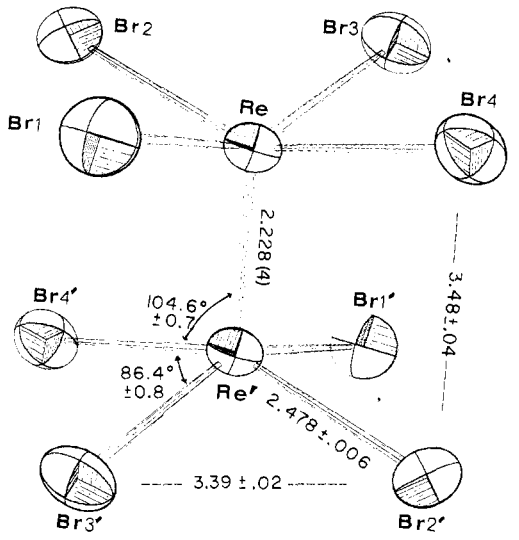

Figure 1.—The $Re_2Br_8^{2-}$ ion showing the atom numbering scheme and mean dimensions. Intervals indicated with ± are root-mean-square deviations from the mean and exceed the standard deviations of individual values used to compute the mean. Primed atoms are related by the center of symmetry to unprimed atoms with the same number.

mensions and the atom numbering scheme. The individual dimensions are given in Table IV. The $Re_2Br_8^{2-}$ ion lies at a crystallographic center of symmetry. Its dimensions are such, however, that it is more chemically meaningful to think of it as having virtual D_{4h} symmetry. The eclipsed configuration and short Re–Re distance are diagnostic[2] of the quadruple Re–Re bond.

The Re–Re bond length, 2.228 (4) Å, is near the middle of the range, roughly 2.22–2.25 Å, covered by other Re–Re quadruple bonds. This is significant since it shows that the quadruple bond distance is relatively constant, 2.235 ± 0.015 Å, provided general stereochemistry remains essentially the same. The increase to 2.29 Å in the case of $Re_2Cl_5(CH_3SCH_2CH_2SCH_3)_2$ becomes meaningful and supports the view that the latter compound contains only a triple bond.[15]

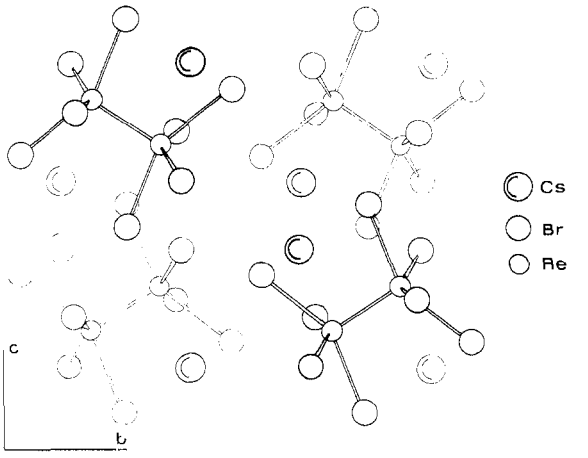

Figure 2.—The $Cs_2Re_2Br_8$ structure projected down *a*.

The crystal packing, shown in Figure 2, is not particularly remarkable. Each $Re_2Br_8^{2-}$ ion is surrounded by four Cs^+ ions, each in approximately symmetrical contact with one of the vertical faces of the right square parallelepiped which it forms. Each Cs^+ ion is surrounded by 11 bromine atoms, four from each of two anions, two from a basal edge of another, and one corner of a fourth. This array of bromine atoms does not approximate to any particular symmetric polyhedron. Eight of the Cs–Br distances are in the range 3.63–3.80 Å, while the other three are appreciably longer, *viz.*, 3.90, 4.11, and 4.17 Å.

(15) M. J. Bennett, F. A. Cotton, and R. A. Walton, *Proc. Roy. Soc., Ser. A*, **303**, 175 (1968).

