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# Monocarbon Carboranes. I. Syntheses and Reactions of the $B_{10}H_{12}CH^-$ and $B_{10}H_{10}CH^-$ Ions and Their C-Trialkylamine Derivatives[1]

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Deamination of $B_{10}H_{12}CNR_3$ with either sodium hydride or sodium metal in refluxing tetrahydrofuran gave the $B_{10}H_{12}CH^-$ ion. In the latter reaction an air-sensitive intermediate was isolated which appears to be $Na_3B_{10}H_{10}CH(C_4H_8O)_{1.8}$. Iodine oxidation of the trisodium salt produced the $B_{10}H_{10}CH^-$ ion in high yield. Halogenated derivatives of $B_{10}H_{12}CNR_3$ and $B_{10}H_{12}CH^-$ have been prepared and the position of substitution determined by a $^{11}B$ nmr study of a specifically labeled bromo derivative.

## Introduction

Recently we reported[4] a method for preparing C-trialkylaminecarbaundecaborane(12) derivatives by reaction of alkyl isocyanides with decaborane(14) followed by alkylation of the amine function. Subsequently a more convenient route to some of these C-trialkylamine derivatives was reported[5] as well as the synthesis of the $B_9H_9CH^-$ and $B_{11}H_{11}CH^-$ ions. The subject of this paper concerns some aspects of the substitution chemistry at both the carbon and boron atoms of the $B_{10}H_{12}CNR_3$ molecule.

## Experimental Section

**Apparatus and Materials.**—Infrared spectra were recorded as KBr disks using a Perkin-Elmer 521 instrument. Intensities of absorptions are reported as strong (s), medium (m), or weak (w). Melting points were obtained in open capillaries and are uncorrected. Mass spectra were obtained with an Atlas CH-4 mass spectrometer using an ionizing voltage of 14–17 ev and a heated inlet system. Proton nmr spectra were obtained with a Varian A-60 spectrometer and the boron ($^{11}B$) nmr spectra with a Varian HA-100 spectrometer operating at 32.1 Mc.

The $B_{10}H_{12}CN(CH_3)_3$ was prepared by the method of Knoth.[5] The decaborane–alkyl isocyanide method[4] was used to prepare $B_{10}H_{12}CNH_2C_3H_7$ and this was methylated with methyl iodide and sodium bicarbonate in tetrahydrofuran–water solution to give $B_{10}H_{12}CN(CH_3)_2C_3H_7$. The $2\text{-}BrB_{10}H_{13}$ was prepared and purified by the procedure of Cohen and Pearl.[6] All reactions were carried out under an atmosphere of prepurified argon.

**$B_{10}H_{12}CH^-$ (I).**—(A) To a suspension of sodium hydride (1.15 g, 0.048 mole) in 150 ml of dry tetrahydrofuran was added $B_{10}H_{12}CN(CH_3)_3$ (2.86 g, 0.015 mole). Gas evolution ($H_2$) was noted initially and then the mixture was refluxed with stirring for 24 hr. The trimethylamine was removed by distillation and isolated as the hydrochloride salt in 86% yield based on $B_{10}H_{12}CN(CH_3)_3$. Excess sodium hydride was decomposed by slow addition of methanol to the reaction mixture. After neutralization with aqueous hydrochloric acid, the solvents were removed *in vacuo*. The solid residues were extracted with 75 ml of water, treated with Darco, and filtered. The filtrate was treated with tetramethylammonium chloride and the white precipitate recrystallized from methanol–acetone to give 2.10 g (69.7% yield) of $(CH_3)_4NB_{10}H_{12}CH$. *Anal.* Calcd for $(CH_3)_4NB_{10}H_{12}CH$: C, 28.95; H, 12.15; N, 6.75. Found: C, 28.72; H, 11.71; N, 6.40. The infrared spectrum of the tetramethylammonium salt included absorptions at $\lambda_{max}$ 2510 (s), 1990 (w), 1280 (w), 1190 (w), 1095 (m), 1063 (m), 1012 (m), 995 (m), 980 (w), 876 (w), 850 (w), 813 (w), and 746 (w) cm$^{-1}$. The proton nmr spectrum (acetone-$d_6$) showed one broad peak at $\tau$ 8.55 (CH).

(B) Reaction of $B_{10}H_{12}CN(CH_3)_3$ (9.57 g, 0.05 mole) with sodium metal (4.59 g, 0.2 g-atom) in tetrahydrofuran at reflux with stirring for 24 hr produced a thick white precipitate. The solid was filtered under argon (with a Schlenk filter[7]) and thoroughly dried *in vacuo* on the filter at room temperature. The dry solid (II) was pyrophoric in moist air and therefore was transferred in an inert-atmosphere box. Treatment of 0.6697 g of II with water gave a basic solution which was neutralized by 38.05 ml of 0.1 *N* hydrochloric acid using phenolphthalein as indicator. A slurry of 0.5560 g of II in dry tetrahydrofuran reacted with 0.414 g of iodine. A 0.3068-g sample of II was treated with 5 ml of water. The volatile products were trap-to-trap distilled at $10^{-2}$ mm (90°). The distillate was analyzed by glpc with an F & M 700 gas chromatograph on a 3-ft column of Porapak Q, 150–200 mesh, at 230°. With dioxane as an internal standard, the distillate was found to contain 0.1049 g of tetrahydrofuran. This data indicated that solid II had the approximate composition $Na_3B_{10}H_{10}CH\cdot[C_4H_8O]_{1.85\pm0.45}$. This stoichiometry was consistent in three experiments.

