occurred. The doublet resonances centered at −4 and +39.2 ppm due to B(4) and B(1,3) appear completely collapsed. The resonances at −16.5 and +15 ppm due to B(2) and B(8,10) appear partially collapsed and the other two doublets due to B(5,7) and B(9) are unchanged. These results are consistent with the existence of a C_{3v} intermediate which is causing the partial scrambling of the labeled boron atoms.

Treatment of 4-$BrB_9H_{12}\cdot S(C_2H_5)_2$[17] with aqueous ethanolic tetraethylammonium hydroxide at room temperature produced $(C_2H_5)_4N[BrB_9H_{11}]$ and the ^{11}B nmr spectrum of this product is presented in Figure 11.[30] The appearance of at least seven resonances in this spectrum suggests that the bromine atom in the product is located at a position which is not on the mirror plane passing through B(2), B(4), and B(9). Therefore rearrangement of the bromine label (possibly as shown in Figure 12) has occurred in this case also.

While these observations do not serve as proof concerning our proposed mechanism for the formation of $B_9H_{12}S^-$ from decaborane, the generation of similarly "rearranged" labeled molecules in these transformations strongly suggests the existence of a common reaction intermediate with effective C_{3v} symmetry (possibly a B_9H_{13} species) in these processes. Further studies concerning the mechanism of formation of $B_9H_{12}S^-$ are in progress.

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Registry No. $(C_2H_5)_4N[B_9BrH_{11}S]$, 51292-99-0; $B_9BrH_{12}\cdot S(C_2H_5)_2$, 51292-00-6; $(C_2H_5)_4N[B_9H_{12}S]$, 51293-01-7; $CsB_9H_{12}S$, 51358-27-1; $(C_2H_5)_4N[B_9H_{12}]$, 51464-40-5; $(C_2H_5)_4N[BrB_9H_{11}]$, 51668-01-0; ^{11}B, 14798-13-1.

[30] The small doublet at +28 ppm is due to an impurity. This product could not be purified further due to its instability.

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Some By-Products of the Oxidative Coupling of Decahydrodecaborate(2−), $B_{10}H_{10}{}^{2-}$

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The involvement of ions other than the primary oxidizing agents in the oxidation of $B_{10}H_{10}{}^{2-}$ produces a variety of substituted species in addition to $B_{20}H_{19}{}^{3-}$ and $B_{20}H_{18}{}^{2-}$. $Fe(NO_3)_3$ yields $B_{20}H_{18}NO^{3-}$; $FeCl_3$ yields 1,6,8-$B_{10}H_7Cl_3{}^{2-}$ and 1,6- (or 2,4) -$B_{10}H_8Cl_2{}^{2-}$; $KClO_3$ yields $B_{10}H_4Cl_6{}^{2-}$ and a free radical. The effects of temperature, reagent concentration, solvent, acidity, and reaction time on the yields of the principal by-products were explored.

Introduction

Over the years, we and other researchers investigating the oxidative coupling of $B_{10}H_{10}{}^{2-}$ have observed extraneous bands in the infrared spectra of the expected products, blue and purple colors, and other evidence of side reactions. Wiesboeck[2] assumed that the blue color produced by $Fe(NO_3)_3$ is due to the same nitroso derivative as the one made with gaseous oxides of nitrogen. He did not isolate the colored material, and since the free radicals formed by $B_{10}H_{10}{}^{2-}$ absorb in the same region of the visible spectrum,[3] we decided to isolate and characterize the colored species in our reactions. In one system the colored species turned out to be the $B_{20}H_{18}NO^{3-}$ ion;[2,4] in another it was a free radical.[3] The extraneous infrared bands were found to belong to partially halogenated decahydrodecaborates. Since the published halogenation methods[5] are unsuitable for the synthesis of specific ions having fewer than eight chlorines, due to the very rapid substitution rate, it seemed worthwhile to explore conditions under which the yield of such chlorinated species is optimized. Moreover, as the molecular structure of one of our products ($B_{10}H_7Cl_3{}^{2-}$) had already been determined by X-ray crystallography,[6] it seemed only appropriate that the synthesis be published too.

