to the atmosphere and to thermal degradation to at least 100° but it is rapidly decomposed by strong mineral acids. Bromine does not destroy the ring system but replaces three of the BH hydrogen atoms to give **3**.

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[1] Paper XV: T. A. Ford, G. H. Kalb, A. L. McClelland, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1032 (1964).

[2] This subject has been reviewed in some detail by P. M. Maitlis, *Chem. Rev.*, **62**, 223 (1962).

[3] N. E. Miller and E. L. Muetterties, *J. Am. Chem. Soc.*, in press.