# HYDRIDE-TRANSFER REACTIONS OF BORINE—I

## SYNTHESIS OF BORON-CARBON BONDS FROM THE **FLUOROETHYLENES**

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Abstract—The effect of diborane on four fluoroethylenes: tetrafluoroethylene, trifluoroethylene, 1:1-difluoroethylene and vinyl fluoride, has been studied at ordinary temperatures, and at higher temperatures. The reactions follow an essentially similar course, and in all cases complex mixtures are obtained. Fluorine in the ethylenes is first replaced by hydrogen, and boron in the products appears mainly as boron trifluoride, ethylboron difluoride, diethylboron fluoride and triethylboron. In the diborane-tetrafluoroethylene reaction polymerization of the olefin takes place with incorporation of some boron in the polymer. Moreover, distribution of boron in the volatile products is in the order  $BF_a > EtBF_a \gg EtBF_a > Et_aBF$ . This order changes as the fluorine content of the olefin decreases. Thus with vinyl fluoride it is,  $EtBF_{2} > Et_{2}BF \gg BF_{3} \sim Et_{2}B$ .

The ethylboron fluorides are the main product of the reaction between tetrafluoroethylene, diborane and triethylboron.

Under conditions similar to those in which fluoroethylenes underwent complete leaction, diborane failed to react with saturated fluorocarbons such as ethyl fluoride.

A possible mechanism for the reactions between diborane and the fluoroethylenes is discussed.

DIBORANE reacts with a variety of electron-donor molecules able to promote dissociation of the hydride into borine<sup>±</sup> fragments. However, compounds containing unsubstituted borine groups are not always found as ultimate products of boron hydride reactions.<sup>(1,2)</sup> This is because co-ordination of BH<sub>3</sub> with donor molecules can sometimes be followed by elimination of molecular hydrogen, or by a hydridetransfer reaction. In either event, a BH<sub>2</sub>-derivative is produced. Such derivatives polymerize, and, moreover, often also disproportionate, giving other products.

In the majority of cases so far investigated the hydride-transfer mode of decomposition proceeds so rapidly that isolation of the borine adduct is impossible. Nevertheless, its transitory existence may be inferred from the nature of the final reaction products, and by the known behaviour of BH<sub>3</sub> in other situations.

It is expected that this paper will be the first in a series concerned with the effect of borine, or its derivatives, on donor molecules where co-ordination is followed by rearrangement and disproportionation.

Olefins represent one class of donor molecule where treatment with borine leads to hydride transfer. Thus, diborane and ethylene yield triethylboron. It has been

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 ‡ It has been recommended by a nomenclature committee of the American Chemical Society that the BH<sub>3</sub> group be termed the borane group. See Chem. Engng. News 34, 560 (1956). However, the Referees objected to the use of this new nomenclature in this paper, because the matter is still being debated. <sup>(1)</sup> A. B. BURG Rec. chem. Progr. 15, 159 (1954).

<sup>&</sup>lt;sup>(2)</sup> F. G. A. STONE Quart. Rev. 9, 174 (1955).

suggested<sup>(3)</sup> that this reaction proceeds through association of borine with one of

the carbon atoms of ethylene, viz. CH<sub>2</sub>·CH<sub>2</sub>·BH<sub>3</sub>. However, in comparison with other Group III acceptor molecules borine has an unusual co-ordination chemistry.<sup>(4)</sup> In view of this it is perhaps more likely that addition of borine to ethylene or other olefins occurs through a kind of  $\pi$ -complex intermediate in which a molecular bond orbital covers both carbon atoms and the boron atom at the same time.<sup>(5)</sup> In the case of ethylene, hydride transfer from boron to carbon would give ethylborine, EtBH<sub>2</sub>. Disproportionation would occur, producing first Et<sub>2</sub>BH and then the final product triethylboron. An alternative route for forming triethylboron would be by reaction between the ethylborines and ethylene, again with hydride transfer.