An 80% yield of $CsB_{10}H_{12}CH$ was obtained from the aqueous, neutralized solution of II by addition of cesium chloride. The analytical sample was recrystallized from hot water. *Anal.* Calcd for $CsB_{10}H_{12}CH$: C, 4.54; H, 4.92. Found: C, 4.53; H, 4.83. The infrared spectrum of the cesium salt of I contained absorptions at $\lambda_{max}$ 3020 (w), 2520 (s), 2000 (w), 1094 (s), 1066 (s), 1019 (s), 1004 (s), 990 (m), 876 (m), 862 (m), 834 (m), 749 (m), and 718 (m) cm$^{-1}$.

**$B_{10}H_{10}CH^-$ (III).**—To a slurry of II (10 g, 0.030 mole) in 100 ml of tetrahydrofuran was added from a dropping funnel a solution of iodine (7.70 g, 0.030 mole) in 50 ml of tetrahydrofuran. The mixture was stirred for an additional 5 hr at room temperature and the volume partly reduced *in vacuo* Filtration gave 7.18 g (76%) of sodium iodide. The filtrate was evaporated to dryness and treated with aqueous tetramethylammonium bromide. The resulting precipitate was recrystallized from methanol–acetone to give 4.76 g (86%) of $(CH_3)_4NB_{10}H_{10}CH$. *Anal.* Calcd for $(CH_3)_4NB_{10}H_{10}CH$: C, 29.21; H, 11.28; N, 6.79. Found: C, 29.61; H, 11.38; N, 6.90. The infrared spectrum included absorptions at $\lambda_{max}$ 2520 (s), 1138 (w), 1120 (s), 1095 (m), 1060 (w), 1012 (m), 984 (m), 840 (m), 800 (w), 750 (m), and 700 (w) cm$^{-1}$. The proton nmr spectrum (acetone-$d_6$) contains a broad singlet at $\tau$ 7.2.

**$B_{10}H_{10}CN(CH_3)_3$ (IV).**—A solution of 10.0 g (0.0524 mole) of $B_{10}H_{12}CN(CH_3)_3$ in 200 ml of dry tetrahydrofuran was treated with 2.24 g of 56.1% sodium hydride–mineral oil dispersion. After gas evolution had ceased, iodine (6.64 g, 0.0262 mole) was added to the mixture. After the solution had decolorized, equal

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quantities of sodium hydride and iodine were added as before. Evaporation of the solvent under reduced pressure followed by washing the solid residues with water to remove sodium iodide gave 9.0 g (94%) of crude IV. The analytical sample was recrystallized from chloroform–acetone, mp 333–334° dec. *Anal.* Calcd for $B_{10}H_{10}CN(CH_3)_3$: C, 25.39; H, 10.04; N, 7.41. Found: C, 25.44; H, 10.03; N, 7.55. The infrared spectrum of IV included absorptions at $\lambda_{max}$ 3020 (w), 2550 (s), 1483 (s), 1463 (s), 1410 (m), 1240 (w), 1130 (w), 995 (m), 942 (s), 848 (m), and 825 (m) cm$^{-1}$. The proton nmr spectrum (acetone-$d_6$) has a sharp singlet at $\tau$ 6.30.

**$B_{10}H_{10}CN(CH_3)_2C_3H_7$ (V).**—(A) This derivative was prepared by the same procedure described for $B_{10}H_{10}CN(CH_3)_3$. The sample was recrystallized from chloroform–acetone, mp 181–182°. *Anal.* Calcd for $B_{10}H_{10}CN(CH_3)_2C_3H_7$: C, 33.19; H, 10.59; N, 6.45. Found: C, 32.91; H, 10.83; N, 6.18. The infrared spectrum of V contained absorptions at $\lambda_{max}$ 3020 (w), 2980 (s), 2940 (m), 2550 (s), 1460 (s), 1410 (m), 1390 (m), 1215 (w), 1180 (w), 995 (s), 960 (m), 939 (s), 872 (w), 848 (m), 820 (m), 780 (w), 755 (m), and 725 (m) cm$^{-1}$. The proton nmr spectrum (acetone-$d_6$) showed signals at $\tau$ 6.13 (multiplet, 2H), 6.41 (singlet, 6H), 7.92 (multiplet, 2H), 8.93 (triplet, 3H).

