amounts of N_2F_4, N_2O, NO_3^-, and NO_2^-. At lower pH values, less N_2 and more N_2F_2 is formed.

Bisulfite Ion. The reaction of this ion with difluoramine yielded 2 mmoles of sulfate ion for every millimole of HNF_2 that was consumed. The major nitrogen-containing species which was produced was ammonia. No nitrogen gas was produced.

Iodide Ion. One millimole of difluoramine reacted quantitatively with 4 mmoles of this ion to give NH_4^+.[20] If less than 4 mmoles of iodide per mmole of HNF_2 is employed, then a corresponding amount of N_2F_4 is formed. The N_2F_4 is apparently the product of the oxidation of unreacted HNF_2 by the iodine liberated.

Cyanide Ion. The reaction of excess CN^- (0.2 *M*) with HNF_2 was run in a solution buffered at pH 8.35 to prevent loss of HCN. The yield of nitrogen-containing material was 50% NH_3, 10% N_2, and 35% N_2F_2. The other products were N_2O and NO. The N_2F_2 and much of the nitrogen result from the reaction of hydroxyl ion with HNF_2. There is probably some contribution to the products from reactions of HCN with HNF_2 or intermediate species, as cyanide ion is in equilibrium with HCN at this pH. At the end of the reaction, a large amount of HCN was pumped out of the solution. No cyanogen was detected.

Thiocyanate Ion. The reaction of SCN^- with HNF_2 was run in an unbuffered system so that the pH of the system was well below 7. All of the HNF_2 was converted to ammonia in essentially quantitative yield. About half of the thiocyanate was converted to HCN. Small amounts of SO_2 were found in each experiment.

Azide Ion. Experiments with this ion were run in solutions buffered between pH values of 7.4 and 7.8. In every experiment more than 90% of the HNF_2 was converted to nitrogen. About 5 to 6% of the HNF_2 was converted to ammonia. The contribution to the reaction products from the reaction of hydroxyl ion with HNF_2 to yield N_2F_2 is subtracted from the over-all reaction. This contribution approached zero in the presence of large amounts of azide ion.

Bromide Ion. Reactions of Br^- with HNF_2 were studied in unbuffered solutions so that pH values were always below 7. Most of the solutions were 0.1 *M* in HNF_2 and 0.6 *M* in bromide ion (NaBr). Approximately one-third of the HNF_2 was converted to ammonium ion and two-thirds of the HNF_2 was oxidized to N_2F_4. Small amounts of nitric oxide were also found. This product is probably a result of the hydrolysis of the N_2F_4.

Chloride Ion. Experiments with Cl^- and HNF_2 were also conducted in unbuffered solutions. The solutions were 0.1 *M* in HNF_2 and from 0.2 to 0.5 *M* in chloride ion (NaCl). In a typical experiment, 39% of the HNF_2 was converted to nitrogen, 40% to N_2F_4, and the remainder to N_2F_2, NO, $ClNF_2$, and NH_3.

Acetate Ion. The reaction of this ion with HNF_2 was studied in solutions which were 0.1 *M* in HNF_2 and 0.35 *M* in sodium acetate and acetic acid. In a typical run, 5.05 mmoles of HNF_2 yielded 0.61 mmole of N_2O after 20 hr; 3.60 mmoles of HNF_2 remained unconsumed. After 40 hr, 1.40 mmoles of N_2O was produced and 2.00 mmoles of HNF_2 remained unconsumed. Only trace amounts of other materials, such as N_2F_2, N_2F_4, NO_3^-, and NO_2^-, were found. Small amounts of carbon dioxide were also formed and reached a level of 0.14 mmole after 40 hr.

Phosphate Ions. The reactions of $H_2PO_4^-$ and HPO_4^{2-} ions with HNF_2 were studied in solutions which were 0.1 *M* in HNF_2 and 0.2 *M* in both of the phosphate ions. The pH was about 7.1. After 20 hr at these initial concentration levels, 38% of the HNF_2 was converted to N_2O, 34% was converted to N_2F_2, and 20% of the HNF_2 was unconsumed. Trace amounts of ammonia and N_2F_4 were also found.

Acknowledgment. The authors express their appreciation to Mr. J. B. Forgie for his assistance in carrying out the experimental part of this study. This research was supported by the Advanced Research Projects Agency through the U. S. Army Research Office (Durham), Contract DA-31-124-ARO(D)-62.