Diborane is now easily prepared, and clearly as a method for preparing organoboron compounds, reaction between this hydride and the carbon-carbon  $\pi$ -bond is capable of wide variation because the hydrogen atoms of ethylene may be substituted by other atoms or groups. Treatment of diborane with these substituted ethylenes should afford hitherto unknown organoboron compounds, or compounds already known but obtained by other and sometimes more difficult methods.

This paper describes the effect on the borine-ethylene reaction of substituting ethylenic hydrogen by fluorine atoms.

### 1. EXPERIMENTAL

### Purification and handling of materials

The tetrafluoroethylene supplied was reported as having no impurities, other than polymerization inhibitor, at concentrations greater than 10 p.p.m. After the inhibitor had been removed by chemical means, an analysis gave M = 100.2. (Calc. for C<sub>2</sub>F<sub>4</sub>: M, 100.0; v.p. (vapour-pressure) 62.24 mm at  $-111.9^{\circ}$ C (in reference 6, 62.27 mm). Purity of other fluorocarbons used in this work was similarly checked after distillation in vacuo: CF<sub>2</sub>:CH<sub>2</sub> (Found: M, 63.8. Calc. for C<sub>2</sub>H<sub>2</sub>F<sub>2</sub>: M, 64.02) v.p. 21.75 mm at -130°C. CFH:CH<sub>2</sub> (Found: M, 46.18. Calc. for C<sub>2</sub>H<sub>3</sub>F: M, 46.04) v.p. 43.65 mm at -111.9°C. CF<sub>3</sub>:CFH (Found: M, 82.04. Calc. for C<sub>2</sub>HF<sub>3</sub>: M, 82.03) v.p. 19.80 mm at -111.9°C.  $C_{2}H_{5}F$  (Found: M, 48.5. Calc. for  $C_{2}H_{5}F$ , M, 48.1) v.p. 195 mm at  $-63.5^{\circ}C$ . The ethylene used had a v.p. of 453 mm at  $-111.9^{\circ}$ C (in reference 7, 455 mm).

The diborane used had a v.p. 225.5 mm at  $-111.9^{\circ}\text{C}$  (in reference 8, 225.0 mm).

All experiments were conducted using a high-vacuum system of conventional design. Vapourpressure measurements on the ethylboron fluorides were made using a tensimeter.<sup>(9)</sup> All temperatures below 0°C were determined using vapour-pressure thermometers.

During the work here described extensive use was made of infra-red spectra as a means of qualitatively identifying constituents of gaseous mixtures. Spectra were recorded, using a Model 21 Perkin-Elmer double-beam spectrometer, and a 4 cm gas cell equipped with KBr windows.

Pure samples of the fluorocarbons, as well as mixtures of known composition, were used to calibrate the mass spectrometer employed in this work.

Microanalyses were made by the Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Gas non-condensable at the temperature of liquid nitrogen was collected in a gas burette by means of an automatic Sprengel pump. As this pump\* has not been described in the chemical literature, yet is extremely useful, a brief description is given here. Pellets of mercury, spilling intermittently from the

\* The apparatus in essentially this form had its origin in the laboratory of Professor Burg, where it was devised by R. I. WAGNER, F. G. A. STONE and A. B. BURG.

- (6) G. T. FURUKAWA, R. E. MCCOSKEY and M. L. REILLY J. Res. nat. Bur. Stand. 51, 69 (1953).
  (7) R. T. SANDERSON Vacuum Manipulation of Volatile Compounds. John Wiley, New York (1948).
  (8) A. B. BURG J. Amer. chem. Soc. 74, 1340 (1952).
  (9) A. B. BURG J. Amer. chem. Soc. 74, 1340 (1952).

- (\*) A. B. BURG and H. I. SCHLESINGER J. Amer. chem. Soc. 59, 780 (1937).