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Synthesis of Sodium Cyanotrihydroborate and Sodium Isocyanotrihydroborate

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A convenient synthetic procedure for sodium cyanotrihydroborate ($NaBH_3CN$) is reported. Sodium isocyanotrihydroborate has also been isolated in mixtures with the normal salt and characterized. The isomerization of $NaBH_3NC$ to $NaBH_3CN$ has been investigated and is found to be H^+ and CN^- catalyzed. Boron nmr data are reported for BH_3CN^-, BH_3NC^-, and $BH_3CNBH_3^-$. The infrared spectra of $NaBH_3NC$, $NaBD_3NC$, and $NaBH_3CNBH_3$ have been recorded and the fundamental vibrations assigned and compared with those reported earlier for $NaBH_3CN$ and $NaBD_3CN$.

Introduction

Wittig and Raff reported the first synthesis of a cyanotrihydroborate in 1951.[2] They prepared the lithium salt by allowing lithium borohydride to react with excess HCN in diethyl ether at 100° under pressure. These authors noted the unusual hydrolytic stability of the product toward acids. Thereafter, only one brief publication appeared on the reducing power of $LiBH_3CN$, and that report indicates limited applicability.[3]

(1) (a) PRF Graduate Fellowship 1969–1970; abstracted in part from the Ph.D. thesis of J. R. Berschied, Kansas State University, 1970. (b) To whom inquiries should be addressed. (c) Kansas State University. (d) Ventron Corp.

(2) G. Wittig and P. Raff, *Z. Naturforsch. B*, **6**, 225 (1951).

(3) G. Drefahl and E. Keil, *J. Prakt. Chem.*, **6**, 80 (1958).

Recent, renewed interest in this compound indicates broader utility in reduction of aldehydes and ketones, and in a simplified reductive amination of these same classes of organic compounds.[4] Convenient and facile isotope exchange of the hydrogens at low pH has also been noted.[5a] Preliminary observations on the redox properties of BH_3CN^- have been reported.[5b]

The relative commercial inaccessibility of $LiBH_3CN$, an inconvenient literature synthesis, and the economic disadvantage inherent to lithium compounds led us to prepare the corresponding sodium salt. We wish to report the synthesis of sodium cyanotrihydroborate in good yield and purity by a much more convenient method. In addition, synthetic conditions are reported under which the iso compound BH_3NC^- may be prepared. The normal and iso compounds have been characterized by their infrared and nmr spectra and these are compared with those of the diborane adduct, $BH_3CNBH_3^-$. The isomerization of $NaBH_3NC$ to $NaBH_3CN$ is also discussed in terms of possible mechanisms.

Experimental Section

Synthesis of $NaBH_3CN$ and $NaBH_3NC$.[6]—A clean, dry, 2-l., three-neck, round-bottom flask was equipped with a pressure-equalized dropping funnel, air-driven mechanical stirrer, and reflux condenser. The condenser outlet was connected to a scrubber flask containing 1 *N* caustic solution, to remove entrained HCN vapors, and then to a gas meter, which measured the quantity of hydrogen evolved. The hydrogen was vented to a fume hood.

To the flask was added 1000 ml of THF (predried over CaH_2 and filtered before use) and 80.2 g (2.09 mol) of 98.5% $NaBH_4$. The flask was then purged with dry N_2. A 16.7 wt % solution of HCN in THF[7] (294 g containing 58.8 g or 2.33 mol of 98% HCN) was placed in the dropping funnel. The system was repurged briefly. The HCN solution was added slowly to the rapidly stirred slurry of $NaBH_4$ at room temperature. Evolution of H_2 occurred slowly as soon as addition was begun. The flask was maintained at about 25° with a water bath, since the reaction is slightly exothermic. The mixture was poststirred for 1 hr and then gradually heated to reflux until H_2 evolution had ceased.