(B) To a solution of $B_{10}H_{12}CN(CH_3)_2C_3H_7$ (3.0 g, 0.0137 mole) in 125 ml of tetrahydrofuran was added sodium metal (2.0 g, 0.065 g-atom). The mixture was refluxed 1.5 hr. Methyl iodide (25.0 g, 0.176 mole) was added and the solution refluxed for another 2 hr. Removal of the solvent *in vacuo* left a gummy residue which was partly dissolved in chloroform. The filtered chloroform solution was partially evaporated to give a white solid. Two recrystallizations from chloroform gave plates, mp 179–181°; mixture melting point with the sample above, 179–180°. The infrared and $^{11}B$ nmr spectra of the products of these two methods are identical.

**4(6)-$BrB_{10}H_{11}CN(CH_3)_3$.**—(A) To a stirred solution of 2-$BrB_{10}H_{13}$ (6.62 g, 0.033 mole) in 100 ml of dry benzene was added slowly at room temperature methyl isocyanide (1.36 g, 0.033 mole). The reaction was continued for 3 hr after which time the yellow-white solids formed were filtered and dried to yield 1.39 g of $BrB_{10}H_{11}CNH_2CH_3$. This product was then dissolved in dry tetrahydrofuran and refluxed with freshly cut sodium metal (in a 3:1 molar excess) until gas evolution stopped. The resultant solution was filtered under argon to remove unreacted sodium and then treated with dimethyl sulfate (1.45 g, 0.011 mole). The solid products formed were filtered, dried, and recrystallized from acetone–methanol to give 1.07 g of material (70% yield based on $BrB_{10}H_{11}CNH_2CH_3$), mp 295–296°. *Anal.* Calcd for $B_{10}H_{11}BrCN(CH_3)_3$: C, 17.78; H, 7.42; N, 5.19. Found: C, 18.20; H, 7.42; N, 5.10. The infrared spectrum had $\lambda_{max}$ 3000 (w), 2520 (s), 1975 (w), 1470 (m), 1450 (m), 1120 (m), 950 (m), 935 (m), 930 (m), and 825 (s) cm$^{-1}$.

(B) A solution of $B_{10}H_{12}CN(CH_3)_3$ (1.9 g, 0.01 mole), bromine (4.8 g, 0.03 mole), and freshly sublimed aluminum chloride (3.9 g, 0.03 mole) in dry tetrahydrofuran was refluxed for 3 hr. The solvent was removed with a rotary evaporator and the resultant solids were recrystallized from acetone–methanol to give 1.7 g of material, mp 296–298°; mixture melting point with sample from part A, 296–297°. *Anal.* Calcd for $B_{10}H_{11}BrCN(CH_3)_3$: C, 17.78; H, 7.42; N, 5.19. Found: C, 17.78; H, 7.46; N, 4.89. The infrared and $^{11}B$ nmr spectra of the products from these two syntheses were identical.

**4(6)-$BrB_{10}H_{11}CN(CH_3)_2C_3H_7$.**—A solution of $B_{10}H_{12}CN(CH_3)_2C_3H_7$ (1.0 g, 0.0045 mole) and bromine (3.68 g, 0.023 mole) in 100 ml of tetrahydrofuran in a Pyrex flask was irradiated with ultraviolet light at room temperature for 1.5 hr. Concentration of the solution under reduced pressure and addition of methanol gave a white precipitate. This solid was recrystallized from methanol–acetone to give 0.74 g (55% yield) of material, mp 179–180°. *Anal.* Calcd for $BrB_{10}H_{11}CN(CH_3)_2C_3H_7$: C, 24.15; H, 8.05; N, 4.70. Found: C, 24.41; H, 8.05; N, 4.46. The infrared spectrum contained $\lambda_{max}$ 2980 (m), 2942 (m), 2885 (w), 2560 (s), 1990 (w), 1460 (s), 1405 (m), 1115 (w), 1015 (w), 935 (m), and 830 (s) cm$^{-1}$. The mass spectrum obtained at low voltage (14 ev) showed the cutoff of the highest mass peak at *m/e* 301 corresponding to a parent ion composition of $^{11}B_{10}{}^{1}H_{24}{}^{12}C_6{}^{14}N^{81}Br$.

**4(6)-$ClB_{10}H_{11}CN(CH_3)_3$.**—A solution of $B_{10}H_{12}CN(CH_3)_3$ (0.57 g, 0.003 mole) in acetone at 10° was treated with excess chlorine gas. The chlorine was bubbled through the solution with stirring for 3 hr. The mixture was concentrated at reduced pressure to yield white solids which were filtered, dried, and recrystallized from acetone–methanol giving 0.40 g (59% yield) of material. *Anal.* Calcd for $ClB_{10}H_{11}CN(CH_3)_3$: C, 21.30; H, 8.89; N 6.22. Found: C, 21.06; H, 8.72; N, 6.14. The infrared spectrum contained $\lambda_{max}$ 3000 (w), 2550 (s), 1980 (w), 1483 (m), 1460 (m), 1130 (w), 1020 (w), 960 (m), 947 (m), 933 (m), 920 (m), and 850 (s) cm$^{-1}$. The mass spectrum obtained at low voltage (14 ev) showed the cutoff of the highest mass peak at *m/e* 229 corresponding to a parent ion of composition $^{11}B_{10}{}^{1}H_{20}{}^{12}C_4{}^{14}N^{37}Cl$.

