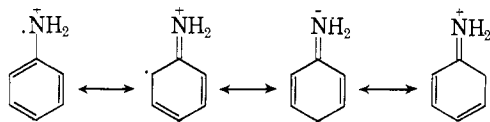


is only 24%. This finding is in keeping with other evidence for high stability, in a rather different environment. When the aniline ion is formed by photoionization in a hydrocarbon glass at low temperature, it survives long enough to be detected spectroscopically.<sup>11</sup> An explanation may lie in resonance stabilization predicted for a molecule that has lost a nonbonding electron—similar to that proposed for Wurster's salt<sup>12</sup>



and as an intermediate in induced decomposition of acyl peroxides by amines.<sup>13</sup> These structures offer a further possible clue to understanding the spectrum of aniline. In the toluene ion, the charge in the  $\pi$ -electron system is thought to furnish the driving force for ring expansion.<sup>4</sup> If so, localization of the charge on the nitrogen atom in the aniline ion might be expected to favor rather different reaction paths.

The principal decomposition path is by reaction VI. Marked preference for the path is doubtless promoted by the high stability of HCN, which seems to be a favored product from many reactive systems containing the necessary elements even though its formation may require extensive rearrangement. Thus, ions formed by loss of HCN are prominent in the mass spectra not only of aniline, but also, for example, of dinaphthylamine,<sup>14</sup> benzonitrile,<sup>14</sup> phthalonitrile,<sup>15</sup>  $\alpha$ -picoline,<sup>15</sup> nicotinonitrile,<sup>15</sup> phthalimide,<sup>15</sup> and 4-carboxyphthalimide.<sup>15</sup> Attention has been drawn to the close parallel between loss of HCN from nitrogen-containing compounds and the well known, highly favored loss of CO in many classes of oxygen-containing com-

(11) I. Norman and G. Porter, *Proc. Roy. Soc. (London)*, **A230**, 399 (1955).

(12) L. Michaelis, M. P. Schubert, and S. Granick, *J. Am. Chem. Soc.*, **61**, 1981 (1939).

(13) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 590-595, and references cited there.

(14) J. H. Beynon, G. R. Lester, and A. E. Williams, *J. Phys. Chem.*, **63**, 1861 (1959).

(15) Unpublished spectra, this Laboratory.

pounds.<sup>14</sup> In other contexts, HCN has been reported to be the main product of the reactions between active nitrogen and a variety of hydrocarbons and hydrocarbon derivatives.<sup>16</sup> It has been found among the products formed by passing a spark discharge through a mixture of nitrogen and formic acid.<sup>17</sup> It is also formed in reactions of methyl radicals with nitric oxide<sup>18</sup> and of hydrogen atoms with methyl-, dimethyl-, trimethyl-, and ethylamines.<sup>19</sup>

The toluene ion rearranges to a seven-membered ring and loses hydrogen to give the stable tropylium ion.<sup>4, 20</sup> Further decomposition occurs largely from this primary product. In contrast, the aniline ion seems to have no strong tendency to lose hydrogen. When it does so, loss occurs chiefly from the amino group, and side-chain and ring hydrogen atoms do not lose identity, as they do in toluene. Nevertheless, rearrangements are involved in most of the processes by which the aniline ion decomposes. In reaction II, all seven hydrogen atoms apparently lose identity; in reaction IV, the five ring hydrogens and one of the two amino hydrogens seem to be scrambled. Even in these two processes, the asymmetry introduced by the nitrogen atom makes a proposal of ring expansion less attractive in aniline than in toluene. Further labeling, especially with C<sup>13</sup>, might help resolve the uncertainty as to whether ring expansion plays any part in the chemistry of aniline under electron impact.

Detailed examination of the mass spectrum of aniline and, especially, the pronounced differences between aniline and toluene emphasize the central role of the nitrogen atom in determining the course of reaction of the aniline ion.

(16) H. G. V. Evans, G. R. Freeman, and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956); A. Schavo, *ibid.*, **37**, 655 (1959).

(17) C. E. Melton and G. A. Ropp, *J. Am. Chem. Soc.*, **80**, 5577 (1958).

(18) V. Pretorius, I. H. Henderson, and C. J. Danby, *J. Chem. Soc.*, 1076 (1955); W. A. Bryce and K. U. Ingold, *J. Chem. Phys.*, **23**, 1986 (1955).