Experimental Part

Reagents and Techniques. Salts of $B_{10}H_{10}{}^{2-}$ were prepared in this laboratory from decaborane;[7] all other chemicals were reagent grade. The infrared spectra of samples pressed into KBr pellets were recorded on a Perkin-Elmer Model 337 spectrophotometer. The visible spectra were recorded on a Cary 14 spectrophotometer. The ^{11}B nmr spectra were obtained at a frequency of 19.25 MHz on a Varian DA-60 spectrometer. Samples were considered free of $B_{20}H_{18}{}^{2-}$ when the uv spectrum showed no traces of the intense bands at 2320 and 2930 Å and free of $B_{20}H_{19}{}^{3-}$ in the absence of the hydrogen-bridge ir band at 1870 cm^{-1}.[8] Overall purity was also ascertained with the aid of tlc. For the halogenated species the best results were obtained on basic alumina with eluents consisting of acetonitrile–2-propanol–water (5:4:1) or acetonitrile–acetone (2:1).

$B_{20}H_{18}NO^{3-}$. Procedure A. To solutions of $(Et_3NH)_2B_{10}H_{10}$ in 15 ml of water weighed samples of $Fe(NO_3)_3\cdot 9H_2O$ (uncrushed lumps) were added *without stirring* and the mixtures were left standing at room temperature. Filtration removed a purple solid which was washed with four 25-ml aliquots of water and dried for 24 hr over P_2O_5. The dry solid was washed repeatedly with dry acetone until only the creamy $(Et_3NH)_3B_{20}H_{19}$ remained undissolved. The washings were evaporated to near dryness, and the residue was recrystallized from acetone–ethanol mixtures till no $B_{20}H_{18}{}^{2-}$ was detectable. The infrared and visible spectra of the products were indistinguishable from those of $(Et_3NH)_2B_{20}H_{18}NO$ made with NO_2.[2,4] When heated above 170° the salt turns colorless before it melts with decomposition. The melting point is a poor criterion of purity since even traces of impurities shift it by as much as 20°. Our purest samples ranged from 175 to 185°. The visible spectrum in CH_2Cl_2 consisted of bands at 6000 and 4000 Å.

Anal. Calcd for $[(C_2H_5)_3NH]_3B_{20}H_{18}NO$: C, 37.8; H, 11.6; B, 37.9; N, 9.81. Found: C, 37.2; H, 11.9; B, 37.6; N, 9.54.

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Procedure B. The crude purple solid, which had been dried over P_2O_5, was washed free of purple color with methanol. Saturated methanolic solution of Me_4NCl was slowly added to the filtered washings until the supernatant liquid was practically colorless, and the precipitate was washed with methanol and recrystallized from acetonitrile–methanol mixtures. Except for bands attributable to the cations the infrared spectrum of $(Me_4N)_3B_{20}H_{18}NO$ resembled that of the Et_3NH^+ salt. The yields are listed in Table I. The solid failed to melt below 250°.

Anal. Calcd for $[(CH_3)_4N]_3B_{20}H_{18}NO$: C, 29.6; H, 11.2; B, 44.4; N, 11.5; neut equiv 162. Found: C, 29.3; H, 10.8; B, 43.8; N, 10.7; neut equiv 166.

$B_{10}H_7Cl_3{}^{2-}$ and $B_{10}H_8Cl_2{}^{2-}$. To aqueous solutions containing $(Et_3NH)_2B_{10}H_{10}$ known amounts of $FeCl_3 \cdot 6H_2O$ were added and the volume was made up to 50 ml. Anhydrous $FeCl_3$ was used with alcohols and with concentrated HCl. The reaction mixture was stirred for a fixed length of time and filtered. In aqueous systems the solid component consisted of $(Et_3NH)_2B_{20}H_{18}$ and $(Et_3NH)_3B_{20}H_{19}$. The filtrate was treated with saturated solutions of Me_4NCl (aqueous or ethanolic, as appropriate) and the resulting precipitate was collected. That precipitates from reactions carried out for brief periods of time contained a certain amount of $B_{10}H_8Cl_2{}^{2-}$ (and possibly also $B_{10}H_9Cl^{2-}$) mixed with $B_{10}H_7Cl_3{}^{2-}$ was indicated by additional spots on the tlc plates, low Cl:B ratio in elemental analyses, and extra bands in the infrared spectra, which will be discussed later. Recrystallization from acetone–water mixtures eventually yields pure 1,6,8-$[Me_4N]_2B_{10}H_7Cl_3$, since the latter is less soluble in water than the corresponding salts of less substituted ions. The white product is negligibly soluble in cold water, acetone, ethanol, and methylene chloride; it is slightly more soluble in methanol and very soluble in acetonitrile. The material failed to melt below 300° and its ultraviolet spectrum contained no bands above 2200 Å. The yields and the infrared spectrum, which contained bands characteristic of chlorodecaborates,[5] will be discussed later. The ^{11}B nmr consisted of bands at δ 7.5 (s, 1), 28.7 (d, 1; $J = 145$ Hz), 36.2 (s, 2), and 40.8 ppm (d, 6; $J = 123$ Hz), all measured relative to trimethyl borate.