**4,6-$Cl_2B_{10}H_{10}CN(CH_3)_2C_3H_7$.**—A solution of $B_{10}H_{12}CN(CH_3)_2C_3H_7$ (1.0 g, 0.005 mole) in dry tetrahydrofuran was allowed to react with excess chlorine gas in a flow system at 25–50° for 5 hr. At the end of this time, the solution was concentrated under reduced pressure and the solids filtered, dried, and recrystallized four times from acetone–methanol to give 300 mg of material, mp 240–243°. *Anal.* Calcd for $Cl_2B_{10}H_{10}CN(CH_3)_2C_3H_7$: C, 25.08; H, 8.02; N, 4.88. Found: C, 25.57; H, 8.33; N, 4.84. The infrared spectrum showed $\lambda_{max}$ 2980 (m), 2940 (w), 2880 (w), 2560 (s), 1975 (w), 1459 (s), 1448 (m), 1405 (m), 1328 (w), 1110 (w), 1050 (m), 982 (m), 922 (s), 895 (m), 830 (s), and 795 (m) cm$^{-1}$. The mass spectrum obtained at low voltage (14 ev) showed the cutoff for the peak of highest mass at *m/e* 293 corresponding to a parent ion of composition $^{11}B_{10}{}^{1}H_{23}{}^{12}C_6{}^{14}N^{37}Cl_2$.

**$Br_2B_{10}H_{10}CH^-$.**—To a solution of $NaB_{10}H_{12}CH$ (0.0055 mole) in 50 ml of water was added dropwise with stirring over a 30-min period a solution of bromine (0.040 mole) in 50 ml of methanol. The bromine color was discharged rapidly. The reaction mixture was neutralized with 20% sodium hydroxide. Addition of tetramethylammonium chloride to this solution precipitated $(CH_3)_4NB_{10}H_{10}Br_2CH$, which was recrystallized from methanol–acetone to give 0.980 g (45% yield) of product. *Anal.* Calcd for $(CH_3)_4NB_{10}H_{10}Br_2CH$: C, 16.43; H, 6.36; N, 3.83. Found: C, 17.20; H, 6.33; N, 3.44. The infrared spectrum contained absorptions at $\lambda_{max}$ 2548 (vs), 2000 (vw), 1150 (m), 1080 (s), 1050 (w), 1025 (m), 984 (m), 885 (s), 865 (w), 839 (m), 788 (vs), 750 (m), and 734 (m) cm$^{-1}$.

**$BrB_{10}H_{11}CH^-$.**—A solution of bromine (0.01 mole) in 50 ml of methanol was added dropwise in 1 hr to a well-stirred solution, maintained at 0°, of $NaB_{10}H_{12}CH$ (0.0055 mole) in 50 ml of water. The reaction mixture was neutralized with 20% aqueous sodium hydroxide and treated with a saturated solution of tetramethylammonium chloride. The resulting precipitate was dissolved in boiling methanol and filtered hot to give 0.480 g (24% yield) of $(CH_3)_4NB_{10}H_{10}Br_2CH$. The filtrate was cooled and treated with a few drops of water to give 0.370 g (25.8% yield) of $(CH_3)_4NB_{10}H_{11}BrCH$. *Anal.* Calcd for $(CH_3)_4NB_{10}H_{11}BrCH$: C, 20.96; H, 8.45; N, 4.89. Found: C, 20.54; H, 8.04; N, 4.61. The infrared spectrum showed $\lambda_{max}$ 2530 (vs), 1990 (vw), 1150 (m), 1080 (s), 1055 (w), 1010 (w), 980 (m), 874 (m), 838 (m), 782 (s), and 745 (m) cm$^{-1}$.

**$Cl_2B_{10}H_{10}CH^-$.**—A rapidly stirred slurry of $NaB_{10}H_{12}CH$ (0.011 mole) and N-chlorosuccinimide (22.8 g 0.170 mole) in 100 ml of water was irradiated with ultraviolet light for 5 hr. The reaction mixture was treated with tetramethylammonium hydroxide. The resulting precipitate was recrystallized from methanol–acetone to give 1.53 g (50% yield) of $(CH_3)_4NB_{10}H_{10}Cl_2CH$. *Anal.* Calcd for $(CH_3)_4NB_{10}H_{10}Cl_2CH$: C, 21.74; H, 8.47; N, 5.07. Found: C, 22.35; H, 8.60; N, 5.19. The infrared spectrum contained $\lambda_{max}$ 2542 (vs), 2000 (vw), 1150 (m), 1082 (m), 1030 (m), 990 (m), 910 (w), 900 (s), 840 (m), 800 (vs), and 760 (m) cm$^{-1}$.

