119 were slightly larger than theoretical for natural abundances, they were on the same order of magnitude as the background currents, because of the relatively low sample pressures used (*ca.* 10^{-6} torr) and so cannot be regarded as very accurate. They are indicative that neglect of ^2H and ^{15}N could give just barely significant differences in the calculated ^{10}B abundances and that the abundances of ^2H and ^{15}N are not significantly different (to determination of ^{10}B abundance) from natural abundances. They are also indicative that ion-molecule reactions leading to $B_{10}H_9N_4^+$, etc., must be negligible under these conditions.

With ordinary laboratory chemicals and equipment, decaborane can be converted to $B_{10}H_8(N_2)_2$, the mass spectrum of which yields many more parameters than are necessary for the determination of the boron isotopic composition, without the complication of overlapping hydrogen fragmentation that is present in the spectrum of decaborane itself.

Experimental Section

Materials.—Decaborane was obtained from Callery Chemical Co. and sublimed before use. Reported methods were used to prepare $B_{10}H_8(N_2)_2$,[8] which was purified by sublimation and crystallization.

Mass Spectra.—Spectra were obtained using a Nuclide Corp. 1290 G spectrometer with a heated inlet system. All parts of the instrument except the filament itself were kept below 100° ($B_{10}H_8(N_2)_2$ decomposes at 125°). Intensities for isotope composition determination were determined by adjusting the magnet to put the desired *m/e* on the detector at an accelerating voltage of 4 kV and then scanning over the peak slowly using the accelerating voltage. Intensities were recorded on a strip-chart recorder and corrected for pressure drop with time by repeating the first intensity measurement of each run at the end of the run.

Appearance potential differences were determined from plots of log (ion current) *vs.* apparent voltage, which were parallel for *m/e* 174, 146, and 118.

Acknowledgment.—The author is indebted to Messrs. J. A. Beran and D. L. Smith for obtaining some of the mass spectra.

CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS,
WASHINGTON, D. C. 20234

Preparation and Some Reactions of Difluoroborane

BY T. D. COYLE, J. COOPER, AND J. J. RITTER

Received November 10, 1967

Difluoroborane is produced by the direct interaction of boron trifluoride with diborane in the gas phase at 100° or above. Pyrolysis of BF_3–B_2H_6 mixtures at 250° for periods of 30 min to 1 hr, followed by rapid quenching, yields HBF_2–BF_3 mixtures free of B_2H_6. An alternative, synthetically useful route is the reaction of $HB(OCH_3)_2$ with excess BF_3. Difluoroborane undergoes rapid H–F exchange with boron trifluoride and H–D exchange with deuterated diborane but does not exchange boron with diborane. Addition of difluoroborane to propene and isobutene yields *n*-propyldifluoroborane and isobutyldifluoroborane, respectively. Reactions with fluoroethylenes give boron trifluoride, ethylfluoroboranes, and less highly fluorinated olefins.

Introduction

Since our preliminary report of the synthesis of difluoroborane,[1] this compound has been intensively investigated by a variety of physical methods, including nuclear magnetic resonance,[2,3] infrared,[4–8] and microwave[9] spectroscopy. Little information has appeared, however, on the chemistry of this compound, which is the only known fluorohydride of three-coordinate boron. In this paper we report our observations on the preparative reactions utilized in the synthesis of HBF_2 and on aspects of its descriptive chemistry.

Results and Discussion

Preparative Reactions.—Two distinct routes have been found for the preparation of difluoroborane, HBF_2. The first of these is the formation of HBF_2 by the direct interaction of BF_3 and B_2H_6 which occurs, in the absence of catalysts, only under relatively vigorous conditions leading also to pyrolysis of diborane. This is in contrast to the facile hydride–halide exchange reactions observed[10] at room temperature between diborane and boron tribromide or trichloride.[11] The most useful synthetic procedure involves pyrolysis of BF_3–B_2H_6 mixtures at 250° for short periods, under which conditions HBF_2–BF_3 product mixtures containing 30–35% HBF_2 and free of B_2H_6 can be obtained. Calculations based on the thermodynamic data of Porter and Wason[6] show that the pressure of

---

[1] T. D. Coyle, J. J. Ritter, and T. C. Farrar, *Proc. Chem. Soc.*, 25 (1964).

[2] T. C. Farrar and T. D. Coyle, *J. Chem. Phys.*, **41**, 2612 (1964).

[3] E. B. Whipple, T. H. Brown, T. C. Farrar, and T. D. Coyle, *ibid.*, **43**, 1841 (1965).

[4] L. Lynds, *ibid.*, **42**, 1124 (1965).

[5] L. Lynds and C. D. Bass, *ibid.*, **43**, 4357 (1965).

[6] R. F. Porter and S. K. Wason, *J. Phys. Chem.*, **69**, 2208 (1965).

[7] M. Perec and L. N. Becka, *J. Chem. Phys.*, **43**, 721 (1965).

[8] M. Perec and L. N. Becka, *ibid.*, **44**, 3149 (1966).

[9] T. Kasuya, W. J. Lafferty, and D. R. Lide, *ibid.*, in press.

[10] H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **53**, 4321 (1931).

[11] The necessary activation can also be provided by subjecting BF_3–B_2H_6 mixtures to an electric discharge.[4] Other potentially useful routes to HBF_2 involve B_2F_4 as a starting material, *e.g.*, the reaction of B_2F_4 with H_2 in a high-frequency discharge[7] or with covalent hydrides in the gas phase: T. D. Coyle and J. J. Ritter, submitted for publication.

B_2H_6 in equilibrium with such mixtures at 250° is less than 0.1% of the partial pressure of HBF_2, and although the equilibrium favors disproportionation at lower temperatures, B_2H_6 is formed only slowly in these mixtures at room temperature or below.

We have as yet found no evidence for the formation of fluorodiborane or any volatile fluorohydrides other than HBF_2 in the BF_3–B_2H_6 system, and such compounds are not detected when HBF_2 undergoes disproportionation to BF_3 and B_2H_6. While such species must almost certainly be involved in the hydride–fluoride exchange, equilibrium concentrations may be too low to allow detection under our conditions. It has, in fact, been suggested[12] on the basis of electronegativity-equalization arguments that B_2H_5F will be unstable because of unfavorable charge distribution on the bridge hydrogen atoms. Both dihaloborane and halodiborane are formed when diborane reacts with boron trichloride[13,14] and tribromide,[14,15] while it is reported[16] that only iododiborane is formed in the reaction with boron triiodide.