When cooled to room temperature, the reaction mixture was purged with N_2 and briefly evacuated. The small amount of undissolved solids was removed by filtration using a filter aid such as Celite. The clear, faintly yellow filtrate was dried on a rotary vacuum evaporator. Approximately half of the solvent was removed before heat was applied; drying was finished at 60° under vacuum. White solid $NaBH_3CN$ (120 g) was recovered, representing 91% yield. *Anal.* Calcd for $NaBH_3CN$: B, 17.21; H, 4.81; CN, 41.40. Found: B, 17.00; H^-, 4.75; CN, 37.52. The good B and H and yet low CN analyses are explained by $B(OH)_3$ impurity which may be removed.[5b] Recrystallization of the impure product can be carried out as described previously[5b] or by dissolving the crude product in THF (20% w/v), filtering the solution, and adding to it a fourfold excess of CH_2Cl_2. After two recrystallizations the $NaBH_3CN$ gave the following analysis: B, 17.17; H^-, 4.81; CN, 40.74 for a 1.0:3.0:0.99 atom ratio.

In other preparations, the reaction mixture was never taken above room temperature. Subsequent examination showed that these unrefluxed solutions contained two anionic species. The normal cyanotrihydroborate predominated but a second isomeric form was also present. We have designated the latter as sodium isocyanotrihydroborate. The isomer mixture is isolated by vacuum stripping the THF at room temperature.

Solubility of $NaBH_3CN$.[6]—Solubilities of $NaBH_3CN$ in water and THF were determined by sampling equilibrated solutions containing excess solute, which were maintained in a constant temperature bath at the temperatures indicated in Table I.

TABLE I
$NaBH_3CN$ SOLUBILITY

Solvent	Temp, °C	*S*, g/100 g of solvent
THF	28	37.2
	46	41.0
	62	42.2
Water	29	212
	52	181
	88	121
Diglyme	25	17.6
Methanol	25	Very soluble
Ethanol	25	Slightly soluble
Isopropylamine	25	Slightly soluble
Diethyl ether	25	Insoluble
Benzene	25	Insoluble
Hexane	25	Insoluble

Samples of the clear saturated solutions were withdrawn through a coarse-porosity filter stick and weighed, and the weight of solute was determined after the solvent had been vacuum evaporated to dryness.

Isomerization of $NaBH_3NC$.[8]—In these experiments a standard taper three-neck round-bottom flask fitted with a condenser connected to a drying tube, a thermometer, and rubber septum was used. Samples were withdrawn through the septum at 30-min intervals by means of a syringe and the infrared spectrum was recorded. The intensity of the cyanide bands was monitored as they are relatively sharp and isolated. A stock solution of the low-temperature product (~2 *M*) in THF, which contained no excess HCN, was used throughout.

Hydrolysis of $NaBH_3NC$.[8]—The hydrolysis of $NaBH_3NC$ in distilled water and acidic solution was studied in the same manner as previously reported for KBH_3CN.[5b]

Synthesis of $NaBH_3CNBH_3$.[8]—The synthesis is similar to the original method.[9] Fisher Certified NaCN (3.5 g) was vacuum dried at 60° for 36 hr. The dried NaCN was then added to 25 ml of THF (dried over Na). To the stirred slurry of NaCN in THF, 200 ml of 1 *M* BH_3·THF (Ventron Corp.) was added. The reaction flask was maintained at 25° with a water bath. After all the BH_3·THF was added, the reaction mixture was stirred for 5 hr, during which time the NaCN dissolved. The solution was then filtered to remove suspended particles and the solvent removed with a Roto-vac at 50°. A white hygroscopic solid was isolated which was identified as $NaBH_3CNBH_3$ by its infrared spectrum and ^{11}B nmr spectrum.[9] The presence of a small amount of H_3BO_3 in the isolated product is indicated by the infrared spectrum of the product. This impurity is difficult to remove.

Spectroscopic Measurements.[8]—Infrared spectra were recorded on Perkin-Elmer No. 457 and 421 spectrophotometers and ^{11}B nmr were obtained on a Varian HA-100 spectrometer.