 <sup>&</sup>lt;sup>(3)</sup> D. T. HURD J. Amer. chem. Soc. 70, 2053 (1948).
 <sup>(4)</sup> W. A. G. GRAHAM and F. G. A. STONE J. inorg. nucl. Chem. 3, 164 (1956).
 <sup>(5)</sup> F. G. A. STONE and W. A. G. GRAHAM Chem. & Ind. (Rev.) 1181 (1955).

reservoir A, trap the gas present in B and carry it down the 3 mm bore capillary C into the gas burette D. In operation, the apparatus is filled with mercury up to line E. Mercury is lifted in neat pistons up the tube F by application of a rough vacuum at G and careful admission of air at H. Mercury is recycled through the valve J, a steel ball ground into place so as to permit the mercury to flow only downwards through this tube. When a length of recycled mercury appears above point K, it is lifted by the air to reservoir A, causing a like amount to spill into the capillary.



FIG. 1.--Automatic Sprengel pump.

When the gas has been quantitatively transferred to the gas burette, pumping is stopped by closing H. Stopcock L is opened to by-pass valve J, stopcock M is opened, and mercury from the main reservoir N flows into the apparatus. Additional pressure is exerted using bulb P. Rising mercury compresses the gas in the burette to one of the calibrated marks and also fills the arm Q, which has previously been highly evacuated, and now serves as the closed end of a manometer from which the gas pressure is read. Volume and temperature are noted and the gas volume calculated. Mercury is again lowered to the operating level by a rough vacuum at R.

Combustion of the gas is carried out by opening suitable stopcocks and using the pump to circulate the gas through the furnaces S (copper oxide at 750°C) and T (copper metal at 400°C). Water formed is removed by a -78.5°C bath at V. Other products are then collected in the burette and measured.

#### The reaction between boron hydride and tetrafluoroethylene

(a) Choice of ratios of reactants. During investigation of the effect of diborane on tetrafluoroethylene at 80-100°C it was found that if the  $B_2H_6:C_2F_4$  molar ratio was 1 : 2, or the mixture even richer in B<sub>2</sub>H<sub>6</sub> than this ratio, serious explosions occurred, but only after the reactants had been heated for some hours. Thus when 510 c.c.\*  $B_2H_6$  was heated with 1019 c.c.  $C_2F_4$  at 80°C in a 11. Pyrex reaction-bulb the mixture exploded 20 hr later, completely destroying the oven used in the experiment. However, no explosions took place when diborane was heated with excess of tetrafluoroethylene, provided initial pressure in the reaction vessel was less than 1.5 atm. Furthermore, no explosions were ever encountered at room temperature even with  $B_2H_6:C_2F_4$  ratios of 1:2 or more. It seemed, therefore, that at temperatures above 80°C, explosions were caused by the action of higher boranes on tetrafluoroethylene, since under conditions involving an excess of diborane there would be the likelihood of borine fragments reacting with themselves giving higher boranes. Then after some hours there would be a sufficient concentration of these higher boranes to react explosively with tetrafluoroethylene. To put this idea on a firmer basis, a 15.7 c.c. sample of C<sub>2</sub>F<sub>4</sub> was added to 12.1 c.c. B<sub>5</sub>H<sub>9</sub> in a glass tube of 30 ml capacity. The tube was sealed off from the vacuum line and allowed to remain at room temperature for an hour, during which time no change was visible. The tube was then placed in a steam-bath, where it exploded with sufficient force to remove the top of the bath.