## Results and Discussion

**$B_{10}H_{12}CH^-$ (I).**—Treatment of $B_{10}H_{12}CN(CH_3)_2C_3H_7$ with excess sodium hydride in tetrahydrofuran initially results in rapid elimination of 1 molecular equiv of hydrogen and then at reflux elimination of 1 equiv of dimethylpropylamine during a 24-hr period. The $B_{10}H_{12}CH^-$ ion is obtained in 63% yield from this reaction.

A second synthesis of $B_{10}H_{12}CH^-$ consists of refluxing a mixture of $B_{10}H_{12}CN(CH_3)_2R$ ($R = CH_3$ or $C_3H_7$) and sodium in tetrahydrofuran for 24–36 hr until a thick white solid forms. The dried solid (II) is pyrophoric in moist air. The hydrolysis of II is represented by

$$\underset{\text{II}}{Na_3B_{10}H_{10}CH(C_4H_8O)_{1.85}} + 2H_2O \longrightarrow NaB_{10}H_{12}CH + 1.85C_4H_8O + 2NaOH \quad (1)$$

The sodium hydroxide formed was titrated with standard acid and the tetrahydrofuran liberated was analyzed by glpc. The results obtained were reproducible and suggest the composition for II indicated in eq 1. Reaction of II with iodine (*vide infra*) is also consistent with this formulation. Hydrolysis of $Na_3B_{10}H_{10}CH(C_4H_8O)_{1.85}$ gave an 80% yield of $CsB_{10}H_{12}CH$. The $^{11}B$ nmr spectrum of I (Figure 1) is quite similar to that of $B_{10}H_{12}CN(CH_3)_3$,[4] suggesting that these two molecules may have closely related structures. Thus we postulate the the $B_{10}H_{12}CH^-$ ion is a nearly regular icosahedron missing one vertex and that the extra two hydrogen atoms bridge boron atoms on nonadjacent edges of the open face. This is the same structure postulated for $B_{10}H_{12}CN(CH_3)_3$[4] and determined by X-ray methods for the isoelectronic $B_{11}H_{13}^{2-}$ ion.[8] The reaction sequence then formally represents a replacement of dimethylpropylamine on the cage carbon atom by a hydride ion.

**$B_{10}H_{10}CH^-$ (III).**—Reaction of $B_{10}H_{12}CN(CH_3)_3$ with sodium in refluxing tetrahydrofuran produces III as a minor product in addition to the $B_{10}H_{12}CH^-$ ion.[5] We find that treatment of II with 1 molar equiv of iodine forms the $B_{10}H_{10}CH^-$ ion in good yield

$$Na_3B_{10}H_{10}CH(C_4H_8O)_{1.85} + I_2 \longrightarrow NaB_{10}H_{10}CH + 2NaI + 1.85C_4H_8O \quad (2)$$

This reaction is reminiscent of the oxidation of $B_{10}H_{14}^{2-}$ by iodine to produce decaborane(14) in high yield.[9] The $^{11}B$ nmr spectrum of III is nearly identical with that shown in Figure 2. There are three apparent doublets at +3.9, +11.0, and +15.5 ppm of relative areas 2:4:4, respectively. This simple $^{11}B$ nmr spectrum can be rationalized in terms of a "closo" octadecahedral structure of $C_{2v}$ symmetry (Figure 3) if it is assumed that two pairs of boron atoms, $B_8$–$B_9$ and $B_{10}$–$B_{11}$, are accidentally equivalent. The configuration of the isoelectronic $B_9H_9C_2(CH_3)_2$ polyhedron has been recently established by X-ray analysis[10] and is the same as we suggest for III. Available evidence[11] does not allow a unique assignment of structure of $B_{11}H_{11}^{2-}$ which is also isoelectronic with III.

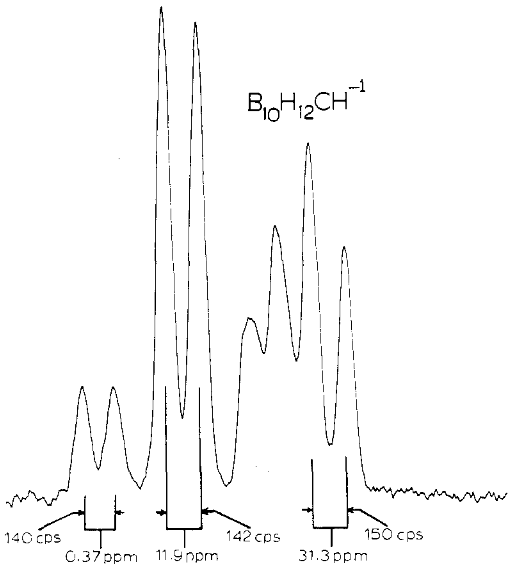

Figure 1.—$^{11}B$ nmr spectrum (32.1 Mc) of $(CH_3)_4NB_{10}H_{12}CH$ in dimethylformamide externally referenced to $BF_3 \cdot (C_2H_5)_2O$.