Anal. Calcd for $[(CH_3)_4N]_2B_{10}H_7Cl_3$: C, 25.9; H, 8.45; Cl, 28.8; B, 29.2. Found: C, 25.1; H, 8.40; Cl, 27.5; B, 28.7.

If the addition of Me_4NCl fails to precipitate halogenated species, as indicated by the absence of the characteristic infrared bands (Table III), the solution is treated with aqueous ammonia and filtered to remove the hydroxides of iron. Slow evaporation of the filtrate yields solid fractions which contain progressively larger amounts of the dichloride as indicated by elemental analyses, tlc, and infrared spectra. Though pure $B_{10}H_8Cl_2{}^{2-}$ was not isolated due to the small amount of material available for work, its tlc spot and infrared spectrum (Table III) were clearly recognizable and will be discussed in the next section.

$B_{10}H_4Cl_6{}^{2-}$. To a solution of $(Et_3NH)_2B_{10}H_{10}$ in hydrochloric or sulfuric acid an aqueous solution of $KClO_3$ was added and the volume made up to 100 ml. The reaction mixture was stirred for a fixed period of time and filtered, and the $(Et_3NH)_2B_{20}H_{18}$ isolated at this stage was recrystallized from hot water and weighed. The filtrate was reduced in volume to 50 ml by rotary evaporation and filtered again. The filtrate was tested for boric acid. The white precipitate was washed with ethanol and recrystallized from hot water after the ultraviolet spectra indicated that $B_{20}H_{18}{}^{2-}$ had been removed. The yields are listed in Table II. The solid failed to melt below 250°. It was soluble in acetone, methanol, and acetonitrile but insoluble in water and ethanol. The ^{11}B nmr spectrum consisted of a broad band with a maximum at 28.4 ppm. The ultraviolet spectrum exhibited a very weak band at 3080 Å.

Anal. Calcd for $[(C_2H_5)_3NH]_2B_{10}H_4Cl_6$: C, 27.2; H, 6.85; N, 5.29; B, 20.4; Cl, 40.2; neut equiv 265. Found: C, 27.8; H, 6.96; N, 5.32; B, 20.3; Cl, 39.5; neut equiv 265.

The Et_3NH^+ salt of the product was dissolved in methanol, the solution was treated with saturated methanolic Me_4NCl, and the resulting precipitate was recrystallized from hot water. It failed to melt below 300°, and its infrared spectrum showed little difference from that of the Et_3NH^+ salt except where the bands attributable to the cations are located. Repeated recrystallization from hot water failed to alter the infrared spectrum of the salt (Table III). The 3080-Å band disappeared from the spectrum of the solid but could be seen in the spectrum of the mother liquor.

Anal. Calcd for $[(CH_3)_4N]_2B_{10}H_4Cl_6 \cdot H_2O$: C, 19.6; H, 6.15; N, 5.70; B, 22.0; Cl, 43.3. Found: C, 19.8; H, 6.19; N, 5.60; B, 21.2; Cl, 42.7.

When the 50-ml filtrate remaining after the removal of $B_{10}H_4Cl_6{}^{2-}$ was allowed to sit at room temperature for 1 month, it turned yellow and a distinct odor of chlorine was noted. The small amount of solid which had accumulated during this time was collected and identified as $(Et_3NH)_2B_{10}Cl_{10}$ by its infrared and ^{11}B nmr spectra[5] and elemental analysis.