Results

$NaBH_4$ and HCN react according to eq 1 in a suitable solvent at ambient temperature and pressure. Monoglyme, diglyme, dimethylformamide, and tetrahydro-

(4) R. F. Borch and H. D. Durst, *J. Amer. Chem. Soc.*, **91**, 3996 (1969).
(5) (a) M. M. Kreevoy and J. E. C. Hutchins, *ibid.*, **91**, 4329 (1969); (b) J. R. Berschied, Jr., and K. F. Purcell, *Inorg. Chem.*, **9**, 624 (1970).
(6) Ventron Corp., Metal Chemicals Division.
(7) Samples of HCN solutions in various solvents were kindly provided by Hampshire Chemical Co.
(8) Kansas State University.
(9) (a) H. L. Jackson and H. C. Miller, U. S. Patent 2,992,885 (1961); (b) V. D. Aftandilian, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **83**, 2471 (1961).

furan (THF)[10] have been found satisfactory as solvents. The crystalline product is isolated by vacuum evaporation of the solvent. Solvent-free $NaBH_3CN$ is a white

$$NaBH_4 + HCN \longrightarrow NaBH_3CN + H_2 \quad (1)$$

crystalline solid which is very hygroscopic. Its density has been measured pycnometrically[11] as 1.199 ± 0.005 g/ml at 28°. It is soluble in water, alcohols, amines, glymes, and THF, but is insoluble in diethyl ether, benzene, and hexane (see Table I).

A THF solution of pure $NaBH_3CN$ exhibits one well resolved quartet in the ^{11}B nmr spectrum. The quartet is centered at +62.2 ppm with respect to external $B(OCH_3)_3$ and the B–H coupling constant is found to be 90 Hz, which agrees with J_{BH} obtained[5b] from the ^1H nmr spectrum of BH_3CN^-. In contrast, the unrefluxed THF reaction mixture shows two quartets of approximate relative intensities 3:1. The strong quartet, centered at +62.5 ppm relative to $B(OCH_3)_3$, is sharp and well defined and is assigned to BH_3CN^-. The other, centered at +45.5 ppm with respect to $B(OCH_3)_3$, is considerably more diffuse, probably due either to N quadrupolar broadening or B–N spin–spin coupling, and is assigned to BH_3NC^-. The ^{11}B–H coupling constants are found to be 91 and 94 Hz, respectively.

Table II lists the infrared fundamentals for BH_3CN^-, BD_3CN^-, $BH_3CNBH_3^-$, and the solid product isolated from the unrefluxed THF solution. From the spectra of the unrefluxed product we see that it consists of a mixture of BH_3CN^- and another species, which we have shown to be $NaBH_3NC$. The ratio of BH_3CN^-:BH_3NC^- in the unrefluxed product was estimated, by comparison of the relative intensities of the two CN bands, to be approximately 4:1. The band assignments for $NaBH_3NC$ are made in the same manner as previously reported for $NaBH_3CN$.[5b] A partial spectrum of $NaBH_3CNBH_3$ has been reported;[9] we have recorded the spectrum independently and here report tentative assignments for all of the fundamental vibrations.

An aliquot of the THF isomer mixture solution containing no HCN was refluxed for 4 hr at 60° after which the infrared spectrum showed no change and the addition of aqueous acid produced vigorous H_2 gas evolution. The infrared spectrum of a second aliquot which had been refluxed for 10 hr in the presence of 0.2 *M* glacial acetic acid indicated that the intensity of ν_{NC} (refers to the CN band of BH_3NC^-) had decreased to 5–10% of its initial value and a corresponding increase in ν_{CN} (refers to the CN band of BH_3CN^-) was observed. Addition of aqueous acid caused only a small amount of gas evolution. Finally, a third portion of the stock solution was refluxed in the presence of 0.04 *M* hydrogen cyanide. After 2 hr the infrared spectrum showed no ν_{NC} absorption and a large increase in intensity of ν_{CN}. Addition of aqueous acid gave no gas evolution. A sample of the solid isomer mixture was heated to 200° under vacuum for 36 hr and no change in the infrared spectrum was observed.