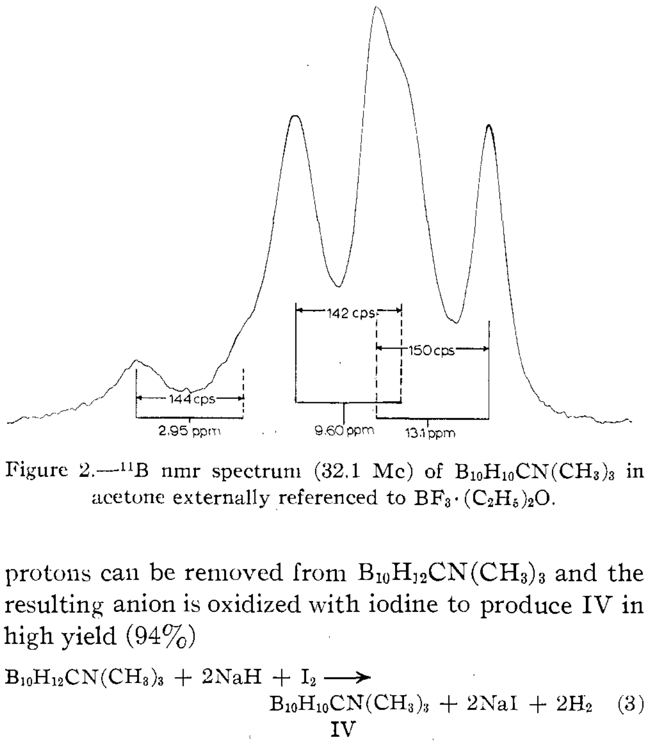

Figure 2.—$^{11}B$ nmr spectrum (32.1 Mc) of $B_{10}H_{10}CN(CH_3)_3$ in acetone externally referenced to $BF_3 \cdot (C_2H_5)_2O$.

**$B_{10}H_{10}CN(CH_3)_2R$ (IV, $R = CH_3$; V, $R = C_3H_7$).**—In a reaction similar to that employed to form III, two protons can be removed from $B_{10}H_{12}CN(CH_3)_3$ and the resulting anion is oxidized with iodine to produce IV in high yield (94%)

$$B_{10}H_{12}CN(CH_3)_3 + 2NaH + I_2 \longrightarrow \underset{\text{IV}}{B_{10}H_{10}CN(CH_3)_3} + 2NaI + 2H_2 \quad (3)$$

Attempted alkylation of $NaB_{10}H_{11}CN(CH_3)_2C_3H_7$ with methyl iodide resulted in partial elimination of methane and a low yield of V was isolated from the products. The $^{11}B$ nmr spectra of $B_{10}H_{10}CN(CH_3)_3$ (Figure 2) is nearly identical with that described for III. Therefore it is suggested that isoelectronic III, IV, and V are structurally related by simple replacement of a hydride ion on the cage carbon atom of III by trimethyl- or dimethylpropylamine to obtain IV and V, respectively.

**Halogenation Reactions.**—The reactions of $B_{10}H_{12}CH^-$ and $B_{10}H_{12}CN(CH_3)_2R$ ($R = CH_3$ or $C_3H_7$) with chlorine, bromine, and iodine under various conditions were studied. As expected, the reactivity of halogens toward these molecules is Cl > Br > I. The C-amine

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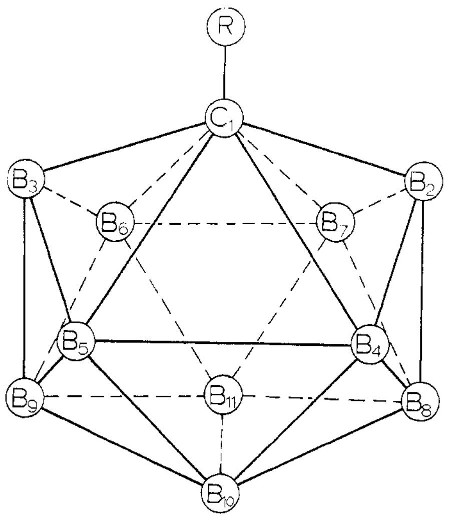

Figure 3.—Proposed structure of $B_{10}H_{10}CR$ (R = $H^-$ or $N(CH_3)_3$)

derivatives are slightly more resistant to halogenation than the $B_{10}H_{12}CH^-$ ion. Reaction of a 1:2 ratio of I and bromine, respectively, at 0° produced a mixture of $BrB_{10}H_{11}CH^-$ and $Br_2B_{10}H_{10}CH^-$. In contrast even at reflux in acetonitrile, $B_{10}H_{12}CN(CH_3)_2R$ did not react with bromine alone. With the aid of aluminum chloride catalyst or ultraviolet irradiation, bromination of $B_{10}H_{12}CN(CH_3)_2R$ gave a monobromo derivative.