Table I. Yield of $B_{20}H_{18}NO^{3-}$

Time,[a] hr	mmol (per 15 ml of H_2O) of $B_{10}H_{10}{}^{2-}$	mmol (per 15 ml of H_2O) of $Fe(NO_3)_3 \cdot 9H_2O$	% converted to $B_{20}H_{18}NO^{3-}$
24	2	7.5	2–4
24	2	15.0	3–5
24	2	22.5	7
24	3	13.5	35
48	3	13.5	14–20
72	3	13.5	11–15
72	4	16.0	4–6

[a] In most instances the solid iron(III) nitrate dissolved over a period of 18–24 hr.

Anal. Calcd for $[(C_2H_5)_3NH]_2B_{10}Cl_{10}$: C, 21.6; H, 4.83; B, 16.2; Cl, 53.2. Found: C, 21.1; H, 4.92; B, 15.9; Cl, 52.6.

Free Radical. To a 50-mg sample of $K_2B_{10}H_{10}$ dissolved in 25 ml of 0.2 *M* $KClO_3$ 10 drops of concentrated H_2SO_4 was added and the solution was allowed to evaporate slowly under an exhaust hood. When the solution had evaporated to near dryness, the pasty cake at the bottom of the vessel became coated with a thin layer of a purple solid, which was washed off with ethyl ether. The visible spectrum of the ether solution consisted of a broad (half-width 3300 cm^{-1}) band with a maximum at 5400 Å. The presence of a free radical with a *g* factor of 2.018 was indicated by the postition of the single 22 G wide line in the esr spectrum of the purple solution. The purple ethereal extract was stirred with water, partially evaporated to remove the ether, and filtered. Addition of saturated aqueous Me_4NCl to the filtrate precipitated a solid the infrared spectrum of which contained bands characteristic of extensively chlorinated $B_{10}H_{10}{}^{2-}$ (see Table III). The appearance of the purple radical in the evaporating solution can be accelerated by heating the original mixture for about 1 hr at 80°. If left deposited on the $KClO_3$–K_2SO_4 cake, the free radical appears to be stable indefinitely. In one instance the purple color persisted for 1 year, and when it was washed off with ether, the resulting solution had visible and esr spectra indistinguishable from those obtained off fresh samples.

A word of caution is appropriate at this point. Although in over a dozen runs we have never had any problems, the mixture used for the free-radical synthesis is *potentially explosive*. Small quantities of reactants should be used and all appropriate safety precautions should be used until after the radical has been extracted.

Results and Discussion

The Yields. The effects of reagent ratio, concentration, and reaction time on the yield of $B_{20}H_{18}NO^{3-}$ are given in Table I. The highest yields are obtained when the borate concentration is high and the reaction time 24-48 hr. If the reaction is allowed to proceed too long after all the iron(III) nitrate has dissolved, most of the nitroso derivative will decompose. In several reactions where the solution was continuously stirred, the decomposition and competition from the simple coupling to $B_{20}H_{19}{}^{3-}$ and $B_{20}H_{18}{}^{2-}$ reduced the yield below 1%. Equally low yields were obtained in 96% ethanol and by using copper(II) nitrate instead of the iron salt. The strong odor of volatile boron hydrides and the effervescence observed in this reaction indicate some decomposition to boric acid. It takes very few polyhedral ions to provide all the electrons needed for the reduction of the nitrate ions.

The yields of $B_{10}H_7Cl_3{}^{2-}$ showed too little variability to be worth tabulating. The molarity of $B_{10}H_{10}{}^{2-}$ was varied from 0.03 to 0.12 and that of $FeCl_3$ from 0.07 to saturation. The molar ratios of the two reagents ranged from 1:1 to 1:20. In pure water at 25° the yields remained below 1% regardless of concentrations, except when saturated $FeCl_3$ was used. Anhydrous $FeCl_3$ in methanol and ethanol, at room temperature or at reflux, yields 1-2% of $B_{10}H_7Cl_3{}^{2-}$ after 2 days. Saturated $FeCl_3$ yields comparable amounts