A second synthetically useful route to difluoroborane is the reaction of boron trifluoride with dialkoxyboranes. A vigorous uptake of 1 mol of BF_3 per mol of dialkoxyborane occurs at low temperatures (−100°), while HBF_2 is formed only in the presence of excess BF_3. The dependence of the reaction course on the reactant ratios suggests that difluoroborane may be produced by the attack of a second molecule of boron trifluoride on a 1:1 $HB(OCH_3)_2$–BF_3 complex. Formation of such a complex, involving $O \rightarrow B$ dative bonding, would be expected to reduce the electron density on the boron atom in dimethoxyborane, either through an inductive electron withdrawal or by reducing the extent of intramolecular $p\pi$–$p\pi$ bonding. Thus, this boron atom in the complex may be rendered more susceptible to nucleophilic attack by a fluorine atom of a second molecule of BF_3. The formally similar reaction of boroxine with boron trifluoride has been studied by Porter and his co-workers.[6,17] Isotope-exchange studies[17] have shown that the boron in HBF_2 produced in the $(HBO)_3$–BF_3 reaction comes exclusively from the boroxine. In our experiments with $H^{11}B(OCD_3)_2$ and $^{10}BF_3$, infrared evidence showed that the dimethoxyborane is at least the predominant source of the boron in the product.

Exchange Reactions of HBF_2.—Difluoroborane readily undergoes H–F exchange with boron trifluoride in the gas phase at room temperature. In mixtures of HBF_2 and BF_3 differing initially in isotopic composition, the infrared spectra showed that isotopic equilibrium was attained in 2–3 hr (Figure 1).

Difluoroborane also exchanges hydrogen rapidly with diborane. When $H^{10}BF_2$ was mixed with $^{11}B_2D_6$ (with some $^{10}BF_3$ present), H–D exchange was detected as soon as the mixture was expanded into the infrared cell. Strong bands of $D^{10}BF_2$ (Figure 2) and of diboranes containing the lighter hydrogen isotope appeared in the spectrum. The exchange reaction was more than 95% complete after 1 hr at room temperature. The spectra of the $H^{10}BF_2$–$^{11}B_2D_6$ mixtures showed bands of diborane consistent with the presence of both terminal and bridging B–H,[18] indicating that hydrogen was distributed rapidly in the diborane molecule. Since hydrogen–deuterium self-exchange is known to be rapid under these conditions,[19] no conclusions can be drawn as to the site of initial exchange in the diborane.

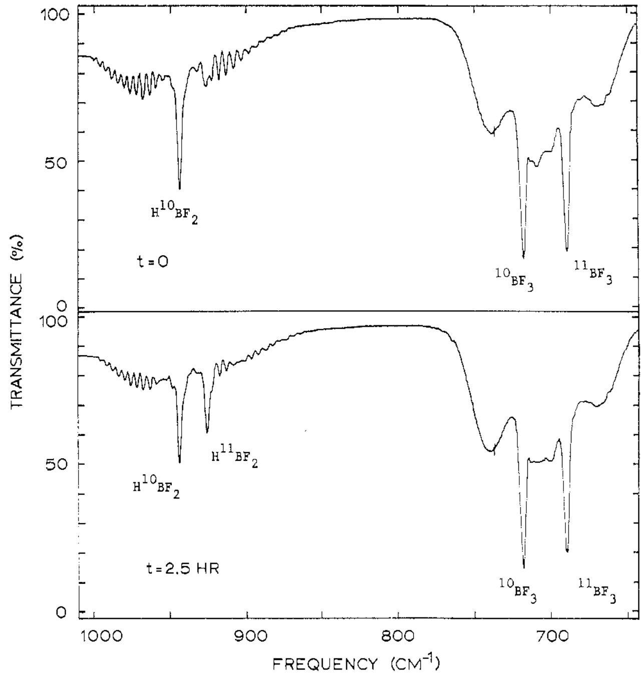


Figure 1.—A portion of the infrared spectrum of a mixture of $H^{10}BF_2$ and BF_3 containing both boron isotopes. Exchange is indicated by the appearance of the ν_6 band of $H^{11}BF_2$ at 926 cm^{-1} and a relative decrease of the 691-cm^{-1} band of $^{11}BF_3$. Initial pressures: $H^{10}BF_2$ ~15 torr; BF_3, ~35 torr.

The spectra of these $H^{10}BF_2$–$^{11}B_2D_6$ mixtures showed no significant growth of bands due to $H^{11}BF_2$ or $D^{11}BF_2$ in 48 hr at room temperature. Thus, any boron exchange, *i.e.*, H–F exchange, between diborane and difluoroborane is very much slower than the H–D exchange.

The facile H–F interchange between HBF_2 and BF_3 is reminiscent of the exchange of halogen atoms in mixtures of boron trihalides[20–22] and may occur by a similar mechanism, perhaps involving a four-center transition state. Other three-coordinate boron hydride species such as BH_3 might reasonably be expected to undergo similar H–F exchange reactions with

---

[12] R. T. Sanderson, *J. Chem. Phys.*, **21**, 571 (1963).

[13] J. V. Kerrigan, *Inorg. Chem.*, **3**, 908 (1964).

[14] J. Cueilleron and J.-L. Reymonet, *Bull. Soc. Chim. France*, 1370 (1967).

[15] S. B. Rietti and J. Lombardo, *J. Inorg. Nucl. Chem.*, **27**, 247 (1965).

[16] H. Mongeot, Thesis, University of Lyon, 1966; quoted in ref 15.

[17] M. Nadler and R. F. Porter, *Inorg. Chem.*, **6**, 1192 (1967).

[18] W. J. Lehmann, J. F. Ditter, and I. Shapiro, *J. Chem. Phys.*, **29**, 1248 (1958).

[19] (a) P. C. Maybury and W. S. Koski, *ibid.*, **21**, 742 (1953); (b) I. Shapiro and B. Keilin, *J. Am. Chem. Soc.*, **77**, 2663 (1955).