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Trifluoromethyl-Substituted Boranes. Trifluoromethyldi-*n*-butylborane and Trifluoromethylboron Difluoride

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Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon. Received January 3, 1967

Abstract: The preparation and properties of trifluoromethyldi-*n*-butylborane and trifluoromethylboron difluoride are reported. Loss of difluorocarbene from the trifluoromethyl group bonded to electron-deficient boron was observed in the presence of catalysts, but in *vacuo* at room temperature the substances were stable for months. Infrared spectra and vapor pressure data for *n*-butylboron difluoride and di-*n*-butylboron fluoride are reported.

In a previous report[1] the preparation of a trifluoromethylboron compound, CF_3BF_2, was described. It was prepared *via* an intermediate, presumed to be $CF_3(n\text{-}C_4H_9)_2B$, but not isolated in a pure state nor further characterized. The synthesis of both of these compounds and their partial characterization is now reported, together with information about other boranes isolated in the course of this study.

Experimental Section

Reagents. Reagents not available commercially were prepared according to literature methods, with minor variations. These include tri-*n*-butylborane,[2] di-*n*-butylboron chloride,[3] sodium-potassium alloy,[4] and trifluoromethyl iodide.[5]

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[2] J. R. Johnson, H. R. Snyder, and M. G. Van Campen, Jr., *ibid.*, **60**, 115 (1938).

[3] R. B. Booth and C. A. Kraus, *ibid.*, **74**, 1415 (1952).

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[5] R. N. Haszeldine, *J. Chem. Soc.*, 584 (1951).

Potassium Di-*n*-butylborate(I). Potassium di-*n*-butylborate(I) was prepared by the reaction

$$(n\text{-}C_4H_9)_2BCl + 2K(Na) \longrightarrow (n\text{-}C_4H_9)_2BK + KCl$$

The method used was similar to that described by Auten and Kraus[6] but adapted to a larger scale and to triethylamine solvent. The apparatus shown in Figure 1 was placed in a glove box and purged with nitrogen (Matheson 99.5%) which was passed over hot copper and P_2O_5 on glass beads prior to use. $(C_2H_5)_3N$ (100 ml) and liquid K-Na alloy (20 ml) were added through A. $(n\text{-}C_4H_9)_2BCl$ (0.1 mole, 16 g) was added over a period of 15 min through the by-pass dropping funnel with stirring. The mixture was stirred for 12 hr. After this time the apparatus was tipped, and the dark brown solution was filtered into the receiver flask. The residue was washed with four 50-ml portions of $(C_2H_5)_3N$, each added to the filtrate. The volume of solution was reduced to *ca.* 50 ml by evaporation in *vacuo*, and the receiver flask was sealed off at B and C. The product gave a negative test for Cl^-. The yield was 63% based on $(n\text{-}C_4H_9)_2BCl$ as estimated from the hydrogen gas released by reaction of an aliquot with aqueous HCl. The reaction was repeated many times with yields ranging from 50 to 63%.

Trifluoromethyldi-*n*-butylborane. Trifluoromethyldi-*n*-butylborane was prepared by the reactions

$$(n\text{-}C_4H_9)_2BK \cdot N(C_2H_5)_3 + CF_3I \longrightarrow (n\text{-}C_4H_9)_2BCF_3 \cdot N(C_2H_5)_3 + KI$$

$$(n\text{-}C_4H_9)_2BCF_3 \cdot N(C_2H_5)_3 + HCl \longrightarrow (n\text{-}C_4H_9)_2BCF_3 + (C_2H_5)_3NHCl$$

Gaseous trifluoromethyl iodide (0.13 mole was bubbled slowly through a solution of potassium di-*n*-butylborate(I) (*ca.* 0.065 mole) in triethylamine at −80°. The characteristic dark brown color of the solution faded to a light amber during the addition. Triethylamine was removed by evaporation at room temperature, and the amber, solid residue was treated with anhydrous HCl. The resulting liquid–solid mixture was separated by filtration under anhydrous HCl. Tri-*n*-butylborane impurity was removed by treating the mixture with excess triethylamine and pumping at 50°. The material removed during this operation, other than triethylamine, was almost entirely tri-*n*-butylborane. Other more volatile impurities found in small amounts (hydrogen, butene, trifluoromethane) also separated during this operation. $CF_3B(n\text{-}C_4H_9)_2$ was recovered from the amine adduct by treatment with excess anhydrous HCl and distilled under a nitrogen atmosphere at 60° (1 mm); yield 30% based on $(n\text{-}C_4H_9)_2BCl$. Further purification was effected by a preparative scale gas chromatographic separation of 2–3% $(n\text{-}C_4H_9)_3B$. The separation was carried out using a 7.5 ft × 12 mm column packed with Chromosorb P (Johns-Manville) coated with 20% by weight Dow Corning Silicone 710 at 92°.