Table II. Yields of $B_{20}H_{18}^{2-}$ and $B_{10}H_4Cl_6^{2-}$

		Molar concn			% conversion to		
Time	Temp, °C	$B_{10}H_{10}^{2-}$	ClO_3^-	H^+	$B_{20}H_{18}^{2-}$	$B_{10}H_4Cl_6^{2-}$	$B(OH)_3$
7 days	25	0.20	0.20	0.5	16	2	
7 days	25	0.20	0.50	0.5	20	5	
7 days	25	0.20	0.70	0.5	30	8	
2 min	80[a]	0.35	0.45	1.0	43		5
30 min	80[a]	0.35	0.90	1.0	96		4
30 min	80[a]	0.40	1.10	1.5[b]	77		9

[a] Steam bath. [b] H_2SO_4 instead of HCl.

Table III. Principal Infrared Bands in the 1300–400-cm^{-1} Region

$B_{10}H_{10}^{2-}$		1085 w	1030 s				
$B_{10}H_8Cl_2^{2-}$	1140 sh	1120 s	1025 m	870 m	795 s	720 m	
$B_{10}H_7Cl_3^{2-}$	1140 w	1120 m	1025 m	870 w	810 m	720 s	520 w
$B_{10}H_4Cl_6^{2-}$	1170 w	1140 m	1020 s	870 m	840 m	770 m	520 w
$B_{10}Cl_{10}^{2-}$	1190 w	1150 m	1010 s	870 m		790 w	520 m

in aqueous solutions at room temperature. After 1 week in concentrated HCl at 25° a 1:3 reagent ratio resulted in 3% conversion to $B_{10}H_7Cl_3^{2-}$. The yield was 5% after 2 weeks. The presence of NaCl (up to 3 *M*) had no detectable effect on the yield. Since high hydrogen ion concentration is more important than chloride concentration, a protonated species such as $B_{10}H_{11}^-$ might be a key intermediate. Such an intermediate has been postulated in the nucleophilic halogenation of polyhedral boranes.[5]

Crude reaction mixtures contain variable amounts of $B_{10}H_8Cl_2^{2-}$ and traces of $B_{10}H_9Cl^{2-}$. The tlc shows no evidence of other isomers or ions having more than three chlorines. In 2 day old reaction mixtures the ratio of $B_{10}H_7Cl_3^{2-}$ to $B_{10}H_8Cl_2^{2-}$ was estimated at 3:1. Longer reaction times raised this ratio, while shorter times made the yields of both products too low for isolation and adequate purification. Attempts were made to isolate pure $B_{10}H_8Cl_2^{2-}$ by fractional crystallization from acetone–water mixtures, since increasing the degree of halogenation decreases solubility in water and increases solubility in acetone. We were not successful as the neutralization equivalents and elemental analyses of the best fractions indicated a trichloride:dichloride ratio no lower than 1:4. In addition to elemental analyses infrared spectra (Table III) and tlc were also used to monitor the progress of crystallization. Under our chromatographic conditions the R_f values increase with increasing degree of halogenation, from $B_{10}H_{10}^{2-}$ to $B_{10}H_7Cl_3^{2-}$.

The relative yields of $B_{20}H_{18}^{2-}$ and $B_{10}H_4Cl_6^{2-}$ obtained in the chlorate oxidation are given in Table II. The yield of free-radical species was low, but the solutions were free of paramagnetic transition metal ions which is an advantage over the previously published reactions.[3] At room temperature the yields of both increase with increasing chlorate:hydroborate ratio, though that of $B_{10}H_4Cl_6^{2-}$ increases more. The effects of temperature are additional evidence for the high activation energy of the coupling process. The yield of $B_{20}H_{18}^{2-}$ after 30 min at 80° is superior to the yields from most other published syntheses of the ion.[8] The missing 4% can be accounted for by decomposition to boric acid. No evolution of hydrogen or volatile hydrides was observed in reactions carried out at room temperature.