(b) Room-temperature reactions. An experiment typical of many at room temperature is described here in detail in order to demonstrate how the products of other experiments mentioned in this paper were separated and identified. A 11. Pyrex bulb was filled with 960 c.c.  $C_2F_4$  and 318 c.c.  $B_2H_6$  (molar ratio  $B_2H_6$ :  $C_2F_4$ , 1:3). After a few days a white solid began forming on the inside of the reaction bulb, but the latter was not reattached to the vacuum system until 33 weeks later, by which time all material containing boron-hydrogen bonds had been consumed by reaction with olefins. On opening the bulb, 15.5 c.c.  $H_2^{\dagger}$  was removed, and the other volatile products were separated by distillation *in vacuo*, giving well-defined fractions at  $-196^{\circ}C(I)$ ,  $-130^{\circ}C(II)$  and  $-96^{\circ}C(III)$ . The white solid remained in the bulb, since it was non-volatile at room temperature.

Fraction I (715 c.c.) was treated with water but no hydrogen was formed showing that all diborane had been used up in the reaction. The volume, however, was reduced to 370 c.c. (average M, 98.4; significantly lower than M, 100.0 calculated for  $C_2F_4$ ). Mass spectrometer analysis of gas which survived water treatment gave:  $C_2F_4$ , 93.87;  $CF_2:CH_2$ , 3.95;  $C_2H_4$ , 0.22;  $C_2H_6$ , 0.11;  $CF_2:CFH$ , 0.04 mole per cent. There was little doubt that the gas absorbed by water was BF<sub>3</sub>, since it was volatile enough to pass a U-trap at  $-130^{\circ}$ C, yet no non-condensable gas was formed on hydrolysis. Quantitative analysis of the solution for fluoride<sup>(10)</sup> ion confirmed this (Found:  $F^-$  equivalent to 341 c.c. BF<sub>3</sub>).

Analysis of II (243.8 c.c.) was more difficult. Previous experiments had shown that only the major part of these  $-130^{\circ}$ C fractions reacted with trimethylamine. Thus they did not entirely consist of boron-containing material. This became obvious when it was found that after the  $-130^{\circ}$ C fractions had been treated with an excess of trimethylamine giving a solid, the gas recovered did not have an infra-red spectrum identical with pure trimethylamine. Separation of mixture II into its constituents was accomplished, therefore, by treatment with excess of Me<sub>3</sub>N (310.9 c.c.) to give a solid *addition* 

compound Me<sub>3</sub>N·BEtF<sub>2</sub>, m.p. 23·9–25·3°C (Found: C, 43·66; H, 10·17; N, 10·50; B, 8·25; F, 27·87. C<sub>5</sub>H<sub>14</sub>BF<sub>2</sub>N requires: C, 43·84; H, 10·30; N, 10·23; B, 7·90; F, 27·74 per cent), and 106·1 c.c. gas. These volumes in themselves imply that II consisted of 224·3 c.c. EtBF<sub>2</sub> and 19·5 c.c. of other material. Confirmation was supplied by treating the recovered gas (106·1 c.c.), trimethylamine plus impurity,

with BF<sub>3</sub> (126·1 c.c.) giving solid Me<sub>3</sub>N·BF<sub>3</sub>, and 17·4 c.c. gas retained at -130 °C. The excess of BF<sub>3</sub> (41·0 c.c.) was condensed at -196 °C. This 17·4 c.c. "impurity" in the EtBF<sub>2</sub> appeared to consist principally of the *olefin* CFH:CFH (Found: M, 65·2;  $C_2H_2F_2$  requires M, 64·0. When 4·01 c.c. were ignited over CuO at 800°C 8·43 c.c. CO<sub>2</sub> was produced. Expected: 8·02 c.c. CO<sub>2</sub>. Mass spectrometer analysis showed the principal peak to be at M/e = 64, and the spectrum differed from all other fluoro-olefins used in this work) presumably as a mixture of *cis*- and *trans*-forms.

Fraction III (44.14 c.c. 247.5 mg) also proved to be a mixture, as did all the -96 C fractions

\* Throughout this paper quantities of material expressed as c.c. refer to the s.t.p. volume.

† It is hardly necessary to point out that the small quantities of hydrogen formed in some of the reactions described in this paper came from the well-established tendency of diborane to decompose.