(10) Although $NaBH_4$ is practically insoluble in THF, the solubility of the cyanotribydroborate product provides the driving force for the desired reaction to occur. In fact, THF is preferred because of its volatility and the fact that an unsolvated product can be obtained.

(11) A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. 1, interscience, New York, N. Y., 1949, pp 288–290.

Discussion

Chemical evidence for the existence of BH_3NC^- follows from the observation that addition of distilled water to a THF solution of the $NaBH_4$–HCN reaction product obtained at room temperature caused immediate evolution of approximately one-fourth of the total hydrogen available. If a sample of the solid product is added to distilled water this amount of H_2 is also evolved. This contrasts with the reported[5b] behavior of $NaBH_3CN$, which is essentially stable to H_2O at pH 7 or greater. Infrared and nmr evidence confirms that the $NaBH_3NC$ undergoes decomposition according to

$$3H_2O + NaBH_3NC \longrightarrow H_3BO_3 + NaCN + 3H_2 \quad (2)$$

These experiments reveal a dramatic difference in the aqueous stabilities of BH_3CN^- and BH_3NC^-. Kreevoy[5a] has proposed a mechanism for the H^+-catalyzed decomposition of BH_3CN^- in acidic solutions, pH 1–2. He concluded that proton attack of the BH_3 group forms some sort of five-coordinate boron intermediate which then decomposes by loss of H_2. If this mechanism were the principal path for both BH_3CN^- and BH_3NC^-, very similar rates of aqueous decomposition should be found for the cyanide and isocyanide. Therefore, it seems necessary to conclude that the mechanisms for $NaBH_3CN$ and $NaBH_3NC$ aqueous decompositions are different. The most obvious possibility is that protonation or solvation of BH_3NC^- leads to BH_3NCH which rapidly decomposes to HCN and other products. Protonation is known to occur[5b] with the weaker base BH_3CN^-, but BH_3CNH is relatively stable.

To substantiate further the existence of both BH_3CN^- and BH_3NC^- in the unrefluxed solution, the ^{11}B nmr spectrum of the diborane adduct of CN^- ($NaBH_3CNBH_3$) was obtained. $NaBH_3CNBH_3$ was first prepared by Muetterties,[9] who also recorded the ^{11}B nmr spectrum; however, he did not report coupling constant or chemical shift data. We find the ^{11}B spectrum to consist of two quartets, one well defined and one broadened, in agreement with the previous work,[9] and the quartets are centered at 62.3 and 41.8 ppm upfield from external $B(OCH_3)_3$, respectively. The coupling constant is 94 Hz for both quartets. It is interesting to note that the integrated intensities of the two quartets are 3:2 (BC:BN). The disagreement between this intensity ratio and the ratio of nonequivalent boron atoms (1:1) is probably a result of different relaxation times for the two boron atoms in each molecule. This is of importance in that the 1:3 ratio of quartets from the unrefluxed THF solutions cannot be taken to indicate that ratio of BH_3NC^- to BH_3CN^-. The ratio of BH_3CN^-:BH_3NC^-, as deduced from the infrared and aqueous decomposition experiments is 4:1. These data do not firmly show that the unrefluxed THF solution does indeed contain both BH_3CN^- and BH_3NC^-. To confirm that the two species in the unrefluxed solution are not BH_3CN^- and $BH_3CNBH_3^-$ but

TABLE II[a]