(19) Z. M. George, A. N. Wright, and C. A. Winkler, *Can. J. Chem.*, **36**, 1171 (1958).

(20) P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957); S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

[CONTRIBUTION FROM THE GORGAS LABORATORY, ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

## Nitrosohydroborates. I

BY ROBERT A. WIESBOECK

RECEIVED APRIL 17, 1963

The first nitrosohydroborate,  $B_{20}H_{18}NO(NHET_3)_3$ , was prepared by the reaction of bistriethylammonium decahydrodecaborate,  $B_{20}H_{10}(NHET_3)_2$ , with nitrogen dioxide or ferric ion and nitric oxide. The nitroso group was readily reduced to the amino derivative producing  $B_{20}H_{18}NH_2^{-3}$ . Halogenation led to  $B_{20}H_{10}F_8NO^{-3}$ ,  $B_{20}H_2Cl_{16}NO^{-3}$ ,  $B_{20}H_4Br_{14}NO^{-3}$ , and  $B_{20}H_{11}I_4NO^{-3}$ . On reduction the corresponding halogenated amino compounds were obtained. They could be reoxidized to the original nitrosoborates. Various physical properties such as infrared, visible, and B<sup>11</sup> n.m.r. spectra for the compounds are presented.

### Introduction

Among the numerous derivatives of boranes and hydroborate ions known there are no compounds reported to date containing an NO group directly attached to one of the boron atoms. One might expect low stability from such a compound and thus only the most stable boranes or borane ions might be capable of forming a stable nitroso derivative. It was therefore interesting to note that the oxidation of decahydrodecaborate salts<sup>1,2</sup> with mild oxidants such as ferric nitrate was accompanied by the appearance of an intense blue color. The fact that the latter did not de-

(1) M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **81**, 5519 (1959).

(2) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, **81**, 5833 (1959).

velop when ferric sulfate or ferric chloride was employed suggested the presence of a nitroso or nitro compound. It was found that ferric ion in combination with nitric oxide or nitrite ion as well as alkyl nitrite and concentrated nitric acid would also produce the same intense color. Extension of this reaction to other boranes, *i.e.*, decaborane and bisacetonitriledodecaborane, did not lead to interesting products. Decaborane was oxidized to boric acid and bisacetonitriledodecaborane produced an unstable, intractable green oil.

### Results and Discussion

**A. The Preparation of  $B_{20}H_{18}NO(NHET_3)_3$ .**—The reaction of decahydrodecaborate ion with ferric ion-nitric oxide essentially parallels that with nitrogen dioxide so that the discussion can be restricted to the

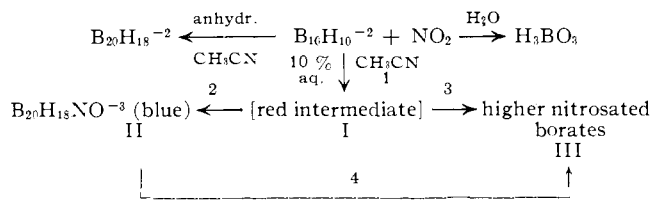
latter. More favorable conditions such as the greater solubility of nitrogen dioxide in solvents allow a more uniform reaction and a homogeneous system which give better reproducibility and higher yields.

When a dilute solution of nitrogen dioxide in methylene chloride was added carefully to a solution of bis-triethylammonium decahydrodecaborate in acetonitrile an intense red color developed immediately which turned dark blue on standing for several hours. The reaction proceeded instantaneously even at  $-45^\circ$  and probably involved the formation of at least one intermediate as indicated by color change. From the initial red solution a red compound (I) was isolated as the tetramethylammonium salt. It could not be obtained analytically pure owing to its reactivity and low stability. It was sensitive to shock and turned blue within a day on storage in a dry atmosphere. The conversion of this red product into the blue nitrosoborane (II) took place immediately on contact with water, more slowly with alcohols, and very slowly in anhydrous media. A carefully dried acetonitrile solution would usually possess a half-life of 6 to 8 hr. at room temperature. Protonic solvents seemed to catalyze the conversion, which proceeded without evolution of a gas. Both the red and the blue compound reacted with more nitrogen dioxide to form a series of higher nitrosated, explosive derivatives which will be reported later.