<sup>(10)</sup> R. J. ROWLEY and H. V. CHURCHILL Industr. Engng. Chem. (Anal.) 9, 551 (1937).

obtained from the many diborane-fluoroethylene reactions conducted at room temperature. Indeed, the small amounts of material prevented characterization of all components of these mixtures. In this particular experiment, III was distilled through a  $-78.5^{\circ}$ C bath four times, giving fractions passing  $-78.5^{\circ}$ C of volumes: 13.56 c.c. (M, 101.3), 9.8 c.c. (M, 105.4), 4.94 c.c. (M, 107), and 4.18 c.c. (M, 111). These fractions were combined (32.48 c.c.) and found to react with 32.49 c.c.  $Me_3N$ , when treated with an excess of this base, giving a liquid addition compound. Combination of that part of III passing a trap at  $-78.5^{\circ}$ C with an exactly equal volume of  $Me_3N$  did at least imply the presence of 32.48 c.c. of boron. The remainder of III could be divided into a fraction retained at  $-46^{\circ}$ C (3.5 c.c.), probably triethylboron, and a fraction at  $-78.5^{\circ}$ C (8.16 c.c., M, 117). These two small fractions also combined in a 1 : 1 ratio with  $Me_3N$ .

Total boron content of III was thus 44·1 c.c. (i.e. only 7 per cent of the boron used in the reaction); the boron content of II, 224·3 c.c.; and the boron content of I, 345 c.c. Hence these volatile reaction products account for  $613\cdot4$  c.c. of the 636 c.c. of boron taken as  $B_2H_6$  for reaction. The remainder of the boron appeared in the white *polymer* (Found: C, 23·98, 24·01; H, 0·32, 0·00; F, 71·44, 70·25; B, 4·16, 6·88 per cent; *M*, isothermal method,<sup>(11)</sup> 650).

(c) Reactions at 80–100°C. In a representative experiment  $B_2H_6$  (116.6 c.c.) was heated with  $C_2F_4$  (438.4 c.c.) at 80°C for 24 hr in a 1 l. Pyrex bulb. White polymer appeared in the bulb within a few hours of starting the experiment. The reaction vessel was attached to the vacuum-line through a tube-opener, and 6.80 c.c.  $H_2$  removed. The volatile products were then separated in a manner

similar to that described under (b) above, giving 134 c.c. BF<sub>3</sub> (characterized as Me<sub>3</sub>N·BF<sub>3</sub>) (Found: C, 28·11; H, 7·19; N, 10·89; C<sub>3</sub>H<sub>9</sub>BF<sub>3</sub>N requires C, 28·38; H, 7·15; N, 11·04 per cent) and 233·6 c.c. ethylenes (Mass spectrometer analysis: C<sub>2</sub>F<sub>4</sub> 95·37; CF<sub>2</sub>:CH<sub>2</sub>, 3·31; CHF:CH<sub>2</sub>, 0·48; and CF<sub>2</sub>:CFH, 0·17 mole per cent) at  $-196^{\circ}$ C. The  $-130^{\circ}$ C fraction consisted of 68·6 c.c. EtBF<sub>2</sub> (again

separated as  $Me_3N \cdot BF_3Et$ ) and 10.0 c.c. material inert towards  $Me_3N$ , probably CFH:CFH. The  $-96^{\circ}C$  fraction consisted of only 22.3 c.c. material. The 22.3 c.c. fraction was treated with 41.6 c.c.  $Me_3N$  forming a liquid complex, 19.2 c.c.  $Me_3N$  being recovered. Treatment of the complex with

excess of  $BF_3$  in an attempt to form  $Me_3N \cdot BF_3$  failed to displace all the Lewis acids combined with the  $Me_3N$ . However, 7.6 c.c.  $Et_2BF$  (identified by its infra-red spectrum) was obtained. It was apparent from this experiment as well as others involving diborane and tetrafluoroethylene that the  $-96^{\circ}C$  fraction contained Lewis acids stronger than  $BF_3$ .

