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Synthesis of Diazonium Derivatives of $B_{10}H_{10}^{2-}$ from Arylazo Intermediates

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Received March 14, 1975 AIC501921

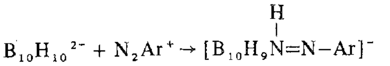
Thermal decomposition of protonated arylazo derivatives of $B_{10}H_{10}^{2-}$ produce diazonium derivatives of $B_{10}H_{10}^{2-}$ plus the arene. A mechanism is suggested which involves electrophilic attack by a proton on the phenyl carbon atom bonded to the azo nitrogen atom. The general utility of this reaction is illustrated by the preparation of a variety of polyhedral B_{10} derivatives.

The stable polyhedral borane anion, $B_{10}H_{10}^{2-}$, undergoes a wide variety of reactions in which the hydrogen atoms are replaced by substituent groups.[1] One of the most useful of these substituents is the diazonium function which may itself function as a leaving group in apparent nucleophilic displacement reactions which produce nitrogen. Thus, the N_2^+ function can be readily replaced by a variety of nucleophiles such as CO, NH_3, CH_3CN, C_5H_5N, H_2S, and OH^-.[2] The first reported synthesis of diazonium derivatives of $B_{10}H_{10}^{2-}$ involved the direct reaction of nitrous acid with $B_{10}H_{10}^{2-}$ followed by reduction of an unstable intermediate to the inner diazonium salt.[3] This method gives only $B_{10}H_8(N_2)_2$ and no

$$B_{10}H_{10}^{2-} \xrightarrow[\text{(2) NaBH}_4]{\text{(1) HNO}_2} 1,10\text{-}B_{10}H_8(N_2)_2 \qquad (1)$$

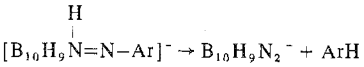
$B_{10}H_9N_2^-$ and has the serious disadvantage that the intermediate may detonate explosively when dry. In a preliminary communication we reported a method of obtaining $B_{10}H_9N_2^-$ and diazonium derivatives of $B_{10}H_9L^-$ from protonated arylazo derivatives[4] and the details of that work are presented here.

Salts of $B_{10}H_{10}^{2-}$, when treated with an aryldiazonium tetrafluoroborate, immediately produce protonated arylazo dyes in nearly quantitative yields.[5] The protonated arylazo species were apically substituted and did not react with a second equivalent of aryldiazonium ion. In addition, the protonated arylazo derivatives were characterized[5] as weak acids in which the nitrogen atom adjacent to the B_{10} polyhedron carried the proton. The protonated arylazo derivatives of $B_{10}H_{10}^{2-}$ and


(2)

$$B_{10}H_{10}^{2-} + N_2Ar^+ \rightarrow [B_{10}H_9\overset{\text{H}}{\text{N}}{=}N{-}Ar]^- \qquad (2)$$

its B-substituted derivatives were found to form the corresponding apical diazonium derivative of the B_{10} polyhedron and the corresponding arene when heated in solution under mild conditions if the aryl group carried electron withdrawing substituents. Due to the general utility of these reactions we believe that they provide the method of choice for the preparation of a wide variety of $B_{10}H_9L^-$ derivatives containing the apical diazonium function.


(3)