The existence of these various competitive side reactions makes it understandable that the blue nitrosoborate II was obtained in good yields only when a 10% aqueous acetonitrile solution of  $B_{10}H_{10}(NH_4)_2$  was employed and when the nitrogen dioxide was added slowly as a very dilute solution in methylene chloride. The use of nitrogen dioxide in high dilution reduced the probability of reaction of I with more  $NO_2$  and permitted the slow conversion of I to II to take place. Since II reacted more slowly with  $NO_2$  than did I, this also depressed the over-all formation of higher nitrosated products and increased the purity of any II isolated. Evaporation of the solvent from the reaction mixture produced a black semisolid which was recrystallized from hot water. The nearly black feathery crystals were stable in air and decomposed at  $165^\circ$  without melting.

The reaction between decahydrodecaborate ion and nitrogen dioxide appeared to be rather complex as indicated by the fact that different solvents led to different products. Aqueous solutions of decahydrodecaborate ion reacted quite rapidly with gaseous nitrogen dioxide. On slow addition, oxidation to boric acid occurred, whereas faster addition gave rise to the formation of a mixture of unidentified green and brown oily materials. If anhydrous acetonitrile was employed the major product was the  $B_{20}H_{18}^{-2}$  ion formed by oxidative coupling.<sup>3</sup> There was evidence for the presence of a small amount of I as indicated by the red color which disappeared slowly most likely due to reduction to an aminoborane as will be discussed subsequently.

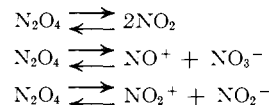
The following scheme summarizes these various reactions



(3) A. R. Pitochelli, W. N. Lipscomb, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **84**, 3026 (1962).

In a 10% aqueous acetonitrile solution steps 1 and 3 were found to be very fast as indicated by the fact that rapid addition of nitrogen dioxide produced I and III while unreacted substrate was still present. Step 2 appeared to be slow with a half-life of approximately 3-4 hr. at  $20^\circ$ .

Although a detailed mechanism could be written for the formation of II, the presently available data do not warrant such a discussion. One can, however, reach some conclusions about the nitrosating species. Among the possible reacting species of the  $NO_2/N_2O_4$  system



preference is given to  $NO^+$  above all others on the following grounds:  $NO_2\cdot$  can be ruled out considering that the reaction proceeds rapidly even at  $-45^\circ$ .  $NO_2^+$  meets the requirements for the reaction with nitrogen dioxide but could not be present in the  $Fe^{+2}$ -NO system. Thus,  $NO^+$  appears most appealing as the reacting species, in particular since acetic acid-nitrite solutions, which are known to contain the  $NO^+$  ion, also lead to the formation of nitrosoborates with decahydrodecaborate ion.

There is evidence that the nitrosation takes place before coupling to the  $B_{20}$  unit occurs since  $B_{20}H_{18}^{-2}$  does not form a nitroso derivative with nitrogen dioxide or nitrous acid.

The composition of the blue nitrosoborate salt was established as  $B_{20}H_{18}NO(NH_4)_3$  by X-ray diffraction<sup>4</sup> since elemental analysis<sup>5</sup> did not distinguish between  $B_{14}H_{13}NO(H_4N)_2$  and  $B_{20}H_{18}NO(NH_4)_3$ . The compound was found to be diamagnetic in the solid state or in solution. The exact number of hydrogen atoms in the molecule is not known, but its diamagnetism suggested the formulation  $B_{20}H_{18}NO^{-3}$ . The triethylammonium salt was very soluble in acetonitrile and moderately soluble in water and ethanol, exhibiting a deep blue color. An extinction coefficient of 26,500 at  $582 \mu$  was measured in acetonitrile.

The infrared spectrum, presented in Table I, showed a strong peak at  $8.45 \mu$  which was removed on hydrogenation. It was, therefore, assigned to the NO absorption. A series of halogenated derivatives, which is discussed in the following section, also exhibited an absorption in the  $8-9 \mu$  region which disappeared on hydrogenation. A comparison with other nitroso compounds indicated a similarity with the NO in the metal-nitric oxide complexes such as the  $Co(NH_3)_5NO^{+2}$  and  $Co(CN)_5NO^{-3}$  ions<sup>6</sup> which absorb at  $8.55$  and  $8.94 \mu$ , respectively.