Chlorination of $B_{10}H_{12}CN(CH_3)_2R$ occurred without the aid of a catalyst to give both mono- and dichloro derivatives. Reaction of $B_{10}H_{12}CH^-$ with chlorine gas even at 0° caused extensive degradation of the carborane molecule to borates. However $Cl_2B_{10}H_{10}CH^-$ was obtained by more gentle reaction with N-chlorosuccinimide and ultraviolet irradiation. Attempts to iodinate I or the C-trialkylamine derivatives even with the aid of aluminum chloride catalyst or a photolamp were unsuccessful.

"Labeled" $BrB_{10}H_{11}CN(CH_3)_3$ was prepared by the reaction sequence

$$\text{2-}BrB_{10}H_{13} + CH_3NC \longrightarrow BrB_{10}H_{11}CNH_2CH_3 \qquad (4)$$

$$BrB_{10}H_{11}CNH_2CH_3 \xrightarrow[(2)\ \ (CH_3)_2SO_4]{(1)\ \ Na\text{–}THF} BrB_{10}H_{11}CN(CH_3)_3 \qquad (5)$$

The "labeled" compound and the monobromo products from both photolytic and catalytic bromination of $B_{10}H_{12}CN(CH_3)_3$ have identical infrared spectra and melting points.

The position of monohalogen substitution on $B_{10}H_{12}CN(CH_3)_2R$ has been investigated by means of the $^{11}B$ nmr spectra of this series of compounds. The boron nmr spectrum of $B_{10}H_{12}CN(CH_3)_3$[4] can be divided into three sections. These are the low-field doublet at −0.6 ppm (1 B), the highest field doublet at +33 ppm (2 B), and the remainder of the spectrum (7 B). Similarly, this type of area comparison can be made with the spectrum of "labeled" $BrB_{10}H_{11}CN(CH_3)_3$ (Figure 4). In this case the area ratio of the low-field doublet at −0.2 ppm to the high-field doublet at +35.4 ppm[12] is 1:1. Similarly a 1:1 ratio is obtained for the areas of the high- and low-field doublets in the spectra of the monochloro and monobromo derivatives from the halogenation reactions. In the halogenation reactions, the elemental analyses assured us that we had a monohalo compound. However, a mixture of monohalo positional isomers could be present. Within the limits of accuracy of the 32-Mc $^{11}B$ nmr spectrometer, this does not seem to be the case. In all instances, we found that the area ratio of the low-field doublet to the high-field doublet was 1:1. The presence of a mixture of isomers would make the ratio 1:(1 + $X$), respectively.

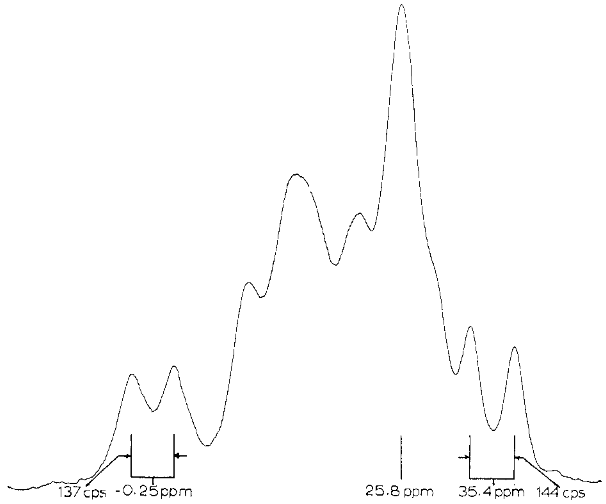

Figure 4.—$^{11}B$ nmr spectrum (32.1 Mc) of 4(6)-$BrB_{10}H_{11}CN(CH_3)_3$ in dimethylformamide externally referenced to $BF_3 \cdot (C_2H_5)_2O$.

The available nmr data only strictly indicate that halogenation occurs at one of four possible equivalent pairs of boron atoms (2,3; 4,6; 8,11; or 9,10; see Figure 5).[13]

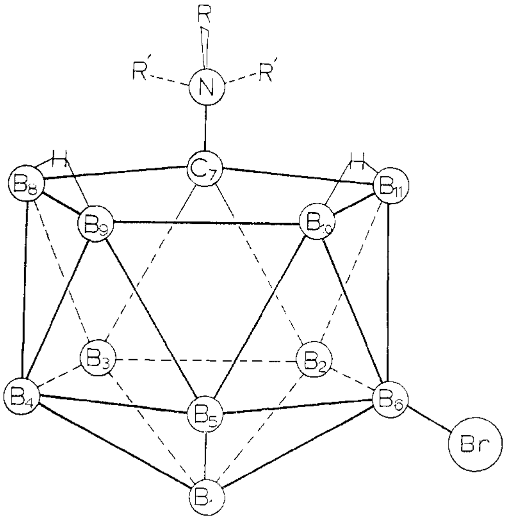

Figure 5.—Proposed structure of 4(6)-$BrB_{10}H_{11}CN(CH_3)_2R$ (R = $CH_3$ or $n$-$C_3H_7$).