The polymer contained a little boron, although volatile products (equivalent to  $225 \cdot 0 \text{ c.c.}$  boron) as usual accounted for the major portion. The diborane taken for reaction corresponded to  $233 \cdot 2 \text{ c.c.}$  boron.

(d) Some properties of the polymer. The polymer proved to be interesting in that it was very soluble in a variety of donor solvents like ether, acetone, triethylamine, ethyl acetate and glacial acetic acid, but insoluble in benzene, carbon tetrachloride, carbon disulphide and chloroform. The molecular weight varied from reaction to reaction with a maximum M, 1183 (Found: C, 23.97; H, 0.33; B, 4.38; F, 71.00 per cent).

#### The reaction between diborane and vinyl fluoride

A 11. bulb containing 124.5 c.c.  $B_2H_6$  and 636.0 c.c.  $CH_2$ :CHF was heated for 10 days at 55°C and then for 2 days at 70°C. The bulb was then opened and its contents examined. No hydrogen had been formed, indicating no loss of BH<sub>3</sub> by pyrolysis. Volatile material was fractionated through U-traps at  $-196^{\circ}C$  (I),  $-130^{\circ}C$  (II), and  $-96^{\circ}C$  (III).

The infra-red spectrum of I (284.0 c.c.) indicated absence of B—H containing material. All  $B_2H_6$  had, therefore, been consumed. This was confirmed when on treatment of I with water, no hydrogen was formed but the volume decreased to 258.5 c.c. (infra-red spectrum corresponded to vinyl fluoride with a trace of ethylene) owing to absorption of 25.5 c.c. BF<sub>3</sub> (indicated in spectrum of I before hydrolysis).

The infra-red spectrum of II (126.7 c.c.) also showed no B—H containing material, but showed the presence of a small quantity of CH<sub>2</sub>:CHF. Refractionation of II through a trap at  $-130^{\circ}$ C yielded 6.8 c.c. CH<sub>2</sub>:CHF, and 119.9 c.c. of pure EtBF<sub>2</sub>.

<sup>&</sup>lt;sup>(11)</sup> R. SIGNER Liebigs Ann. 478, 246 (1930). See STEYERMARK Quantitative Organic Microanalysis. Blakiston (1951).

Fraction III was distilled through a trap at  $-45^{\circ}$ C, where 83.8 mg (19.1 c.c.) Et<sub>3</sub>B (infra-red spectrum identical with triethylboron specimen prepared via Grignard reagent) was retained. An 81.4 c.c. sample Et<sub>2</sub>BF (identified by infra-red spectrum) was recovered in the  $-96^{\circ}$ C trap.

The various components of the mixture account for 245.9 c.c. boron, 99 per cent of the boron taken as diborane for reaction. No polymerization of vinyl fluoride was observed.

Several other reactions between  $B_2H_6$  and  $CH_2$ :CHF were carried out under the same conditions of temperature and pressure, using slightly different reaction ratios. No difficulties were encountered. However, when 142.5 c.c.  $B_2H_6$  and 571.5 c.c.  $CH_2$ :CHF were heated at 80°C, an explosion, without breakage of the bulb, occurred after a few hours. On opening the reaction vessel, the walls of which were entirely black, 1190 c.c.  $H_2$  was removed, and 161.5 c.c. condensable gas recovered. This gas was identified as 143.0 c.c.  $BF_3$ , 4.8 c.c.  $B_2H_6$ , 1.0 c.c.  $CH_2$ :CHF and 3.0 c.c.  $EtBF_2$ . The black solid appeared to be a mixture of carbon, boron, and solid boron hydride.