Fusion with potassium metal[7] and spectrophotometric analysis of the resultant soluble fluoride[8] gave 2.95 F per $(n\text{-}C_4H_9)_2BCF_3$: mol wt by vapor density, 190.7 (calculated, 193.85). Vapor pressures between 40 and 145° are described by the equation $\log p_{mm} = 8.611 - (2827/T)$; extrapolated bp 221°

Acid Strength of Trifluoromethyldi-*n*-butylborane toward Ammonia. The Lewis acid strength of $(n\text{-}C_4H_9)_2BCF_3$ toward NH_3 was determined by Brown's method.[9] Observed pressures in the system at 23 and 92° were 0.9 and 52.3 mm, respectively. Calculated pressures (corresponding to the vapor pressures of $(n\text{-}C_4H_9)_2BCF_3$ as if it were the sole component) were 0.6 and 8.1 mm for these temperatures. The calculated degrees of dissociation of $(n\text{-}C_4H_9)_2BCF_3 \cdot NH_3$ were 0.337 and 0.845 at 23 and 92°, respectively.

Trifluoromethylboron Difluoride. CF_3BF_2 was prepared by the reactions

$$(n\text{-}C_4H_9)_2BCF_3 + BF_3 \longrightarrow (n\text{-}C_4H_9)_2BF + CF_3BF_2$$

$$(n\text{-}C_4H_9)_2BCF_3 + 2BF_3 \longrightarrow 2(n\text{-}C_4H_9)BF_2 + CF_3BF_2$$

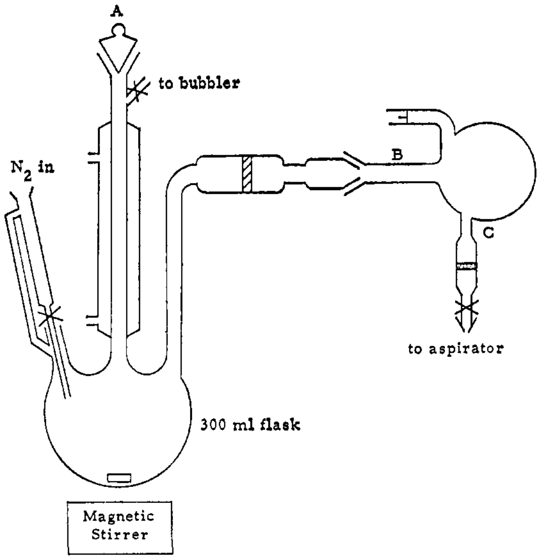

Figure 1. Reaction vessel.

$CF_3B(n\text{-}C_4H_9)_2$ (24.5 mmoles) and excess BF_3 were mixed and allowed to stand at room temperature for 24 hr. Separation of the products by fractional condensation gave BF_3, $(n\text{-}C_4H_9)BF_2$ (6.72 mmoles), $(n\text{-}C_4H_9)_2BF$, and CF_3BF_2 (1.31 mmoles). Additional amounts of CF_3BF_2 were obtained by successive treatment of the remaining $(n\text{-}C_4H_9)_2BCF_3$ with more BF_3. The compound identified as CF_3BF_2 had a vapor-phase molecular weight of 117.5 ± 1.5 (calculated, 117.8). It formed 1:1 adducts with $(CH_3)_3N$ and $(C_2H_5)_3N$ from which it could be recovered by the action of anhydrous HCl. Analysis for fluorine by fusion with potassium metal[7] and spectrophotometric analysis of soluble fluoride[8] gave 5.1 F per CF_3BF_2. The infrared spectrum showed strong absorption peaks at 1080 and 1190 cm^{-1}; medium absorption peaks at 850, 845, 1040, 1255, and 1460 cm^{-1}; weak absorption peaks at 690, 725, and 1160 cm^{-1}; and a broad weak absorption from 1350 to 1400 cm^{-1}.

CF_3BF_2 decomposed quantitatively to BF_3 and a white, nonvolatile residue in the presence of oxygen gas, moisture, glyptal resin, and other catalysts of undetermined nature, but it was stable for periods of months *in vacuo* in the absence of these substances.