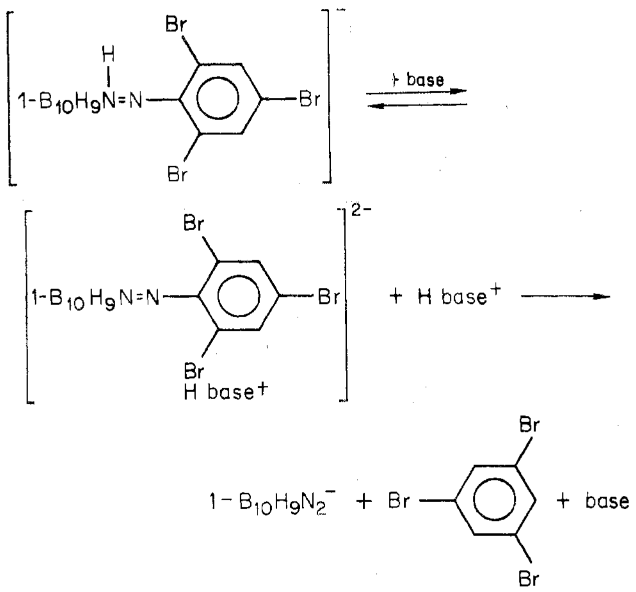
$$[B_{10}H_9\overset{\text{H}}{\text{N}}{=}N{-}Ar]^- \rightarrow B_{10}H_9N_2^- + ArH \qquad (3)$$

Results and Discussion

When a solution of $K_2B_{10}H_{10}$ in acetonitrile was treated with 2,4,6-tribromophenyldiazonium tetrafluoroborate at −35° the dark, red, protonated arylazo derivative was formed. If the solution was allowed to come to room temperature and treated with excess sodium propionate, the intensity of the color rapidly decreased and after several hours $(CH_3)_4N[1\text{-}B_{10}H_9N_2]$ was isolated in 52% yield. The neutral B-substituted derivatives $1,10\text{-}N_2B_{10}H_8N(CH_3)_3$, $1,6\text{-}N_2B_{10}H_8N(CH_3)_3$, $1,10\text{-}N_2B_{10}H_8NC_5H_5$, and $1,10\text{-}N_2B_{10}H_8S(CH_3)_2$ were prepared from the correspondingly substituted $B_{10}H_{10}^{2-}$ ions using only slightly more vigorous conditions.

Formation of the diazonium function from the protonated arylazo derivative was found to proceed only very slowly at room temperature in the absence of a weak base. On the other hand, the dianion, $ArN_2B_{10}H_9^{2-}$, was completely unreactive in acetonitrile at the reflux temperature. The most rapid formation of the diazonium function was obtained in the presence of a weak base which apparently had the effect of buffering the arylazo derivative.

These data are consistent with a mechanism for the formation of the diazonium function in which the dianion, $ArN_2B_{10}H_9^{2-}$, is first formed by reaction of the acidic proton with a base, followed by electrophilic attack on the phenyl carbon atom attached to nitrogen by the proton of the conjugate acid of the base.



The B-perchloroarylazo derivative, 1-(1-Br-4-$N_2C_6H_4$)-$B_{10}Cl_9^{2-}$, was obtained by chlorination of the 4-bromoazo compound in acetonitrile at low temperature in the presence of excess base. The perchloro diazonium compound could not be formed from this derivative when treated in the usual manner. On the basis of the infrared spectrum, a major side product of the chlorination reaction appeared to be a mixture of $B_{10}H_xCl_{9-x}N_2^-$ species. Separated experiments on the chlorination of $B_{10}H_9N_2^-$ showed that only partial chlorination of this anion is possible under the conditions employed.

The usefulness of the 1-$B_{10}H_9N_2^-$ ion depends upon the unique ease with which it reacts with nucleophiles to give a large number of $B_{10}H_{10}^{2-}$ derivatives. The displacement reactions described by Knoth[2] apply equally well to 1-$B_{10}H_9N_2^-$ and 1,10-$B_{10}H_8(N_2)_2$. As a specific example, $(CH_3)_4N$[1-$B_{10}H_9N_2$] was heated in pyridine solution at the reflux temperature for several hours to produce a nearly quantitative yield of $(CH_3)_4N$[1-$B_{10}H_9NC_5H_5$].