[20] L. H. Long and D. Dollimore, *J. Chem. Soc.*, 4457 (1954).

[21] L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.*, **24**, 242 (1956).

[22] T. D. Coyle and F. G. A. Stone, *ibid.*, **32**, 1892 (1960).

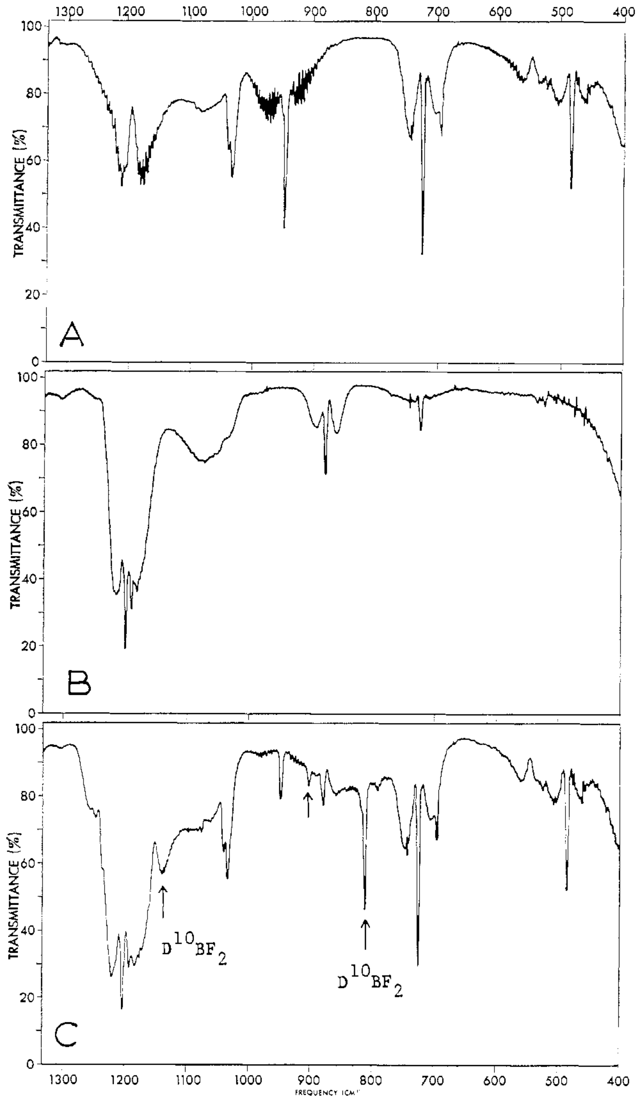
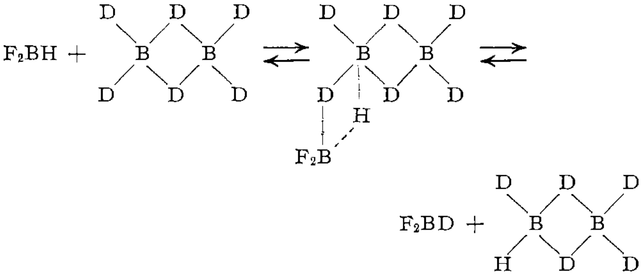
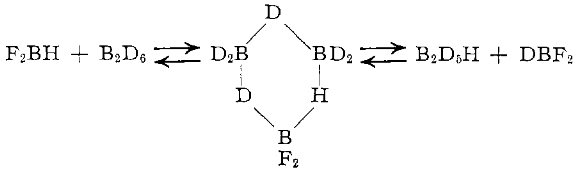


Figure 2.—Infrared spectra showing isotope exchange between $H^{10}BF_2$ and $^{11}B_2D_6$: (A) $H^{10}BF_2$–$^{10}BF_3$ mixture, 60% $H^{10}BF_2$, p = 25 torr; the band at 1031 cm^{-1} is due to SiF_4; (B) $^{11}B_2D_6$, p = 12.5 torr; (C) spectrum obtained 1.5 hr after combining samples in A and B; temperature 25°.

BF_3 or with HBF_2.[23] The absence of H–F exchange and of isotope dilution in the $H^{10}BF_2$–$^{11}B_2D_6$ system thus suggests that the principal pathway in the H–D exchange reaction at room temperature may not involve free BD_3. Hydrogen isotope exchange could occur by mutual displacement without cleavage of the bridge



or *via* a triborane intermediate in which one bridge bond is preserved



The exchange behavior of difluoroborane is similar in some respects to that of diethoxyborane, which rapidly exchanges hydrogen, but not boron, with diborane in the gas phase at room temperature.[24] Diethoxyborane, like the methyl analog, reacts with BF_3 to form HBF_2. As noted above, however, this reaction appears to involve predominantly alkoxy–fluorine exchange, with little or no H–F exchange.

Boron isotope exchange between HBF_2 and B_2H_6 might have been expected to result from the equilibration of difluoroborane, diborane, and boron trifluoride in this system, together with self-exchange of diborane. The mass action product, $p(HBF_2)/p(B_2H_6)^{1/6}p(BF_3)^{2/3}$, for the initial pressures in these experiments was greater than the equilibrium constant.[6] Thus, disproportionation of HBF_2 was favored. However, the approach to equilibrium is quite slow at room temperature. Addition of a trace (*ca.* 1 mol %) of BCl_3 to the cell after 48 hr resulted in a slow decrease in the total concentration of HBF_2 and the appearance of bands of $H^{11}BF_2$ and $^{11}BF_3$ which we attribute to acceleration of the equilibration by BCl_3. As noted in the Experimental Section, traces of the heavier boron trihalides were observed in other experiments to promote the reaction of BF_3 with B_2H_6.

It should also be noted in this context that several reports[13,14,17] suggest that exchange reactions of boron trihalides and diborane may be subject to catalysis (or inhibition) by other constituents of the mixture or by oxide materials present in the reaction vessel.

Reactions of Difluoroborane with Olefins.—Difluoroborane adds readily to ethylene, forming ethyldifluoroborane.[1] Since the pyrolysis procedure provides a convenient route to HBF_2, the direct addition of this hydride to olefins offers a useful procedure for synthesis of organodifluoroboranes that does not require the use of an organometallic reagent.