BH_3CN^- [b]	BH_3CN^-; BH_3NC^-	$BH_3CNBH_3^-$	Assignment
2240	2240; 2290	2270, 2225	$\nu^{a_1}_{BH}$
2180	2180; 2070	2260	$\nu^{a_1}_{CN}$
1127	1127; 1105	1130, 1100	$\delta^{a_1}_{BH}$
890	890; 760	925, 745	$\nu^{a_1}_{BC,BN}$
2320	2320; 2350	2340, 2370	ν^{e}_{BH}
1195	1195; 1175	1205, 1185	δ^{e}_{BH}
870	870; 645	865, 635	ρ^{e}_{BH}
360	360; 330	365, 340	$\delta^{e}_{BCN,BNC}$
Not present	Not present	Not active	$\tau^{a_2}_{BH_3}$
BD_3CN^- [b]	BD_3CN^-; BD_3NC^-		
2180	2180; 2075		$\nu^{a_1}_{CN}$
1661	1661; 1640		$\nu^{a_1}_{BD}$
920	920; 940		$\delta^{a_1}_{BD}$
800	800; 665		$\nu^{a_1}_{BC,BN}$
1761	1761; 1745		ν^{e}_{BD}
875	875; 855		δ^{e}_{BD}
675	675; 525		ρ^{e}_{BD}
330	330; 300		$\delta^{e}_{BCN,BNC}$

[a] Frequencies in cm^{-1}; abbreviations: ν, stretch; δ, bend; ρ, rock; τ, torsion. [b] Reference 5b.

a mixture of the cyanide and isocyanide, we need only compare the infrared bands of Table II.

The infrared spectrum, Table II, of the low-temperature reaction product conclusively substantiates the existence of $NaBH_3NC$ in several ways. Most convincing are the bands at 2070 cm^{-1}, characteristic of nitrogen-coordinated cyanide,[12a] and at 760 cm^{-1}, which is in the region expected for a B–N stretching vibration,[12b] and neither of these bands is found in the $BH_3CNBH_3^-$ spectrum. The absorption bands in $BH_3CNBH_3^-$ correspond very closely to the assignments in BH_3CN^- and BH_3NC^- with two exceptions—the single band at 2260 cm^{-1} assigned to ν_{CN} and the two bands at 925 and 745 cm^{-1} assigned to ν_{BC} and ν_{NB}. The strong, sharp band at 2260 cm^{-1} is characteristic of bridging cyanide. The absence of this band in the unrefluxed product is very good evidence that the product is not a BH_3CN^- and $BH_3CNBH_3^-$ mixture. The high- and low-energy shifts of ν_{BC} and ν_{BN}, respectively, are interesting and will be discussed in a paper on the normal-coordinate analyses of the ions.

The existence of isomeric forms of cyanotrihydroborate can be explained in terms of the sequence

$$HCN \longrightarrow H^+ + CN^- \quad (3)$$

$$H^+ + BH_4^- + THF \longrightarrow THF\cdot BH_3 + H_2 \quad (4)$$

$$CN^- + THF\cdot BH_3 \longrightarrow THF + (NCBH_3^- + CNBH_3^-) \quad (5)$$

Dissociation of the weak acid HCN could be followed by protonation of borohydride in the presence of the coordinating solvent to liberate hydrogen and form $THF\cdot BH_3$,[13] which is known to exist in THF solution[14] and to be stable under these conditions. Replacement of THF by the stronger Lewis base, CN^-, as in eq 5, could follow with donation through the carbon or nitrogen lone pair to form either BH_3CN^- or BH_3NC^-.

(12) (a) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **39**, 712 (1963); (b) K. Niedenzu, "Boron-Nitrogen Chemistry," American Chemical Society, Washington, D. C., 1964, Chapter 6.

(13) A. D. Norman and W. L. Jolly, *Inorg. Syn.*, **11**, 15 (1968).

(14) (a) J. R. Elliott, *et al.*, *J. Amer. Chem. Soc.*, **74**, 5211 (1952); (b) H. E. Wirth, F. E. Massoth, and D. X. Gilbert, *J. Phys. Chem.*, **62**, 870 (1958).