The properties of 1-$B_{10}H_9N_2^-$ suggest considerable resonance interaction between the diazonium function and the B_{10} polyhedron. Thermal decomposition of solid $(CH_3)_4N$[1-$B_{10}H_9N_2$] with release of N_2 does not occur at temperatures below 120°. The cyclic voltammogram of $(CH_3)_4N$[1-$B_{10}H_9N_2$] in CH_3CN has two irreversible oxidation waves occurring at −1.50 and +1.75 vs. SCE. This oxidation sequence may result in the formation of a coupled species such as $B_{20}H_{16}(N_2)_2$.[6,7] The high potential required to oxidize the mono-diazonium species, compared with that of the similar anion, 1-$B_{10}H_9S(CH_3)_2^-$, at +1.08 and +1.28 V, can be attributed to the strong electron-acceptor capability of the diazonium function which through apparent resonance interaction with the B_{10} polyhedron decreases electron density at the unsubstituted apical position.

Experimental Section

Apparatus, Materials, and Procedures. Ultraviolet–visible spectra were recorded on a Beckman Model DB spectrophotometer. Infrared spectra were determined using a Perkin-Elmer Model 137 spectrophotometer. Proton NMR spectra were obtained on a Varian T-60 spectrometer; 80.5 MHz ^{11}B NMR spectra were recorded on an instrument designed by Professor F. A. L. Anet. Controlled-potential cyclic voltammetry was carried out on an instrument based on the design of Hawley.[8] Analyses were carried out by Schwarzkopf Microanalytical Laboratories, Woodside, N.Y. Pyridine was distilled from KOH. Silica gel (60–200 mesh) was obtained from J. T. Baker Co. and 2,4,6-tribromophenyldiazonium tetrafluoroborate[9] was prepared from Eastman practical grade 2,4,6-tribromoaniline. $K_2B_{10}H_{10}$[10] was twice recrystallized from ethanol. Cs[1-$B_{10}H_9S(CH_3)_2$][11] and $(CH_3)_4N$[1-$B_{10}H_9N(CH_3)_3$][3,9] were prepared by literature methods.

$(CH_3)_4N$[1-$B_{10}H_9N_2$]. Into a 2 l. three-neck flask fitted with a mechanical stirrer, thermometer, addition funnel, and N_2 inlet was placed 10.0 g (51 mmol) of $K_2B_{10}H_{10}$ in 1 l. of acetonitrile. The flask was flushed with N_2 and placed in a Dry Ice–2-propanol bath and cooled to −35°. To this solution 21.8 g (51 mmol) of 2,4,6-tribromophenyldiazonium tetrafluoroborate dissolved in 200 ml acetonitrile was added dropwise over 0.5 hr. The solution was stirred another 0.5 hr and then warmed to room temperature at which time 2 g of solid sodium propionate was added. The slurry was stirred for 5 hr and the volume was reduced to 200 ml on a rotary evaporator and filtered. The solution was then evaporated to dryness and the solid was thoroughly dispersed in 100 ml of water and filtered. The solid was washed three times with 50 ml portions of water and identified as 1,3,5-tribromobenzene by its infrared spectrum. The combined aqueous solution was treated with excess $(CH_3)_4NCl$ and filtered. The solid was washed with water, cold ethanol, and diethyl ether to yield 7.5 g of crude product. The crude product was further purified by chromatography through a 30 mm × 300 mm column packed with silica gel eluting with 5:1 (v/v) dichloromethane–acetonitrile. The first slightly pink fractions were evaporated to dryness and dissolved in 800 ml of boiling 95% ethanol. Decolorizing charcoal was added and the solution was filtered while hot. The ethanol solution was cooled to ice bath temperature, filtered, and washed with cold ethanol and ethyl ether to yield 4.9 g (44%) of colorless crystals of $(CH_3)_4N$[1-$B_{10}H_9N_2$]. An additional 0.9 g (8%) of product was obtained by evaporating the filtrate. The infrared spectrum contains bands at 2500 (s), 2230 (s), 1160 (m), 1130 (m), 1000 (s), 950 (s), and 820 (w) cm^{-1} and the ultraviolet spectrum exhibits absorptions at 273 (14,200) and 219 (9210) [λ_{max}, nm (ϵ)]. Anal. Calcd for $(CH_3)_4NB_{10}H_9N_2$: C, 21.90; H, 9.65; B, 49.28; N, 19.15. Found: C, 22.14; H, 9.82; B, 49.56; N, 19.48.