Examination by infrared and nmr spectroscopy of the products obtained from the reaction of HBF_2 with propene and isobutene showed them to be *n*-propyl- and isobutyldifluoroborane, respectively. Thus, in the gas-phase hydroboration of these olefins with HBF_2, addition is anti-Markownikoff in the sense that the boron atom becomes attached to the least substituted olefinic carbon atom.

(23) From a study of boron isotope exchange in the reaction of $LiBH_4$ with BF_3 in ether (J. W. Kury and W. L. Jolly, University of California Radiation Laboratory Report UCRL-4432, 1954), it was concluded that no exchange occurs between BH_3 and BF_3, fluoroboranes, or fluoroborohydrides. However, some or all of these species will involve four-coordinate boron in ether solution. Halogen exchange occurs at 0° between three- and four-coordinate boron in the reactions of $(C_2H_5)_3NBF_3$ with BCl_3 and of $(C_2H_5)_3NBCl_3$ with BF_3 [T. D. Coyle, *Proc. Chem. Soc.*, 172 (1963)]. Experiments performed in this laboratory indicate, however, that H–F exchange is not a significant process in the reaction of $(C_2H_5)_3NBH_3$ with BF_3 under comparable conditions.

(24) W. J. Lehmann, T. P. Onak, H. G. Weiss, and I. Shapiro, *J. Chem. Phys.*, **30**, 1214 (1959).

The hydroboration of unsymmetric olefins with B_2H_6 and organoboranes similarly gives, under most circumstances, the products of anti-Markownikoff addition. This observation and the *cis* addition stereochemistry of the reaction are rationalized in terms of a four-center transition state and the polarity of the B–H bond.[25] It has been reported,[26,27] however, that addition of $HBCl_2$ to propene and isobutene in gas- or liquid-phase reactions gives products, identified on the basis of boiling points, as isopropyl- and *t*-butyldichloroborane, *i.e.*, that Markownikoff addition occurs. Addition of $HBCl_2$ and H_2BCl in the anti-Markownikoff sense has, however, been observed[28–30] in reactions carried out in ether solvents.[31]

Reaction of HBF₂ with Vinyldifluoroborane.—This reaction was of interest in connection with studies of bis(dihaloboryl)ethanes obtained from reactions of diboron tetrahalides with unsaturated organometallic compounds[32] and because of its relation to the problem of dihydroboration of acetylenes. In general, the latter reactions occur preferentially in such a way as to place two boron atoms on the same carbon, although some formation of vicinal diboron compounds may occur, and, in some cases, steric factors may inhibit the second addition.[33]

The recovery of small amounts of the stable, known[34] compound, 1,2-bis(difluoroboryl)ethane, indicated that addition of HBF_2 to $C_2H_3BF_2$ occurs to a minor extent (<5%) with attachment of boron to the unsubstituted carbon atom

$$HBF_2 + CH_2{=}CHBF_2 \longrightarrow F_2BCH_2CH_2BF_2$$

The major reaction resulted, however, in the essentially quantitative formation of 1 mol of BF_3 per mol of HBF_2 (or $C_2H_3BF_2$) and of an involatile liquid with a composition closely approaching $(C_2H_4BF)_n$. These observations are consistent with a reaction sequence involving predominant addition of the boron atom to the α-carbon atom of vinyldifluoroborane, followed by rapid elimination of BF_3 and polymerization of the organoboron fragment

$$HBF_2 + CH_2{=}CHBF_2 \longrightarrow [CH_3CH(BF_2)_2] \longrightarrow BF_3 + (1/n)(CH_3CHBF)_n$$

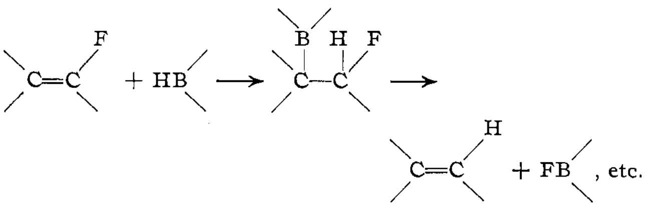
The proposed intermediate, 1,1-bis(difluoroboryl)ethane, may be viewed as a heteroatom analog of a β-haloorganoborane. The postulated elimination is similar to the eliminations, involving transfer of a β-halogen atom to boron, which have been invoked to account for the instability of the hydroboration products of vinyl chloride[35] and 3-chlorocyclohexene[36] and which are believed to be involved in the hydroboration reactions of fluoroolefins.[37–39]

An analogous addition–elimination sequence has been observed in the reaction of dimethylborane (from tetramethyldiborane) with 3,3,3-trifluoropropene, the "carbon analog" of vinyldifluoroborane.[38] The addition occurs principally to place the boron on the 2-carbon atom. The intermediate β-haloorganoborane decomposes with the elimination of dimethylfluoroborane

$$HB(CH_3)_2 + CH_2{=}CHCF_3 \longrightarrow CH_3CH(CF_3)B(CH_3)_2 \xrightarrow{100°} (CH_3)_2BF + CH_3CH{=}CF_2$$

As in the vinyldifluoroborane–difluoroborane reaction, addition of boron to the terminal carbon atom is also observed. Similarly, the hydroboration of 3,3,3-trifluoropropene with diborane occurs predominantly with attachment of boron at the 2 position.[39]

Reactions of HBF₂ with Fluoroethylenes.—The reactions of HBF_2 with mono-, di-, and trifluoroethylenes all gave essentially similar results. In each case, ethylboron compounds (principally $C_2H_5BF_2$), BF_3, and a fluoroethylene containing one less fluorine atom than the reactant olefin were obtained, together with unreacted starting materials. The results are consistent with the reaction scheme suggested by Stone and his co-workers[37] in their study of the reactions of the fluoroethylenes with diborane. Successive additions and eliminations were proposed



leading ultimately to ethylene, which would undergo final B–H addition to form ethylboranes. Difluoroborane was proposed as one intermediate in this reaction sequence.

Some insight into the details of the reaction is afforded by the interaction of $CH_2{=}CF_2$ with DBF_2.

---

[25] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[26] L. Lynds and D. R. Stern, *J. Am. Chem. Soc.*, **81**, 5006 (1959).

[27] D. R. Stern and L. Lynds, British Patent 853,379 (1960).