Infrared spectra. Only the "fingerprint" region below 1300 cm^{-1} is included in the Table III since that is where the effects of chlorination are most visible. The tabulated frequencies are for the Me_4N^+ salts, and the characteristic cation band at 950 cm^{-1} provides an excellent reference point for both the wave numbers and the relative intensities of the anionic bands. The four chlorinated ions exhibit at least six bands. As the degree of halogenation increases, one band fails to shift, one shifts to lower frequencies, and four shift to higher frequencies. The spectrum of $B_{10}H_4Cl_6^{2-}$ has additional weak bands at 745 and 685 cm^{-1}. Most of the intense bands in the spectra of the other ions have shoulders. An extensive study of a large number of ions of the general type $B_{10}H_{10-n}Cl_n^{2-}$, where $n = 4$–9, has revealed[9] that the relative intensities and positions of these bands are very sensitive not only to the degree of halogenation but also to differences in the isomeric structures.

Though pure $B_{10}H_8Cl_2^{2-}$ was not isolated, examination of spectra of mixtures in which the dichloride:trichloride ratio ranged from 4:1 to 0 (single crystals) enabled us to identify the principal bands and deduce their relative intensities. Thus the 795 and 810 cm^{-1} bands were clearly resolved in all our mixtures, and since they appeared equally intense in a 1:4 mixture, it was obvious that the former is naturally more intense than the latter. The presence of a shoulder 50 cm^{-1} to the left of the principal B-H stretching band (*ca.* 2500 cm^{-1}) observed in the spectra of the three partially halogenated ions suggests that at least one apex remains unsubstituted in all of them. This has been confirmed in the $B_{10}H_7Cl_3^{2-}$ case by X-ray crystallography, which assigned the 1,6,8 positions to the chlorines.[6] Since the $B_{10}H_8Cl_2^{2-}$ is an intermediate in the formation of the trichloride it has to have the 1,6 or the 2,4 structure. We were unable to decide between the two. It should be pointed out that the spectra of $B_{20}H_{18}^{4-}$, $B_{20}H_{18}^{2-}$, and $B_{20}H_{19}^{3-}$ are fortunately quite free of major bands in the 1300-1000-cm^{-1} region[8] and have large open gaps below 900 cm^{-1} which facilitates the detection of halogenated species in the presence of simple coupled ions.

^{11}B Nmr Spectra. The spectrum of $B_{20}H_{18}NO^{3-}$ has already been published.[2,10] The assignment of the nmr bands of $B_{10}H_7Cl_3^{2-}$ presents no problems since the structure of the ion is known.[6] The singlet at 7.5 and the doublet at 28.7 ppm can be assigned to the halogenated and unhalogenated apices, respectively. The singlet at 36.2 ppm must belong to the two symmetrically equivalent borons at positions 6 and 8. Bands belonging to the other nonapical borons are not resolved and show up as one big doublet at 40.8 ppm. The assignments are also supported by a comparison of the observed coupling constants, 145 and 123 Hz, with those of $B_{10}H_{10}^{2-}$, in which the corresponding borons have values of 140 and 125 Hz.[10,11]

It is interesting to compare the effects of halogenation on the halogenated and the remaining protonated apical and

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(11) E. L. Muetterties, J. H. Balthis, Y. T. Chia, W. H. Knoth, and H. C. Miller, *Inorg. Chem.*, 3, 444 (1964).

nonapical borons. In $B_{10}H_{10}^{2-}$ the two borons appear at 23 and 53 ppm, respectively,[10,11] whereas in $B_{10}Cl_{10}^{2-}$ they appear at 23.4 and 28.7 ppm.[5] It is thus surprising that in 1,6,8-$B_{10}H_7Cl_3^{2-}$ the halogenated apex is shifted that far downfield while the other apex moves up. An examination of the ^{11}B nmr spectra of several ions containing four, five, six, seven, and eight chlorines[9] showed that subsequent halogenation of the nonapical borons shifts the apical boron upfield until it ends up where it is seen in the perchloro ion. Halogenation shifts all nonapical borons downfield; consequently in both $B_{10}H_7Cl_3^{2-}$ and $B_{10}H_4Cl_6^{2-}$ (28.4 ppm) they appear at positions intermediate between $B_{10}H_{10}^{2-}$ and $B_{10}Cl_{10}^{2-}$. The shift is greater for the chlorinated boron. While we may attribute the downfield shifts to the "inductive electron withdrawal" by the chlorines, we have no ready explanation for the reverse trend exhibited by some of the apical borons.