1,10-$N_2B_{10}H_8N(CH_3)_3$. Five grams (20 mmol) of $(CH_3)_4N$[1-$B_{10}H_9N(CH_3)_3$] was dissolved in 200 ml of CH_3CN and the flask was cooled to −35°. To this 8.7 g (20 mmol) of 2,4,6-tribromophenyldiazonium tetrafluoroborate in CH_3CN was added slowly over 0.5 hr. The solution was allowed to warm to room temperature when 2 g of sodium propionate was added and the stirring was continued overnight. The acetonitrile was then refluxed for 2 hr, the solution was cooled and filtered, and the dissolved product was deposited on 50 g of silica gel by removing the solvent under reduced pressure. This was added to the top of a previously packed silica gel column (30 mm × 300 mm) and eluted first with hexane to remove the tribromobenzene, then with CH_2Cl_2. The yellow CH_2Cl_2 fractions were recrystallized from ethanol using decolorizing charcoal yielding 2.5 g (59%) of colorless crystals of 1,10-$N_2B_{10}H_8N(CH_3)_3$. Anal. Calcd for 1,10-$N_2B_{10}H_8N(CH_3)_3$: C, 17.72; H, 8.43; B, 53.18; N, 20.67. Found: C, 17.92; H, 8.59; B, 51.18; N, 19.20.

The infrared spectrum included peaks at 2510 (s), 2220 (s), 1120 (s), 1000 (m), 970 (w), 920 (w), 890 (w), and 830 (w) cm^{-1}.

1,10-$N_2B_{10}H_8S(CH_3)_2$, 1,6-$N_2B_{10}H_8N(CH_3)_3$, and 1,10-$N_2B_{10}H_8NC_5H_5$. The method of preparation of these compounds was identical with the preparation of 1,10-$N_2B_{10}H_8N(CH_3)_3$ described above, but began with Cs[1-$(CH_3)_2SB_{10}H_9$], $(CH_3)_4N$[2-$(CH_3)_3NB_{10}H_9$], or $(CH_3)_4N$[1-$C_5H_5NB_{10}H_9$] to yield 45% 1,10-$N_2B_{10}H_8S(CH_3)_2$, 36% 1,6-$N_2B_{10}H_8N(CH_3)_3$, and 24% 1,10-$N_2B_{10}H_8NC_5H_5$. The compounds 1,10-$N_2B_{10}H_8S(CH_3)_2$ and 1,6-$N_2B_{10}H_8N(CH_3)_3$[12] were identical in all respects with the products prepared by the previously reported method. Anal. Calcd for $N_2B_{10}H_8NC_5H_5$: C, 26.89; H, 5.87; B, 48.42; N, 18.81. Found: C, 26.67; H, 5.37; B, 47.14; N, 18.77.

The infrared spectrum of 1,10-$N_2B_{10}H_8NC_5H_5$ included peaks at 2500 (s), 2200 (s), 1630 (m), 1250 (m), 1200 (w), 1160 (w), 1040 (w), 1010 (w), 860 (w), and 780 (s) cm^{-1}.

[$(CH_3)_4N$]$_2$[1-(1-Br-4-$N_2C_6H_4$)$B_{10}Cl_9$] and $CsB_{10}Cl_9N_2$. A solution of 2.0 g of $(CH_3)_4N$[1-(1-Br-4-$N_2C_6H_4$)$HB_{10}H_9$] in 100 ml of acetonitrile was made basic with 2 g of 50% NaH and cooled to −35°. The solution was stirred while Cl_2 was slowly bubbled into the solution. After the exothermic phase of the reaction was over the cooling bath was removed and Cl_2 was passed through the solution at ambient temperature for 5 hr. The solution was filtered and the solvent was removed at reduced pressure. The residue was dissolved in basic H_2O–acetone and precipitated by addition of excess $(CH_3)_4NCl$. The solid was dissolved in acetone–ethanol and the acetone was slowly removed under reduced pressure. The solution was filtered to yield