[28] D. R. Pasto and P. Balasubramaniyan, *J. Am. Chem. Soc.*, **89**, 295 (1967).

[29] T. A. Shchegoliva, E. M. Shashkova, V. G. Kiselov, and B. M. Mikhailov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **2**, 365 (1964).

[30] G. Zweifel, *J. Organometal. Chem.* (Amsterdam), **9**, 215 (1967).

[31] We have carried out a few experiments on the reactions of $HBCl_2$ with propene and isobutene in the absence of solvent. The proton magnetic resonance spectra of the organodichloroboranes recovered from the reaction mixture clearly showed them to be exclusively the *n*-propyl and isobutyl derivatives, *i.e.*, the anti-Markownikoff products. In our experiments, BCl_3 and B_2H_6 were present in the $HBCl_2$ used, and may conceivably have influenced the direction of addition. The literature suggests, however, that rigorous exclusion of these contaminants from $HBCl_2$ is experimentally difficult. In the earlier hydroboration studies[26] with $HBCl_2$, this compound was observed to disproportionate to BCl_3 and B_2H_6 at 25°. The half-time for the disproportionation is said to be approximately 30 min [L. Lynds and C. D. Bass, *Inorg. Chem.*, **3**, 1147 (1964)]. It is known [D. J. Pasto and C. C. Cumbo, *J. Am. Chem. Soc.*, **86**, 4343 (1964)] that the presence of BF_3 reverses the direction of addition of BH in the hydroboration of 4-*t*-butylethoxycyclohexene, in tetrahydrofuran. However, BF_3 has no effect on the hydroboration of styrene, in which there is no alkoxy substituent capable of functioning as a Lewis base toward BF_3. It seems likely, therefore, that the direction of addition of $HBCl_2$ in the absence of solvent is the same as observed with $HBCl_2$ in ether and with HBF_2.

[32] T. D. Coyle and J. J. Ritter, *J. Organometal. Chem.* (Amsterdam), in press.

[33] Reference 25, Chapter 16.

[34] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **81**, 6368 (1959).

[35] M. F. Hawthorne and J. Dupont, *J. Am. Chem. Soc.*, **80**, 5830 (1958).

[36] P. Binger and R. Köster, *Tetrahedron Letters*, 156 (1961).

[37] B. Bartocha, W. A. G. Graham, and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **6**, 119 (1958).

[38] J. M. Birchall, R. N. Haszeldine, and J. F. Marsh, *Chem. Ind.* (London), 1080 (1961).

[39] J. R. Phillips and F. G. A. Stone, *J. Chem. Soc.*, 94 (1962).

The deuteriovinyl fluoride isolated was exclusively $CH_2{=}CFD$. This strongly implies that the initial addition involves attachment of boron to the 2-carbon and hence that the elimination step involves a fluorine in the β position relative to the boron atom. Addition in the opposite direction, followed by α elimination, would be expected to lead to formation of a carbene intermediate which could undergo an intermolecular insertion or rearrangement to an olefin. The observed 97% recovery of carbon as C_2 fragments argues against the significant occurrence of insertion reactions, while the isomeric purity of the monodeuterated vinyl fluoride would seem to exclude the carbene rearrangement.

The formation of *cis*-difluoroethylene in the reaction of HBF_2 with trifluoroethylene can similarly be viewed in terms of an addition–elimination sequence. It is of interest that Stone and his co-workers observed formation of both 1,1- and 1,2-difluoroethylenes in the reactions of diborane with tri- and tetrafluoroethylene. This may reflect the presence of processes other than β elimination in the formation of the olefin or may indicate that the extent of addition in different directions to unsymmetrical fluoroethylenes varies for the several intermediates possible in the reaction with diborane.

Experimental Section

Apparatus and Techniques.—Manipulations were carried out using standard vacuum-line techniques. Infrared spectra in the range 4000–400 cm^{-1} were recorded with a commercial double-beam grating spectrophotometer. Gaseous samples and reaction mixtures for isotope exchange studies were contained in borosilicate glass cells fitted with glass and fluorocarbon polymer O rings. Infrared spectroscopic identifications of reaction products were based on comparison with literature spectra or with spectra of authentic samples prepared by alternate routes. Nuclear magnetic resonance spectra were obtained with a standard commercial 60-MHz proton magnetic resonance spectrometer or with the modified spectrometer described in a previous publication from this laboratory.[40] Mass spectrometric analyses were performed by Mr. W. Dorko of the Microchemical Analysis Section of the NBS.

Reagents.—Except as noted, starting materials were obtained from commercial sources and were purified by vacuum line fractionation before use. Isotopically labeled boron compounds were derived by standard procedures from ^{10}B- or ^{11}B-enriched boron trifluoride obtained from Oak Ridge National Laboratory in the form of calcium fluoride or dimethyl ether complexes. Dimethoxyborane was prepared by the methanolysis of diborane, according to the procedure of Burg and Schlesinger.[41] Vinyldifluoroborane was prepared by the reaction of tetravinyltin with boron trifluoride.[42] Unless otherwise specified, no significant impurities were detectable in the infrared spectra of the compounds used in this work.

The Interaction of B_2H_6 with BF_3.—To the limits of detection by infrared spectroscopy, no boron isotope exchange was observed between ^{10}B-enriched BF_3 and isotopically normal B_2H_6, and no new species were formed, when equimolar mixtures were heated at 60° for 16 hr at 1 atm total pressure. After pyrolysis at 100° for 16 hr, however, the volatile fraction obtained following removal of noncondensables and higher boron hydrides showed, in addition to infrared absorption bands of BF_3 and unreacted B_2H_6, bands attributable to HBF_2. Under these conditions, isotopic dilution of the BF_3 and the presence in the HBF_2 of boron derived from both reactants were evident from the infrared spectrum of the reaction mixture. Typically, samples containing 5–10% HBF_2 could be prepared in this manner. In the presence of small amounts (0.3 mol %) of BBr_3, comparable amounts of HBF_2 were formed at 60° or below, without degradation of B_2H_6. Minute yields of purified HBF_2 were obtained after repeated fractionation in the vacuum line.