General Observations. If the compounds discussed in this paper are regarded as undesirable side products, the conditions which suppress them are clearly indicated. However, we were also interested in conditions which would make these reactions into useful synthetic methods. Though our best yield of the nitroso derivative was below the best value reported by Wiesboeck,[2] the reaction with $Fe(NO_3)_3$ is so sensitive to conditions that we have no doubt the yield can be raised considerably by further modifying the reaction conditions within the optimum reaction times. In addition to the general advantages of not having to work with gaseous reactants, our reaction shows no evidence of producing any of the explosive red intermediate reported in the reaction where NO_2 was used.[2] However, increasing the yield of the chlorinated species may prove to be more difficult, since the coupling rate is much greater than the rate of halogenation.

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Registry No. $(Et_3NH)_2B_{10}H_{10}$, 12430-35-2; $Fe(NO_3)_3$, 10421-48-4; $(Et_3NH)_3B_{20}H_{18}NO$, 12551-45-0; $(Me_4N)_3B_{20}H_{18}NO$, 51668-02-1; $FeCl_3$, 7705-08-0; 1,6,8-$[Me_4N]_2B_{10}H_7Cl_3$, 36569-15-0; $(Me_4N)_2B_{10}H_8Cl_2$, 51668-03-2; $KClO_3$, 3811-04-9; $(Et_3NH)_2B_{10}H_4Cl_6$, 51668-04-3; $(Me_4N)_2B_{10}H_4Cl_6$, 51745-61-0; $(Et_3NH)_2B_{10}Cl_{10}$, 51668-05-4; $(Me_4N)_2B_{10}Cl_{10}$, 51668-06-5; $K_2B_{10}H_{10}$, 12447-89-1; ^{11}B, 14798-13-1.

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Synthesis and Mechanism of Hydrolysis of Amine-Cyanoboranes[1]

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Hydrolysis of cyanoborane adducts of morpholine and dimethylamine are described by the expression rate = $k[R_2NH{\cdot}BH_2CN][OH^-]$ over the range pH 6–12.5. At constant pH (12.4), k is insensitive to an 18-fold change in total buffer concentration suggesting specific lyate ion catalysis. For a given concentration of lyate ion, rates are 60–70% slower in water than in deuterium oxide and exchange of the nitrogen-bonded proton with solvent is rapid compared to the rate of hydrolysis. The addition of H_2O_2 to the alkaline hydrolysate significantly retards the rate. Cyanoborane adducts of trimethylamine and *N*-methylmorpholine react very slowly and at rates independent of alkali up to 0.9 *M* OH^-. The proposed mechanism for hydrolysis of the secondary amine adducts involves the removal by OH^- of the nitrogen-bonded proton in a rapid preequilibrium followed by the rate-determining decomposition, probably *via* a dissociative pathway, of substrate conjugate base analogous to the accepted mechanism for base hydrolysis of amminecobalt(III) complexes. The presence of a nitrogen-bonded proton also seems to be important in influencing the mechanism of halogenation of such cyanoboranes. Synthesis of secondary amine–cyanoboranes *via* the reaction of BH_3CN^- with the corresponding amine salt is accompanied by scrambling of the hydrogen between nitrogen and boron.

Introduction

The cyanotrihydroborate anion BH_3CN^-, first prepared by Wittig[2] in 1951 as the lithium salt, has drawn attention in recent years as a useful reducing agent[3-5] and has been the subject of investigations of hydrogen exchange and hydrolysis,[6] of rearrangement to the isocyanotrihydroborate isomer,[7] and of the spectra, structure, and bonding in substituted borane adducts[5] and metal cyanotrihydroborate complexes.[8-10] Such studies have been aided by the greater accessibility of this ion through its preparation as the sodium salt,[7] a factor which has also facilitated development of its derivative chemistry. Thus, recent work of Spielvogel and coworkers has been concerned with the structure of species obtained on acidification of solutions of BH_3CN^- in tetrahydrofuran,[11] and the utilization of such solutions for the synthesis of new nitrogen base donor–cyanoborane addition compounds has been noted.[11,12]

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