Table I. The 80.5 MHz ^{11}B NMR Spectra of $B_{10}H_{10}^{2-}$ Derivatives[a]

Compd	Rel intensity	Chemical shifts, $\delta^b (J_{B-H}, Hz)$
$(CH_3)_4N[1\text{-}B_{10}H_9N_2]$	1:1:4:4	−22.0 (150), +13.4, +17.2 (130), +25.8 (140)
$1,6\text{-}N_2B_{10}H_8N(CH_3)_3$	1:1:1:2:2:2:1	−9.0 (140), +10.8, +17.9, +20.5 (140), +27.3 (120), +29.6 (120), +33.9 (140)
$[(CH_3)_4N_2][1\text{-}(1\text{-}Br\text{-}4N_2\text{-}C_6H_4)B_{10}Cl_9]$	1:9	−1.6, +8.5[e]
$(CH_3)_4N[1\text{-}C_5H_5NB_{10}H_9]$	1:1:8	−0.5, +2.5 (120), +31.3[c]
$1,10\text{-}N_2B_{10}H_8\text{-}NC_5H_5$	1:1:4:4	−25.6, +9.2, +17.2 (130), +22.4 (140)
$1,10\text{-}(CH_3)_2\text{-}SB_{10}H_8N_2$	1:1:4:4	−19.5, +4.1, +18.4 (130), +23.0 (130)
$1,10\text{-}N_2B_{10}H_8N(CH_3)_3$	1:1:4:4	−32.2, +8.4, +19.4 (130), +25.4 (130)
$CsB_{10}Cl_9N_2$ [d]	1:1:8	−12.0, +2.4, +7.2[e]

[a] Obtained in CH_3CN solution except where noted. [b] Relative to $BF_3 \cdot O(C_2H_5)_2$. [c] Overlapping doublets. [d] Obtained in $(CH_3)_2SO$ solution. [e] Broad overlapping singlets.

1.3 g (36%) of $[(CH_3)_4N]_2[1\text{-Br-4-}N_2C_6H_4)B_{10}Cl_9]$. Anal. Calcd for $[(CH_3)_4N]_2[BrC_6H_4N_2B_{10}Cl_9]$: C, 22.14; H, 3.73; B, 14.23; N, 7.37; Cl, 42.01; Br, 10.52. Found: C, 22.60; H, 3.82; B, 13.69; N, 7.37; Cl, 41.95; Br, 10.69. The infrared spectrum contained peaks at 1640 (w), 1290 (w), 1150 (m), 1000 (s), 950 (s), 875 (m), 840 (m), and 715 (m) cm^{-1}.

The remainder of the ethanol from the filtrate was removed to yield 1.1 g of $(CH_3)_4NB_{10}H_xCl_{9-x}N_2$ which exhibited both a small peak at 2500 cm^{-1} due to B–H and a strong absorption at 2250 cm^{-1} due to the diazonium function. The mixture was chromatographed on a silica gel column to obtain fractions in which the 2500 cm^{-1} peak in the infrared spectrum was no longer apparent and then passed through a sodium form cation exchange column. Excess CsCl was added to the aqueous solution to obtain a low yield of the apparently impure mixed salt $Cs[1\text{-}N_2B_{10}Cl_9] \cdot CsCl$. Anal. Calcd for $CsB_{10}Cl_9N_2 \cdot CsCl$: Cs, 35.13; Cl, 46.87; B, 14.29; N, 3.70. Found: Cs, 33.48; Cl, 49.20; B, 12.58; N, 5.05; H, 0.0; C, 0.0. The infrared spectrum contained peaks at 2250 (s), 1140 (s), 1010 (s), and 825 (s) cm^{-1}.

Solutions of $[(CH_3)_4N]_2[1\text{-}(1\text{-Br-4-}N_2C_6H_4)B_{10}Cl_9]$ in CH_3CN were protonated changing the color from yellow to the dark red characteristic of the protonated dye. These solutions were refluxed over periods up to several weeks and only trace amounts of the diazonium function formed.