**B. The Chemistry of  $B_{20}H_{18}NO^{-3}$ .**—The chemistry of  $B_{20}H_{18}NO^{-3}$  is characterized by its stability toward oxidants and bases. Mineral acids lead to decomposition only on heating. The nitroso group is readily reduced to the amino derivative and nearly all hydrogens of the borane can be substituted by halogens to a varying degree.

(1) **Halogenation.**—Recently Knoth and co-workers<sup>7</sup> reported the halogenation of the  $B_{10}H_{10}^{-2}$  and  $B_{12}H_{12}^{-2}$

(4) A. Kaczmarezky, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962).

(5) The compound was reported in a previous communication [*J. Am. Chem. Soc.*, **83**, 4108 (1961)] as  $B_{14}H_{13}NO(NH_4)_2$ , which could not be distinguished from  $B_{20}H_{18}NO(NH_4)_3$  by elemental analysis or equivalent weight determination. Subsequent X-ray analysis by Prof. W. N. Lipscomb and co-workers at Harvard University—which is hereby gratefully acknowledged—established the structure as  $B_{20}H_{18}NO^{-3}$ .

(6) W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958).

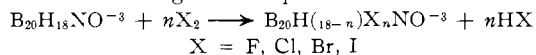
(7) W. H. Knoth, H. C. Miller, D. C. England, G. W. Parshall, and E. L. Muettterties, *J. Am. Chem. Soc.*, **84**, 1056 (1962).

TABLE I  
INFRARED SPECTRA<sup>a</sup> OF THE TETRAETHYLAMMONIUM SALTS OF  
NITROBORATES

$B_{20}H_{18}NO^{-3}$	$B_{20}H_{10}F_8NO^{-3}$	$B_{20}H_2Cl_{16}NO^{-3}$	$B_{20}H_4Br_{14}NO^{-3}$	$B_{20}H_{11}I_7NO^{-3}$
3.40 (s)	3.39 (s)	3.40 (s)	3.40 (s)	3.40 (s)
4.02 (s)	3.45 (s)	3.48 (s)	3.48 (s)	3.48 (s)
6.90 (s)	3.96 (m)	3.85 (w)	3.90 (w)	3.95 (m)
7.21 (m)	6.85 (s)	6.78 (s)	6.88 (s)	6.88 (s)
7.30 (m)	7.15 (m)	6.88 (s)	7.21 (m)	7.21 (m)
7.59 (m)	7.25 (m)	7.35 (m)	7.70 (w)	7.28 (m)
8.45 (s)	8.45 (s)	8.11 (m)	8.11 (m)	7.34 (m)
10.00 (m)	8.55 (s)	8.82 (s)	8.48 (m)	7.72 (w)
11.23 (m)	9.96 (m)	9.90 (m)	8.56 (m)	8.25 (m)
12.80 (m)	11.15 (w)	10.55 (m)	8.85 (m)	8.48 (m)
13.25 (w)	12.52 (m)	12.22 (w)	9.08 (s)	8.54 (m)
	12.65 (m)		11.82 (m)	9.40 (m)
			12.52 (m)	10.00 (m)
				10.65 (m)
				11.48 (w)
				12.82 (m)
				13.10 (m)

<sup>a</sup> Spectra obtained in Nujol mull with Nujol bands included in tabulation.

ions to a series of partly or totally halogenated borate ions such as  $B_{10}H_8I_4^{-2}$ ,  $B_{10}I_{10}^{-2}$ ,  $B_{12}H_2Cl_{10}^{-2}$ , and  $B_{12}Cl_{12}^{-2}$ . Similar reactions were found to occur when  $B_{20}H_{18}NO^{-3}$  (I) was subjected to halogenation. Nearly all of the hydrogens of I could be substituted by halogen in a buffered aqueous or partly aqueous solution at temperatures ranging from 0 to 70°. The over-all reaction proceeded according to the equation



The alkali salt of I had to be used since the triethylammonium cation also underwent halogenation. The chlorination of  $K_3B_{20}H_{18}NO$  (III) in the above-mentioned fashion produced the ion  $B_{20}H_2Cl_{16}NO^{-3}$  (IV) in nearly quantitative yield. The compound resisted all attempts to achieve complete chlorination even at elevated temperatures. The bromination of III led to  $B_{20}H_{14}Br_4NO^{-3}$  (V) and iodination to  $B_{20}H_{11}I_7NO^{-3}$  (VI). The latter reacted with excess iodine at temperatures above 30–35° to produce an unidentified green oil. It was also possible to prepare a fluorine derivative  $B_{20}H_{10}F_8NO^{-3}$  (VII). However, continued fluorination beyond this level resulted in the destruction of the nitrosoborate ion and a colorless solution was obtained.