If rearrangement of the decaborane structure has not occurred during the formation of the so-called "labeled" $BrB_{10}H_{11}CN(CH_3)_3$ (eq 4 and 5), then the

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[12] The $^{11}B$ nmr chemical shift values have an accuracy of ±1.5 ppm.

[13] The numbering system of these new cage molecules has not yet been clearly defined. At the suggestion of Dr. R. M. Adams, we have revised the numbering system previously used for $B_{10}H_{12}CNH_2R$[4] to that given in Figure 5.

nmr study suggests that the high-field doublet represents the $B_4$ and $B_6$ atoms.

The 1:1 ratio of the high- and low-field doublets at +30.9 and −0.7 ppm, respectively, in the spectrum of the $BrB_{10}H_{11}CH^-$ ion leads us to suggest that halogenation of I also occurs initially at the $B_4$ atom (numbering is the same as Figure 5). Deamination of "labeled" $BrB_{10}H_{11}CN(CH_3)_3$ with sodium in ethereal solvents is much more sluggish than with $B_{10}H_{12}CN(CH_3)_3$. Thus far, a "labeled" $BrB_{10}H_{11}CH^-$ ion has not been obtained. Dihalogenation of both I and $B_{10}H_{12}CN(CH_3)_2C_3H_7$ yields $^{11}B$ nmr spectra in which the high-field doublet originally at +31.3 and +35 ppm, respectively, is completely absent. The stereochemistry of thse products is therefore probably 4,6-$Br_2B_{10}H_{10}CH^-$ and 4,6-$Cl_2B_{10}H_{10}CN(CH_3)_2C_3H_7$.

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# Hydrazinium(+2) and Hydroxylammonium Hexafluorouranates(V)[1,2]

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In the reaction between uranium hexafluoride and hydrazinium(+2) fluoride in liquid hydrogen fluoride at room temperature, with excess uranium hexafluoride, the product is hydrazinium(+2) bishexafluorouranate(V), $N_2H_6(UF_6)_2$, and, with excess hydrazinium(+2) fluoride, the product is hydrazinium(+2) heptafluorouranate(V), $N_2H_6UF_7$. The analogous reaction with hydroxylammonium fluoride produces mixtures of hydroxylammonium and nitrosyl hexafluorouranates(V). X-Ray powder patterns, infrared spectra, and magnetic susceptibilities of the solids are given. In the Raman spectra of the hydrogen fluoride solutions of these materials, the 628-$cm^{-1}$ band was assigned to the principal symmetric vibration of $UF_6^-$ ion. The thermal decompositions in argon are discussed in terms of the schemes

$$N_2H_6(UF_6)_2 \xrightarrow{120^\circ} N_2H_5UF_5 + UF_4 \cdot nHF \xrightarrow{250^\circ} NH_4F \cdot 3UF_4 \xrightarrow{300^\circ} 3UF_4 \cdot HF \xrightarrow{380^\circ} UF_4$$

$$(NH_3OH)UF_6 + NOUF_6 \xrightarrow{110^\circ} (NH_3OH)UF_5 + NOUF_6 \xrightarrow{170^\circ} \text{unknown} \xrightarrow{350^\circ} UF_4$$

Hydrazinium(+2) fluoride solubility in hydrogen fluoride at 0° was found to be 15 g of $N_2H_6F_2$/100 g of HF. $N_2H_6^{2+}$ is the only important cationic species in such solutions.

## Introduction

The complex fluorides of uranium(V) have been the subject of research in several laboratories in the past few years. Such compounds were prepared by allowing uranium pentafluoride to react with ammonium and alkali fluorides at elevated temperatures under anhydrous conditions.[4] The silver and thallium complexes were prepared in the same way.[5] Uranium pentafluoride also reacts with soluble binary fluorides in hydrogen fluoride at room temperature forming complex fluorouranates (V).[6]

Fluorination of a complex fluorouranate(IV) with elemental fluorine at carefully controlled temperatures[7] and fluorination of uranium tetrafluoride in the presence of alkali fluorides in hydrogen fluoride at room temperature[8] have been reported as alternate approaches to these compounds. Reduction of uranium hexafluoride is, however, a logical counterpart of oxidation methods. Under certain conditions uranium hexafluoride is reduced by ammonia to give ammonium hexafluorouranate(V)[9] and by nitrogen monoxide[10] or nitrosyl chloride[10] to give nitrosyl hexafluorouranate(V).

It was shown also that hyrazinium(+2) fluoride can be used to reduce uranium hexafluoride at 0° in hydrogen fluoride or carbon tetrachloride to give hydrazinium(+2) heptafluorouranate(V).[11] This study has been continued in this laboratory and hydroxylammonium fluoride has been introduced as another reducing and complex-forming agent.

The properties of the reacting solutions were studied previously. It was shown[12] that uranium hexafluoride

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Paper presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

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