$(CH_3)_4N[1\text{-}C_5H_5NB_{10}H_9]$. In a 100 ml flask fitted with a reflux condenser and N_2 inlet were placed 3.1 g (14 mmol) of $(CH_3)_4N[1\text{-}B_{10}H_9N_2]$ and 50 ml of pyridine to give a clear solution. After several minutes at reflux a yellow precipitate had begun to form. After 3 hr at reflux the precipitate was separated by filtration and washed with acetone and diethyl ether giving 3.4 g (95%) of $(CH_3)_4N[1\text{-}C_5H_5NB_{10}H_9]$. Anal. Calcd for $(CH_3)_4N[C_5H_5NB_{10}H_9]$: C, 39.97; H, 9.69; B, 40.00; N, 10.35. Found: C, 39.82; H, 9.87; B, 40.23; N, 10.22. The infrared spectrum contained peaks at 2500 (s), 1630 (m), 1600 (m), 1540 (m), and 12.69 (m) cm^{-1}.

Acknowledgment. The authors wish to thank Dr. R. J. Wiersema for his assistance in obtaining the electrochemical data and for measuring ^{11}B spectra and Professor F. A. L. Anet for use of the 80 MHz NMR spectrometer. This research was supported in part by the Office of Naval Research and the National Science Foundation under Grant No. GP-14372X1.

Registry No. $(CH_3)_4N[1\text{-}B_{10}H_9N_2]$, 55913-46-7; $1,10\text{-}N_2B_{10}H_8N(CH_3)_3$, 55822-55-4; $1,10\text{-}N_2B_{10}H_8NC_5H_5$, 55822-56-5; $[(CH_3)_4N]_2[1\text{-}(1\text{-Br-4-}N_2C_6H_4)B_{10}Cl_9]$, 55904-73-9; $CsB_{10}Cl_9N_2$, 55886-11-8; $(CH_3)_4N[1\text{-}C_5H_5NB_{10}H_9]$, 55913-47-8; $K_2B_{10}H_{10}$, 12447-89-1; $(CH_3)_4N[1\text{-}B_{10}H_9N(CH_3)_3]$, 55904-74-0; $(CH_3)_4N[1\text{-}(1\text{-Br-4-}N_2C_6H_4)HB_{10}H_9]$, 55975-91-2; 2,4,6-tribromophenyldiazonium tetrafluoroborate, 4639-13-8; pyridine, 110-86-1.

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High-Resolution Boron-11 Nuclear Magnetic Resonance Spectroscopy.[1] V. Analysis of the Boron-11 Nuclear Magnetic Resonance Spectrum of Tetraborane(8)–Carbonyl at 32.1 MHz

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Received March 27, 1975 AIC502321

The boron-11 NMR spectrum of tetraborane(8)–carbonyl at 32.1 MHz has been interpreted in terms of the presence of two stereoisomers. This conclusion is based on the results of computer line-narrowed, proton-decoupled, and partially relaxed Fourier transform NMR spectra. The existence of isomers at −20° implies either isomers are formed during the synthesis and do not interconvert or isomer interconversion at −20° is slow with respect to the NMR chemical shift time scale.

Broad lines and overlapping resonances have previously made ^{11}B spectral interpretation and assignment of resonances arduous.[3] Utilization of techniques such as computer line-narrowing,[4,5] partially relaxed Fourier transform[6,7] NMR (PRFT), and complete proton decoupling[8,9] has made it possible to extract significantly more information from ^{11}B spectra recorded at any field strength. Because of our interest in the NMR parameters of low molecular weight boron hydrides and the structural implications of these data, we have applied the aforementioned methods in an attempt to elucidate the ^{11}B NMR spectrum of tetraborane(8)–carbonyl, $B_4H_8 \cdot CO$.

Tetraborane(8)–carbonyl was first synthesized[10] by Burg