The results of pyrolysis experiments carried out at higher temperatures are summarized in Table I. In each case the stated quantities of BF_3 and B_2H_6 were heated in a 200-ml bulb under the conditions indicated. At the end of the reaction period, the contents were frozen at −196°, the bulb was opened into the vacuum line, and hydrogen formed in the pyrolysis was removed with a Toepler pump and measured. Material volatile at room temperature was fractionated through a −115° trap to remove B_5H_9. The infrared spectrum of the volatile fraction showed in each case that the sample contained only BF_3 and HBF_2. (Traces of B_2H_6 were found in the products of similar experiments when the reaction mixtures were allowed to cool slowly to room temperature but were absent if the mixture was frozen immediately upon removal from the oven.) The HBF_2 content of the gas mixture was determined by measurement of the hydrogen produced by hydrolysis in distilled water at 100° overnight. The major part of the BF_3 could be removed from these product mixtures by rapid distillation through a −130° trap; final traces were separated by slow distillation through a −165° trap, through which a portion of the HBF_2 slowly passes.

Table I

Products from the Reaction of B_2H_6 with BF_3

Reactants, mmol			Products, mmol				Yield,	Conversion,
BF_3	B_2H_6	Conditions	H_2	BF_3	HBF_2	B_5H_9	%[a]	%[b]
2.23	1.12	150°, 48 hr	2.03	1.64	0.77	0.04	23.0	87.0
2.19	0.55	150°, 48 hr	0.92	1.72	0.63	0.02	19.2	89.4
2.22	1.14	250°, 0.5 hr	2.16	1.61	0.82	0.04	24.6	89.6
2.22	0.55	250°, 0.5 hr	0.92	1.70	0.73	0.02	22.1	93.6

[a] Yield of HBF_2 based on maximum attainable from reaction mixture. [b] Based on BF_3 consumed, assuming $4BF_3 + B_2H_6 \rightarrow 6HBF_2$.

Reactions of Dimethoxyborane with Boron Trihalides.—Dimethoxyborane reacted vigorously with an equimolar quantity of boron trifluoride at −100° or below to yield a liquid product, which is apparently an addition compound, having slight vapor pressure at −78.5°. On standing at room temperature, this product evolved diborane, and the melting point of the liquid rose slowly. In one experiment, 11.51 mmol of $HB(OCH_3)_2$ and an equal quantity of BF_3 were combined in a 100-ml bulb, allowed to react at low temperature, and then held at room temperature for 64 hr. Fractionation gave 1.21 mmol of B_2H_6 [H equivalent to 63% of the inital $HB(OCH_3)_2$].

The less volatile products were found to be $HB(OCH_3)_2$, $B(OCH_3)_3$, CH_3OBF_2 (all identified from their infrared spectra), and a liquid, with an infrared spectrum like that of the original addition product, which slowly evolved B_2H_6 on standing.

In contrast to the results obtained at 1:1 reactant ratios, reaction of $HB(OCH_3)_2$ with excess BF_3 gave HBF_2 as a significant product. In a typical preparative run, $HB(OCH_3)_2$ (3.88 mmol) and BF_3 (7.84 mmol) were condensed into a 100-ml bulb. A vigorous reaction (complex formation) again occurred as the mixture warmed to the melting point. When the mixture was warmed to room temperature, the liquid in the bulb underwent a further rapid reaction, and a white crystalline deposit quickly covered the walls of the bulb. After 20 min, the bulb was opened. The fraction passing −140° consisted of 3.61 mmol of a mixture of B_2H_6, HBF_2, and BF_3. The B_2H_6 content was estimated from the infrared spectrum to be about 10%. Hydrogen liberated on hydrolysis of the mixture was 80.1% of the total in the original $HB(OCH_3)_2$. The remaining material, consisting principally of

---

[40] R. B. Johannesen, T. C. Farrar, F. E. Brinckman, and T. D. Coyle, *J. Chem. Phys.*, **44**, 962 (1966).

[41] A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4020 (1933).

[42] F. E. Brinckman and F. G. A. Stone, *ibid.*, **82**, 6218 (1960).

CH_3OBF_2 and some of the liquid addition product, liberated 0.91 mmol of hydrogen on hydrolysis (equivalent to 23.3% of the hydride originally present). Experiments in which the ratio of $HB(OCH_3)_2$ to BF_3 was between 1:1 and 1:2 gave mixtures of HBF_2, B_2H_6, and BF_3 similar in composition to that obtained with the 1:2 reactant ratio, in amounts approximately equal to the excess over 1:1 of the BF_3 taken.

To ascertain the source of the boron in HBF_2 as originally formed in the reaction, a small sample[43] of $H^{11}B(OCD_3)_2$ was combined with a twofold excess of $^{10}BF_3$ in a cold finger attached directly to an infrared cell. The cold finger was then inserted in a Dry Ice–ethanol bath and the spectrum of the gas in contact with the mixture was recorded. Within a few minutes, small amounts of HBF_2 were detected. Comparison of the bands of HBF_2 at 926 and 944 cm^{-1} showed that the HBF_2 initially produced was highly enriched in ^{11}B but that equilibration with the excess $^{10}BF_3$ present in the infrared cell occurred within minutes.

In order to determine whether this reaction could be extended to the preparation of dichloroborane, reactions of boron trichloride with dimethoxyborane in 1:1 and 1:2 ratios were investigated. A mixture of BCl_3 (3.78 mmol) and $HB(OCH_3)_2$ (3.73 mmol), in a 100-ml bulb, reacted near the melting point of the mixture to give a product which was liquid at room temperature. Fractionation of the contents of the bulb after 17 hr at room temperature gave a trace of B_2H_6, CH_3Cl (0.45 mmol), BCl_3 (0.18 mmol), and CH_3OBCl_2 (2.02 mmol), together with an involatile white solid that evolved CH_3OBCl_2 and traces of B_2H_6 and CH_3Cl on standing.

Experiments in which $HB(OCH_3)_2$ and BCl_3 were taken in *ca.* 1:2 molar ratio gave no evidence for the rapid secondary reaction observed in the BF_3–$HB(OCH_3)_2$ system. The products of the reaction of 3.89 mmol of $HB(OCH_3)_2$ and 7.75 mmol of BCl_3, held at room temperature in a 100-ml bulb for 6 hr, consisted of B_2H_6 (0.12 mmol), B_2H_5Cl (0.07 mmol), $HBCl_2$ (trace), and CH_3OBCl_2 and BCl_3 (*ca.* 3.3 mmol each), together with an involatile white solid which evolved CH_3OBCl_2, CH_3Cl, and B_2H_6 on standing. The total hydrogen appearing in the volatile products was 27.3% of that contained in the original $HB(OCH_3)_2$.