#### The reaction between diborane and 1:1 difluoroethylene

In a typical experiment,  $CF_2:CH_2$  (646.5 c.c.) and  $B_2H_6$  (158.0 c.c.) were heated in a 1 l. Pyrex bulb at 50°C for 10 days, and then at 65°C for 4 days. On opening the bulb, no hydrogen gas was found. The reaction products were taken into the vacuum system and distilled through traps at -196°C (I), -130°C (II) and -96°C (III). Infra-red spectrum of I (506 c.c.) indicated it to be a mixture of BF<sub>3</sub> and fluoroethylenes. Treatment with water gave no hydrogen, but removed 138.0 c.c. BF<sub>3</sub>, leaving 368 c.c. fluoroethylenes (Mass spectrometer analysis: CF<sub>2</sub>:CH<sub>2</sub>, 59.9; CFH:CH<sub>2</sub>, 36.9; C<sub>2</sub>H<sub>4</sub>, 1·2; CFH:CFH, 1·42; CF<sub>4</sub>, 0·2 mole per cent). Fraction II consisted of 115.1 c.c. EtBF<sub>2</sub>, and III 62.1 c.c. Et<sub>2</sub>BF. Both boron fluorides were identified by their spectra. No polymerization of CF<sub>2</sub>:CH<sub>2</sub> had occurred, and boron in the volatile products accounts for 99.7 per cent of the boron taken as B<sub>2</sub>H<sub>6</sub>.

### The reaction between diborane and trifluoroethylene

A mixture of  $CF_2$ :CFH (649.0 c.c.) and  $B_2H_6$  (159.3 c.c.) was heated at 55°C for 10 days, and then at 65°C for 3 days. No hydrogen was formed. Infra-red analyses of the products showed absence of absorption bands corresponding to B—H. Products were identified as 290.4 c.c. fluoroethylenes (Mass spectrometer analysis: CF<sub>2</sub>:CFH, 90.8, CF<sub>2</sub>:CH<sub>2</sub>, 8.3; CH<sub>2</sub>:CHF, 0.2; C<sub>2</sub>H<sub>4</sub>, 0.1 mole per cent), 165.0 c.e. BF<sub>3</sub>, 103.9 c.c. EtBF<sub>2</sub>, 84.0 c.c. fluorocarbon (infra-red spectrum corresponding to the compound CFH:CFH) and 21.9 c.c. boron containing material condensed at -96°C (established as a mixture of Et<sub>2</sub>BF and Lewis acids stronger than BF<sub>3</sub> by trimethylamine treatment).

#### The reaction between diborane and ethylene

In one experiment,  $C_2H_4$  (662.0 c.c.) and  $B_2H_6$  (150.5 c.c.) were heated in a 1 l. bulb at 60°C for 10 days. No hydrogen gas was formed, and no  $C_2H_4$  or  $B_2H_6$  were recovered. Pure Et<sub>3</sub>B, 1.0634 g (243.0 c.c.) was condensed at -45°C. The only other product was  $Et_2B_2H_4$ , 24.85 c.c. (Found: M, 85.2;  $Et_2B_2H_4$  requires M, 83.8. Infra-red spectrum different from any other observed in this work showed bands corresponding to B-H, B-C and C-H) condensed at -96°C.<sup>(12)</sup>

A mixture of  $C_2H_4$  and  $B_2H_6$  (molar ratio  $4\cdot 4:1$ ) heated under milder conditions again gave  $Et_3B$  as the main product, but a small quantity (3.7 c.c.)  $EtB_2H_5^{(12)}$  (condensed at  $-130^{\circ}C$ . Infra-red different from any other spectrum observed in this work, but nevertheless showed presence of B—C, B—H and C—H) was also isolated.

### The effect of diborane on ethyl fluoride

A mixture of  $C_2H_5F$  (635.4 c.c.) and  $B_2H_6$  (317.4 c.c.) was allowed to remain at room temperature for 11 months, by which time formation of solid boranes was observed. The reaction bulb was then opened, 102.4 c.c.  $H_2$  removed, and gas condensable in liquid nitrogen examined. The mixture consisted of 262.3 c.c.  $B_2H_6$ , 623.7 c.c.  $C_2H_5F$  (identified by infra-red spectrum) corresponding to 98.4 per cent of this compound taken for reaction, and 5.1 c.c.  $B_5H_9$  (identified by comparing the infra-red spectrum with that of a pure sample).