All of the halogenated nitrosoborates were isolated as the water-insoluble tetraalkylammonium salts. The crystalline, nearly black compounds were soluble in acetonitrile, producing a dark blue solution from which they were recrystallized. Extinction coefficients and the corresponding wave lengths at which the maximum was observed are presented in Table II.

TABLE II  
EXTINCTION COEFFICIENTS OF  $B_{20}H_{(18-n)}X_nNO(NEt_4)_3$  IN  
ACETONITRILE

	Ext. coeff.	$\lambda_{max}$ , m $\mu$
$B_{20}H_{10}F_8NO^{-3}$	19,400	600
$B_{20}H_2Cl_{16}NO^{-3}$	21,000	588
$B_{20}H_4Br_{14}NO^{-3}$	20,300	570
$B_{20}H_{11}I_7NO^{-3}$	17,300	575
$B_{20}H_{18}NO^{-3}$	26,500	582

It can be seen that the halogenation gave rise to a general decrease in intensity of the absorption coupled with a slight shift in wave length. There was also observed a general broadening of the maxima of the halogenated derivatives when compared with the parent compound.

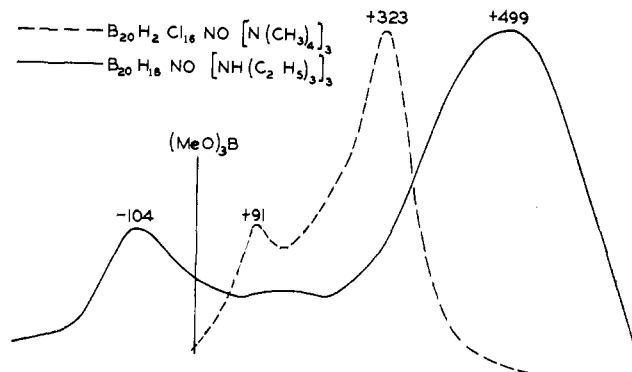
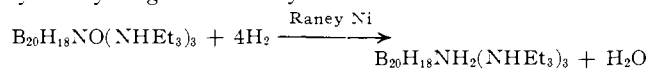


Fig. 1.— $B^{11}$  n.m.r. spectra.

The infrared absorptions of the halogenated nitrosoborates reflected a similar nonuniform picture with shifts of the NO absorption in both directions. The substitution of most of the hydridic hydrogen in  $B_{20}H_{18}NO^{-3}$  by chlorine did not simplify the poorly resolved  $B^{11}$  n.m.r. spectrum (see Fig. 1).

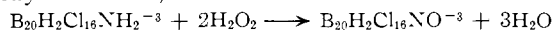
(2) Oxidation-Reduction Reactions.—An alcoholic solution of I was readily reduced by Raney nickel-catalyzed hydrogenation to yield the amino derivative.



The same reaction was obtained with hydrazine, hydroxylamine, and sodium dithionite in aqueous solution. The resulting slightly yellow aminoborane exhibited great stability and showed an N-H stretching and deformation absorption in the infrared at 2.80 and 6.40  $\mu$ , respectively. From the presence of both stretching and deformation absorption, it was concluded that reduction to an  $NH_2$  group had taken place. Deuteration in  $D_2O$  occurred readily at room temperature and led to a shift of the 6.40  $\mu$  peak to 8.75  $\mu$  while the N-D stretching absorption appeared to be covered up in the B-H region at 3.9–4.0  $\mu$ . The amino group was of low basicity and rather unreactive. Acylation could be achieved only under forced conditions.

The reduction of the halogenated nitroso compounds produced readily the corresponding colorless amino derivatives  $B_{20}H_{10}F_8NH_2^{-3}$ ,  $B_{20}H_2Cl_{16}NH_2^{-3}$ ,  $B_{20}H_4Br_{14}NH_2^{-3}$ , and  $B_{20}H_{11}I_7NH_2^{-3}$ .