Reaction of HBF_2 with Unsaturated Compounds. Olefins.— Reactions were carried out in sealed glass bulbs with reactants in the gas phase. Since highly purified samples of HBF_2 were observed to undergo slow disproportionation to B_2H_6 and BF_3 under the conditions of these experiments, HBF_2–BF_3 mixtures containing 70–90% of the hydride were used to repress the formation of B_2H_6 and to avoid major accumulation of the products of hydroboration of the olefin by B_2H_6. The use of hydride mixtures containing different amounts of BF_3, with and without B_2H_6 present, had no apparent effect on the nature or stereochemistry of the addition reaction.

In a typical reaction, propene (2.00 mmol) was combined with 2.25 mmol of a BF_3–HBF_2 mixture containing 85% (1.91 mmol) of HBF_2 (as indicated by gas density). After 23 hr at room temperature, the contents of the bulb were fractionated in the vacuum line through traps held at −78.5 and −130° into a −196° trap. The −196° fraction (0.50 mmol) consisted of BF_3, with traces of B_2H_6 and HBF_2. The infrared spectrum of the −78.5° fraction (0.14 mmol) indicated the presence of a 1,1-dialkyldiborane. The −130° fraction (1.55 mmol) was identified as *n*-propyldifluoroborane on the basis of the molecular weight (found, 92.3; calcd, 91.8) and infrared and nuclear magnetic resonance spectra. The infrared spectrum of the product was identical with that of $C_3H_7BF_2$ prepared by the reaction of tetra-*n*-propyltin with boron trifluoride[42,44] and distinctly different from that obtained from tetraisopropyltin (Figure 3).

The proton magnetic resonance spectrum of the hydroboration product was that of the *n*-propyl isomer (Figure 4). The ^{19}F nmr spectrum of the pure liquid at 56.4 MHz consisted of four broad lines of approximately equal intensity with a separation of *ca.* 81 Hz, centered 62 ppm to low field of the peak from an external perfluorocyclobutane reference (+76 ppm relative to external trichlorofluoromethane). The values agree with previously reported ^{19}F nmr parameters for the *n*-propyl isomer.[45] The chemical shift of isopropyldifluoroborane was found to be +82 ppm on the CCl_3F scale; the quartet splitting was 95 Hz.

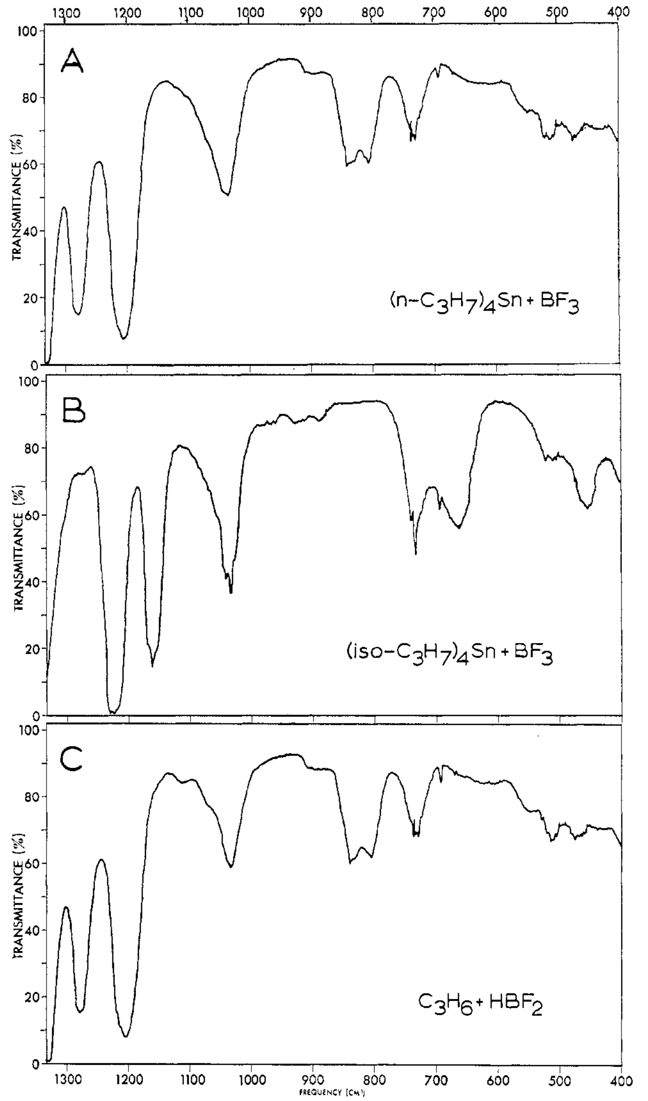


Figure 3.—Infrared spectra of propyldifluoroboranes: (A) product of reaction of tetra-*n*-propyltin with boron trifluoride; (B) product from tetraisopropyltin and boron trifluoride; (C) product of addition of difluoroborane to propene.

The gas-phase reaction of HBF_2 with isobutene (2-methylpropene) led to extensive polymerization of the olefin. Small amounts of a product (10.5% based on olefin taken) were isolated. The molecular weight (found, 105; calcd for $C_4H_9BF_2$, 105.9) and infrared spectrum were consistent with formulation as a butyldifluoroborane. The proton magnetic resonance spectrum consisted of a weak multiplet of at least six lines ($J \sim 7$ Hz) centered at −1.87 ppm and a doublet ($J \sim 7$ Hz) at −0.93 ppm (external tetramethylsilane, 0), with observed relative intensities

---

[43] T. C. Farrar, J. Cooper, and T. D. Coyle, *Chem. Commun.*, 610 (1966).