One reasonable mechanism to explain the 4:1 ratio of cyanide to isocyanide assumes SN2 attack by CN^- on $THF\cdot BH_3$ with the activation energy for $THF\cdots BH_3\cdots CN^-$ somewhat less than that for $THF\cdots BH_3\cdots NC^-$. This is in keeping with the fact that the carbon lone pair is more easily involved in bond formation than is the nitrogen lone pair.[15] Such a scheme is also supported by the isomerization studies discussed below.

The results of the isomerization experiments can be summarized as follows. Isomerization of BH_3NC^- will not take place in 24 hr at 60° in THF solutions (about 2 *M* in cyanoborohydride species) in the absence of acids. (This statement is qualified to the extent that small amounts of H_3BO_3 were present as an impurity in our experiments; however, H_3BO_3 does not catalyze isomerization.) Addition of acetic acid (final concentration, 0.2 *M*) induces slow isomerization (~10 hr) with no H_2 evolution or formation of other CN species. Addition of hydrocyanic acid (final concentration, 0.04 *M*) induces complete isomerization in about 2 hr. Cyanide ion alone (slurry of NaCN) does not cause isomerization. Thus it appears that the isomerization reaction

$$BH_3NC^- \xrightarrow[THF]{HCN} BH_3CN^- \quad (6)$$

is acid catalyzed and further accelerated by the presence of CN^-. An isomerization scheme, compatible with that given for the BH_4^-–HCN reaction and similar to that for aqueous decomposition, *cf.* (2), is

$$BH_3NC^- + H^+\cdot THF + BH_3CN^- \longrightarrow HCN + BH_3CNBH_3^- + THF \quad (7)$$

$$HCN \longrightarrow H^+\cdot THF + CN^- \quad (8)$$

$$CN^- + BH_3CNBH_3^- \longrightarrow 2BH_3CN^- \quad (9)$$

Hydrogen ion attacks the isocyanide which then dissociates to form HCN and $BH_3CNBH_3^-$; the latter arises from the presence of *ca.* ~1.6 *M* BH_3CN^- in the isomer mixture. Experiments in this laboratory have shown that BH_3CN^- rapidly forms $BH_3CNBH_3^-$ in THF solutions of $BH_3\cdot THF$; therefore formation of the diborane adduct is preferred over $BH_3\cdot THF$; *cf.* (4). In addition, we have observed that, in THF, $BH_3CNBH_3^-$ will react with excess CN^- to form BH_3CN^-; *cf.* (9). It is not known at this time whether (9) should be considered an SN1 or SN2 reaction.

This sequence explains both the H^+ and CN^- dependence we observed. While it is known that hydrogen ion will protonate BH_3CN^- in water, and presumably in THF, HCN dissociation of BH_3CNH is not significant in anhydrous THF. More detailed studies using soluble CN^- salts are planned to establish quantitatively the conditions and mechanisms for this reaction and that by which $BH_3CNBH_3^-$ is prepared.[16]

(15) K. F. Purcell, *J. Amer. Chem. Soc.*, **89**, 6139 (1967).

(16) NOTE ADDED IN PROOF.—Further study of the $NaCN–BH_3\cdot THF$ reaction has revealed that unless either a considerable excess of $BH_3\cdot THF$ is used or longer (>5 hr) reaction times are allowed, significant amounts of BH_3CN^- and BH_3NC^- will be isolated with $BH_3CNBH_3^-$. The presence of these adducts in the product can be readily verified by ^{11}B and infrared spectra of the THF reaction solutions or by infrared spectra of the solid products as isolated.