Attempts to arrest the reduction at the hydroxylamine stage by the use of Zn-H<sub>2</sub>O or sulfurous acid were unsuccessful. The amino derivative was produced in all cases. It was not possible to oxidize the unsubstituted amine ion  $B_{20}H_{18}NH_2^{-3}$  to the original nitrosoborane as no reaction took place with mild oxidizers and more vigorous conditions led to the destruction of the hydroborate. However, the desired oxidation was easily achieved with the halogenated derivatives. These were reconverted to the original nitrosoborate by oxidizing agents such as dilute hydrogen peroxide, peroxyacetic acid, and ferric ion.



Oxidation occurred merely on standing in air so that the compounds had to be stored in an atmosphere free of oxygen. The identity of the blue oxidation product was established by comparison of the infrared and visible spectra which exhibited the same extinction coefficients as those of the corresponding starting materials.

### Experimental

**Materials.** Bistriethylammonium decahydrodecaborate was most conveniently purified by recrystallization from acetonitrile-methylene chloride mixtures. A 25% solution of the borate in acetonitrile was diluted at room temperature with one-half volume of methylene chloride. After standing for 2 hr. more methylene chloride was added to achieve complete precipitation.

The compound crystallized in nice prisms containing one methylene chloride of crystallization. The latter was readily removed on heating to 40–50° in vacuum.

Commercial nitric oxide was used after passing through a wash bottle containing 10% sodium hydroxide solution.

**Nitrogen dioxide** was condensed in an atmosphere of oxygen and dried by passing it through a U-tube filled with Drierite.  $B^{11}$  N. m. r.—The  $B^{11}$  nuclear magnetic resonance spectra were obtained in acetonitrile solution with a Varian Model V 4300B high resolution n. m. r. spectrometer at a frequency of 12.8 Mc.

**Infrared spectra** were recorded on a model 137 Perkin-Elmer Infracord spectrophotometer. Nujol oil mulls were employed throughout.

**Visible Spectra.**—The spectra were measured with a model DK-1 Beckman spectrophotometer using commercial Eastman spectrograde acetonitrile as solvent.

**The Preparation of  $B_{20}H_{18}NO(NHET_3)_3$ .** I.—Ten grams (0.031 mole) of triethylammonium decahydrodecaborate was dissolved in 30 ml. of 10% aqueous acetonitrile in a three-neck flask equipped with two gas inlet tubes and a magnetic stirrer. A stream of nitrogen was introduced through the shorter inlet tube which ended above the surface of the liquid while nitric oxide was passed in through the second inlet tube close to the stirring bar, at a rate of 2–3 bubbles per second. It was essential that all unreacted nitric oxide was carried out of the flask by nitrogen. After 30 min., the solution was cooled to 0° and a solution of 9 g. of ferric chloride nonahydrate in 10 ml. of water was added dropwise. This caused the solution to turn red and finally deep blue. The stream of nitric oxide was maintained for another hour and the solution was then poured into a mixture of 70 ml. of water and 300 ml. of methylene chloride. Extraction with a total of 4 l. of methylene chloride and removal of the solvent under vacuum produced 6–7 g. of a black material. Crystallization was achieved by adding 10 ml. of acetonitrile and quickly diluting with 400 ml. of hot water. Brilliant purple-black needles precipitated as the solution cooled. Concentration to 100 ml. produced a second crop; a total yield of 2.2 g. of feathery, nearly black crystals was obtained.

II.—A solution of 20 g. (0.062 mole) of bistriethylammonium decahydrodecaborate in 1000 ml. of 10% aqueous acetonitrile was placed into a 2-l. three-neck flask equipped with mechanical stirrer and two dropping funnels. After cooling to 0° a solution of 0.062 mole of nitrogen dioxide in 700 ml. of cold (0°) methylene chloride was dropped in over a period of 4 hr. while stirring vigorously.<sup>8</sup> The reaction mixture turned red and toward the end of the addition deep blue. It was dried over magnesium sulfate and filtered. The filter cake was washed with 50 ml. of acetonitrile and the combined filtrate evaporated under vacuum. The blue-black, oily residue was dried for 3 hr. at room temperature under high vacuum. Boiling water (400 ml.) was added and the solution was filtered through a fritted glass filter funnel while still hot. The filtrate was allowed to cool very slowly by placing it in a warm dewar flask. Shiny, blue-black crystals (5.6 g.) were obtained. The compound was soluble in acetonitrile, water, and alcohol and decomposed at 165° without melting.