Properties of $(n\text{-}C_4H_9)_2BF$ and $(n\text{-}C_4H_9)BF_2$. $(n\text{-}C_4H_9)_2BF$ and $(n\text{-}C_4H_9)BF_2$, isolated during the preparation of CF_3BF_2, have been previously reported.[9,10] Vapor pressure and infrared spectral data were determined in this work and are reported here. Di-*n*-butylboron fluoride gave vapor density molecular weights of 142.5, 145.0, and 144.0 (calculated, 143.85). Vapor pressure data in the range 25 to 87° correspond to the equation $\log p_{mm} = 7.954 - (2130/T)$; extrapolated bp 147°; $\Delta H_{vap} = 9.76$ kcal/mole. The infrared spectrum was determined using a Beckman IR 7 with NaCl and CsI interchanges from 200 to 4000 cm^{-1}. The spectrum showed strong absorption peaks at 1350, 2860, and 2980 cm^{-1}; medium absorption peaks at 1120, 1290, 1380, and 1480 cm^{-1}; and weak absorption peaks at 725, 900, 975, 1180, and 2790 cm^{-1}.

n-Butylboron difluoride gave a vapor density molecular weight of 104.6 (calculated 105.8). Vapor pressures in the range −47 to 22° correspond to the equation $\log p_{mm} = 7.935 - (1558/T)$; extrapolated bp 35.5°; $\Delta H_{vap} = 7.13$ kcal/mole. The infrared spectrum in the range 200–4000 cm^{-1} showed strong absorption peaks at 1360, 1400, and 2970 cm^{-1}; medium absorption peaks at 1200, 1270, 1310, 1430, and 2860 cm^{-1}; and weak absorption peaks at 480, 510, 730, 810, 905, 975, and 3680 cm^{-1}.

Discussion

The loss of difluorocarbene from the trifluoromethyl group, when bonded to trivalent boron, is thermodynamically favored, at least when other boron substituents are not π-electron donors. Stability toward this reaction for both $(n\text{-}C_4H_9)_2BCF_3$ and CF_3BF_2 was

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enhanced when the substances were in the form of adducts with Lewis bases such as triethylamine. It was found desirable to generate the uncomplexed borane in the last step of the synthesis whenever possible by destruction of the adduct with dry HCl. It should be noted in this connection that Chambers, Clark, and Willis[11] reported the $CF_3BF_3^-$ anion is stable under a wide variety of conditions. It has not been possible to produce a trifluoromethyl-substituted trivalent boron from this compound.

The comparative degree of dissociation of the ammonia adduct of $(n\text{-}C_4H_9)_2BCF_3$ indicates that this compound has about the same Lewis acid strength as $(CH_3)_3B$; $(CH_3)_3BNH_3$ is 98.5% dissociated at 91.5°.[9] $(n\text{-}C_4H_9)_2BCF_3$ is expected to be a stronger Lewis acid than $(n\text{-}C_4H_9)_2BCH_3$ because of the strong electrophilic character of the trifluoromethyl group. No quantitative information is available about the acid strength of this hydrocarbon analog of $(n\text{-}C_4H_9)_2BCF_3$ but, qualitatively, it is known to be a much weaker acid than $(CH_3)_3B$ so that the expected order of acid strengths is observed.

The structure of CF_3BF_2 is confirmed by vapor state molecular weight, by fluorine analysis, and by the products of its decomposition. The infrared spectrum shows absorptions characteristic of C–F vibrations at 1080 and 1190 cm^{-1}, and absorptions characteristic of B–F vibrations at 1255 and 1460 cm^{-1}.

The loss of difluorocarbene by CF_3BF_2 is rapid and quantitative when catalyzed. The difluorocarbene must be generated in an excited electronic state since its usual mode of decay to C_2F_4, C_3F_6, etc., was not observed; only the nonvolatile polymer was formed. In a related study[12] it was observed that the reaction of CF_3HgI with excess BBr_3 gave BF_3 in sufficient amount to account for essentially all of the fluorines of the trifluoromethyl groups.

The preparation of CF_3BF_2 by the reactions

$$(n\text{-}C_4H_9)_2BCF_3 + BF_3 \longrightarrow (n\text{-}C_4H_9)_2BF + CF_3BF_2$$

$$(n\text{-}C_4H_9)_2BCF_3 + 2BF_3 \longrightarrow 2(n\text{-}C_4H_9)BF_2 + CF_3BF_2$$

may represent a group redistribution reaction by a bridge-bond mechanism[13] or a transfer of difluorocarbene in an elimination–capture equilibrium process. This matter is currently under investigation.

Acknowledgment. The authors are deeply grateful to the Office of Naval Research for financial support for this work.

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