Acknowledgment.—The authors wish to express their gratitude to Professor Emily Dudek of Brandeis University, who initially determined and interpreted the ^{11}B nmr spectra of BH_3CN^- and BH_3NC^-. Subsequent nmr work was performed by J. R. B. We wish to thank Professor R. L. Middaugh, of Kansas University, for help with the nmr spectra. K. F. P. and J. R. B. also thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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Boron–Nitrogen Compounds. XXXIV.[1a] Preparation and Some Properties of 2-Halo-1,3,2-diazaboracycloalkanes

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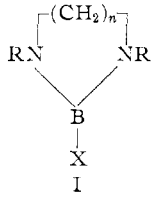
A series of 2-halo-1,3,2-diazaboracycloalkanes has been prepared by (a) the interaction of trialkylamine–trihaloboranes with alphatic α,ω-diamines, (b) displacement of dimethylamino groups of 2-dimethylamino-1,3,2-diazaboracycloalkanes with halogen through interaction with boron trihalides, and (c) a transhalogenation reaction. The 2-halo-1,3,2-diazaboracycloalkanes are thermally rather stable but are very reactive toward moisture and oxygen. The boron-bonded halogen is readily replaced by organic groups through interaction with Grignard reagents. All compounds have a characteristic BN absorption in the 1510–1540-cm^{-1} region of their infrared spectra and the proton magnetic resonance spectra are consistent with their structure. In the mass spectra, the parent peaks P^+ are generally less abundant than the $(P - 1)^+$ peaks.

The first synthesis of heterocyclic σ-bonded boron–nitrogen–carbon compounds was reported by Goubeau and Zappel in 1955.[2] Since that time, several preparative routes have be enexplored to afford the 1,3,2-diazaboracycloalkane system, I.[3] However, with few



I

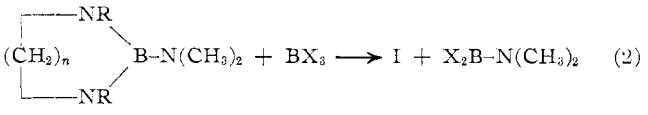
exceptions, only those derivatives in which X = alkyl or aryl have been described. In particular, derivatives of I with X = halogen are exceedingly rare with only four chloro compounds being known.[4,5] These latter compounds were obtained by treating boron trichloride with the appropriate aliphatic α,ω-diamines in the presence of an excess of triethylamine. With the exception of a Wurtz–Fittig reaction,[4] the chemistry of 2-halo-1,3,2-diazaboracycloalkanes has not been investigated.

The present study concerns the preparation of a series of 2-halo-1,3,2-diazaboracycloalkanes and some of their properties. In a slight modification of the previously described procedure,[4] the preparation of 2-chloro-1,3,2-diazaboracycloalkanes is facilitated when triethylamine–trichloroborane, $(C_2H_5)_3N \cdot BCl_3$, rather than boron trichloride is treated with α,ω-diamines in the presence of an excess of triethylamine providing a smooth reaction according to eq 1; boron tribromide or

$$(C_2H_5)_3N \cdot BX_3 + (C_2H_5)_3N + HRN(CH_2)_nNRH \longrightarrow 2(C_2H_5)_3NHX + I \quad (1)$$

boron triiodide may be used in the place of the chloride. However, in order to reduce side reactions, both nitrogen atoms of the diamine must be secondary. Otherwise, trimerization of I, R = H, occurs readily with the intermolecular elimination of HX and a borazine derivative is obtained along with higher aggregated species. It is worth noting that the reaction described in eq 1 does not work well if boron trifluoride is utilized.

An alternate procedure for the preparation of compounds of type I with X = halogen involves the interaction of 2-dimethylamino-1,3,2-diazaboracycloalkanes[6] with boron trihalides as illustrated by eq 2. Replacement of the boron-bonded exocyclic dimethylamino group can be accomplished with boron trihalides (BCl_3, BBr_3) or with complexes thereof such as trifluoroborane etherate. The reaction works particularly well with the latter whereas when boron triiodide was used, little or no product could be isolated. However, care must be taken to avoid an excess of the boron trihalide; otherwise, B–N ring bonds are attacked and the heterocyclic system may be cleaved.



$$+ BX_3 \longrightarrow I + X_2B\text{–}N(CH_3)_2 \quad (2)$$

Halogen exchange between boron trihalides and 2-

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