*Anal.* Calcd. for  $C_{18}H_{66}B_{20}N_4O$ : C, 37.85; H, 11.65; B, 37.89; N, 9.81. Found: C, 36.26; H, 11.36; B, 37.36; N, 10.46.

**Attempted Isolation of the Intermediate I.**—A solution of 6 mmoles of  $NO_2$  in 30 ml. of methylene chloride was added dropwise to a stirred solution of 6 mmoles of bistriethylammonium decahydrodecaborate in 50 ml. of 10% aqueous acetonitrile at –20°. Then 20 g. of Drierite was added and the mixture was filtered while cold. The filtrate was concentrated to one-half of its original volume under vacuum. Addition of 20 mmoles of tetramethylammonium chloride in 120 ml. of cold methanol precipitated a flocculent red material which was collected quickly on a fritted glass filter and dried under vacuum. The compound was recrystallized from dry acetonitrile on cooling to –30°. It was highly shock sensitive and slowly turned into the blue  $B_{20}H_{18}NO(NMe_4)_3$  on storage at room temperature.

**The Preparation of  $B_{20}H_{18}NH_2(NHET_3)_3$ .**—Two grams of  $B_{20}H_{18}NO(NHET_3)_3$  in 500 ml. of 1:1 ethanol-methanol was reduced in an autoclave with 0.2 g. of Raney nickel and 500 p.s.i. hydrogen at 60–70° for 2 hr. The Raney nickel was filtered from the hot solution. On standing in the refrigerator overnight white platelets precipitated. Concentrating the mother liquor to one-fifth of its volume increased the yield to 1.8 g. The compound was soluble in acetonitrile and water.

*Anal.* Calcd. for  $C_{18}H_{88}B_{20}N_4$ : C, 38.80; H, 12.30; B, 38.84; N, 10.05. Found: C, 37.51; H, 11.96; B, 39.00; N, 10.30.

**The Preparation of  $B_{20}H_{18}NHCOCH_3(NEt_4)_3$ .**—A mixture of 10 mmoles of  $B_{20}H_{18}NH_2(NEt_4)_3$ , 50 ml. of acetic acid, and 50 ml. of acetic anhydride was heated to 80° for 48 hr. The resulting slightly brown solution was evaporated under vacuum and the oily

(8) Care must be exercised to add the nitrogen dioxide solution at the indicated rate, otherwise a different red compound is formed which is highly explosive.

residue recrystallized from acetonitrile-ethanol using decolorizing carbon to remove the brown impurity. The white feathery crystals (1.2 g.) melted at 210° with decomposition.

*Anal.* Calcd. for  $C_{26}H_{82}B_{20}N_4O$ : C, 45.70; H, 12.09; B, 31.66; N, 8.20. Found: C, 45.52; H, 11.95; B, 31.42; N, 8.11.

**The Preparation of  $B_{20}H_{18}NO(NMe_4)_3$ .**—A solution of 2 mmoles of  $K_3B_{20}H_{18}NO$  and 25 mmoles of  $KHCO_3$  in 60 ml. of water was placed in a three-neck flask and cooled to 0°. While stirring, 20 mmoles of fluorine diluted with 90 volume % helium were introduced through a capillary tube reaching to the bottom of the flask. The blue solution was poured into excess aqueous tetramethylammonium chloride and the precipitate isolated by filtration. Repeated recrystallization from warm acetonitrile-ethanol yielded 0.4 g. of greenish black crystals which decomposed at 140° without melting.

*Anal.* Calcd. for  $C_{12}H_{46}B_{20}F_8N_4O$ : C, 22.84; H, 7.34; B, 34.30; F, 24.09; N, 8.88. Found: C, 22.70; H, 7.38; B, 34.19; F, 23.95; N, 8.75.