[44] In the course of preparing the comparison samples from the isomeric tetrapropyltins and boron trifluoride, it was observed that the *n*-propyltin compound was considerably more reactive toward BF_3 than the isopropyl analog. Thus, *n*-$C_3H_7BF_2$ was obtained in good yield from a sealed bulb reaction in 20 hr at 110°. Only traces of *i*-$C_3H_7BF_2$ were recovered after 42 hr at 110°, and the reaction required further heating for 109 hr at 150°. Infrared and proton magnetic resonance spectra demonstrated that the propyl groups were transferred without isomerization under these vigorous conditions.

[45] T. D. Coyle and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6223 (1960).

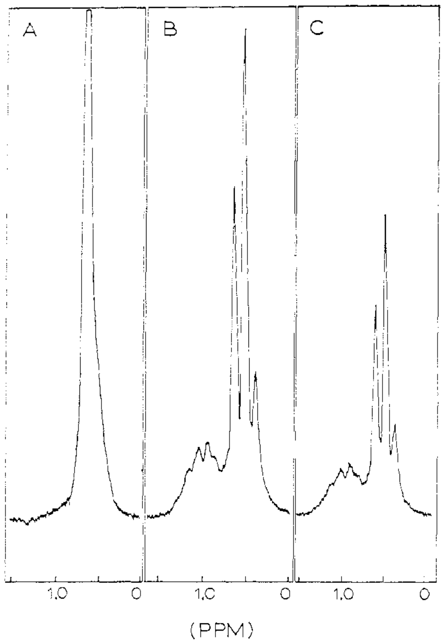


Figure 4.—Proton magnetic resonance spectra of propyldifluoroboranes. Chemical shift scale is relative to external tetramethylsilane: (A) product from tetraisopropyltin and boron trifluoride; (B) product from tetra-*n*-propyltin and boron trifluoride; (C) product of addition of difluoroborane to propene.

approximately 1:7. The observed spectrum clearly excluded *t*-, *sec*-, or *n*-butyl structures and is consistent with the presence of an isobutyl group in which the chemical shifts of the CH_3 and CH_2 resonances are identical, or nearly so. The ^{19}F spectrum was typical of a BF_2 group, with a chemical shift of +81 ppm relative to CCl_3F and $J \sim 88$ Hz.

Vinyldifluoroborane.—A mixture of 2.90 mmol of vinyldifluoroborane and 3.11 mmol of difluoroborane (0.78 mmol of BF_3 initally present) gave, after 18 hr at room temperature, 2.81 mmol (net) of BF_3 containing traces of HBF_2 and 0.09 mmol of 1,2-bis(difluoroboryl)ethane, identified from the infrared spectrum. The other major product was a colorless liquid, involatile at room temperature. Prolonged pumping (18 hr) on this material at 0–25° yielded small quantities of a more volatile product, condensing at −78.5°, which decomposed partially on warming to BF_3 and an involatile oil. The gross composition of the major involatile product was evaluated by difference from the quantities of reactants and of the characterized volatile products. In three separate experiments, the C:B:F ratio was found to range from 2.00:1.03:1.04 to 2.00:1.06:1.10. Reaction of 0.235 g of this material with glacial acetic acid at 80° for 20 hr gave 2.94 mmol of gas determined by mass spectrometric analysis to be principally ethane with traces of butane. The proton magnetic resonance spectrum indicated the absence of protons bonded to unsaturated carbon.

Fluoroethylenes.—Reactions of HBF_2 with fluoroethylenes are summarized in Table II. Product mixtures were separated in the vacuum line into fractions retained in traps held at −115, −130, and −196°. The −196° fractions, which were mixtures of HBF_2, BF_3, and fluoroethylenes, were hydrolyzed with water. The HBF_2 was determined by measurement of evolved hydrogen. The fluoroethylene mixtures were recovered from the hydrolysis bulbs, measured, and analyzed mass spectrometrically. The BF_3 was determined by difference. The −130° fractions consisted of $C_2H_5BF_2$. When CHF=CHF was present, this olefin was retained in the −130° fractions, from which it could be separated by removal of the $C_2H_5BF_2$ with $(CH_3)_3N$. The recovered $(C_2H_5)_2BF$ was contained in the −115° fractions.

Table II

Reaction of HBF_2 with Fluoroethylenes

	Olefin			
	$CH_2{=}CHF$	$CH_2{=}CF_2$	$CHF{=}CHF$	$CHF{=}CF_2$
Conditions	89 hr, room temp	14 days, 40°	9 days, 40°	17 days, 40°
Reactants (mmol)				
Olefin	3.46	3.33	3.22	3.23
HBF_2[a]	2.6	3.0	2.5	2.5
Recovered (mmol)				
HBF_2	0.15	0.16	0.17	0.42
$C_2H_5BF_2$	0.85	0.54	0.46	0.18
$(C_2H_5)_2$-BF,	0.12	0.02	...	...
BF_3 (net)	1.40	2.24	1.81	1.86
Other	2.26 ($CH_2{=}CHF$)	1.67 ($CH_2{=}CF_2$) 0.98 ($CH_2{=}CHF$)	2.42 ($CHF{=}CHF$) 0.04 (unident.)	2.34 ($CHF{=}CF_2$) 0.43 ($CHF{=}CHF$) 0.02 (unident.)

[a] Reactant mixtures contained 6–12% BF_3. Quantity of HBF_2 is estimated from vapor density of HBF_2–BF_3 and from infrared spectra and is believed to be correct to within ±0.2 mmol or less.

In one experiment, $CH_2{=}CF_2$ was treated with DBF_2 under conditions similar to those in Table II. The proton magnetic resonance spectrum of the resulting fluoroethylene mixture showed that both the difluoroethylene and a deuterated vinyl fluoride were present. The spectrum of the latter was compared with spectra calculated for the three possible isomers of C_2H_2DF using parameters for vinyl fluoride,[46] with coupling constants suitably adjusted for the presence of a single deuterium atom. The observed spectrum agreed with that calculated for $CH_2{=}CDF$.

Acknowledgments.—We thank Dr. F. E. Brinckman for communicating the results of unpublished work on the BF_3–B_2H_6 system and for helpful discussions during the course of this work. We are indebted, also, to Dr. R. B. Johannesen for assistance in nuclear magnetic resonance measurements and to Dr. John R. Phillips for the gift of a sample of tetraisopropyltin.

(46) C. N. Banwell and N. Sheppard, *Proc. Roy. Soc.* (London), **A263**, 136 (1961).