**The Preparation of  $B_{20}H_2Cl_{16}NO(NEt_4)_3$ .**—Ten mmoles (5.8 g.) of  $B_{20}H_{18}NO(NHET_3)_3$  was added to a solution of 35 mmoles of potassium hydroxide in 100 ml. of water. The mixture was heated on the steam bath while a vigorous stream of nitrogen was introduced to remove all liberated triethylamine. The solution was cooled to 10–15° and 10 g. of potassium bicarbonate in 50 ml. of water was added. A stream of chlorine was passed through the liquid with rapid stirring. The temperature was maintained below 60° by means of an ice bath and the pH was controlled by adding more bicarbonate solution during the reaction. After saturation the gas introduction was continued for another 30 min. Addition of excess tetraethylammonium chloride precipitated a flocculent blue material which was isolated by filtration and washed with water until the wash water was free of chloride. After drying under vacuum the compound was recrystallized from acetonitrile-ethanol. A yield of 8.2 g. of black crystals was obtained which decomposed at 160° without melting.

*Anal.* Calcd. for  $C_{24}H_{82}B_{20}Cl_{16}N_4O$ : C, 23.89; H, 5.18; B, 17.93; Cl, 47.02; N, 4.64. Found: C, 23.73; H, 5.19; B, 17.80; Cl, 47.00; N, 4.48.

**The Preparation of  $B_{20}H_4Br_{14}NO(NMe_4)_3$ .**—A solution of 10 mmoles of  $K_3B_{20}H_{18}NO$  in 100 ml. of water was prepared as described in the preceding example and 20 g. of  $KHCO_3$  added. Bromine (200 mmoles) was dropped into the stirred solution while cooling with ice water. A reflux condenser was attached to the flask and the mixture was warmed to 50–60° for 2 hr. to achieve complete reaction. Excess bromine was subsequently removed under reduced pressure and an aqueous solution of tetramethylammonium chloride was added. The precipitate was filtered, washed with plenty of water, and dried under vacuum. Recrystallization from warm acetonitrile-ethanol produced 12 g. of shiny black crystals.

*Anal.* Calcd. for  $C_{12}H_{40}B_{20}Br_{14}N_4O$ : C, 9.05; H, 2.53; B, 13.60; Br, 70.28; N, 3.52. Found: C, 8.89; H, 2.46; B, 11.40; Br, 70.30; N, 3.53.

**The Preparation of  $B_{20}H_{11}I_7NO(NMe_4)_3$ .**—Ten mmoles of  $K_3B_{20}H_{18}NO$ , dissolved in 100 ml. of water, was prepared as described earlier and buffered with 20 g. of potassium bicarbonate. To this solution was added 25 g. of iodine dissolved in 160 ml. of 10% potassium iodide. The mixture was stirred for 3 hr. while the temperature was maintained at 20°. Addition of an excess of aqueous tetramethylammonium chloride precipitated a black material which was collected on a fritted glass filter and washed with alcohol until free of iodine. The compound was recrystallized several times from a small amount of warm acetonitrile by adding ethanol, producing 7.8 g. of black shiny platelets.

*Anal.* Calcd. for  $C_{12}H_{17}B_{20}I_7N_4O$ : C, 11.05; H, 3.46; B, 15.81; I, 64.92; N, 4.09. Found: C, 11.13; H, 3.59; B, 15.50; I, 64.2; N, 4.13.

**The Preparation of  $B_{20}H_2Cl_{16}NH_2(NEt_4)_3$ .**—A solution of 10 mmoles of  $K_3B_{20}H_{18}NO$  in 100 ml. of water was chlorinated in the aforementioned manner. Excess chlorine was removed by a sweep of nitrogen and 1 ml. of hydrazine diluted with 10 ml. of water was added. The blue color of the solution faded away on standing at room temperature within 20–30 min. Addition of excess tetraethylammonium chloride, dissolved in water, caused a white precipitate which was recrystallized from hot acetonitrile by adding ethanol until the turbidity point was reached. The white crystalline compound (6.7 g.) was dried under vacuum and stored in an oxygen-free atmosphere; reoxidation to the nitrosoborane occurred readily in air.

*Anal.* Calcd. for  $C_{24}H_{64}B_{20}Cl_{16}N_4$ : C, 24.17; H, 5.41; B, 18.14; Cl, 47.57; N, 4.70. Found: C, 23.64; H, 5.50; B, 17.84; Cl, 47.19; N, 4.68.

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