Other mixtures of diborane and ethyl fluoride also failed to react over periods of months at room temperature.

(12) H. I. SCHLESINGER, L. HORVITZ and A. B. BURG J. Amer. chem. Soc. 58, 407 (1936).

Synthesis of ethylboron fluorides from diborane, triethylboron and tetrafluoroethylene (a) A mixture of  $B_2H_6$  (156 c.c.),  $Et_3B$  (160.6 c.c.) and  $C_2F_4$  (620.7 c.c.) was allowed to remain in a 1 l. bulb for a period of 1 year. During this time a quantity of white polymer formed, but in much smaller amount than when diborane and tetrafluoroethylene are alone mixed. After the bulb had been attached through a tube-opener to the vacuum line, 5.1 c.c.  $H_2$  was removed. Other products were separated in the usual manner into 391.5 c.c. fluoroethylenes, 1.5 c.c.  $BF_3$ , 385 c.c.  $EtBF_2$ , 65.8 c.c.  $Et_2BF$  and 16.4 c.c.  $Et_3B$ . Infra-red spectrum of all fractions showed a complete absence of bands corresponding to B—H.

(b) After a mixture of  $B_2H_6$  (145.8 c.c.),  $Et_3B$  (186.9 c.c.) and  $C_2F_4$  (662 c.c.) had been heated at 55°C for 10 days the products were,  $BF_3$  (68.2 c.c), fluoroethylenes (439 c.c.),  $EtBF_2$  (251 c.c.),  $Et_2BF$  (58.1 c.c.) and  $Et_3B$  (88 c.c.). No  $H_2$  or B—H-containing material was formed, but some polymer was observed in the reaction bulb.

#### Characterization and properties of ethylboron fluorides

For physical studies. EtBF<sub>2</sub> was readily liberated from its trimethylamine complex by treatment at room temperature with the stronger Lewis acid boron trifluoride. Thus a 226 c.c. sample of  $Me_3N\cdot BEtF_2$ , prepared by mixing equal volumes of  $Me_3N$  and  $EtBF_2$  at  $-78\cdot5^\circ$ C, was treated with 246.0 c.c. BF<sub>3</sub>. Liquid phase disappeared within an hour, and solid  $Me_3N\cdot BF_3$  formed together with 224.8 c.c. ethylboron difluoride (Found: *M*, 78·3, 78·1; F, 20·1 per cent. C<sub>2</sub>H<sub>3</sub>BF<sub>2</sub> requires *M*, 77·9; F, 20·44 per cent) condensed at  $-130^\circ$ C, and 20·3 c.c. BF<sub>3</sub> recovered at  $-196^\circ$ C.

Vapour-pressures of  $EtBF_2$  over the range  $-95^{\circ}C$  to  $-45^{\circ}C$  (Table 1) imply the relevant physical constants summarized in Table 4.

t, °C	-95	<b>−83·6</b>	<b>−78</b> ·5	-63.5	-45.2
$P_{\rm mm}$ (found)	5·8	17∙4	26·6	81·5	262
$P_{\rm mm}$ (calc.)	6·2	17 <u>-</u> 4	26·6	81·5	261·8

TABLE 1.-VAPOUR TENSIONS OF LIQUID EtBF<sub>2</sub>

The compound Et<sub>2</sub>BF (Found: M, 87·6; C, 55·3; H, 11·1 per cent. C<sub>4</sub>H<sub>10</sub>BF requires M, 87·9: C, 54·7; H, 11·1 per cent) combined in a 1 : 1 ratio with trimethylamine forming a liquid adduct + -Me<sub>3</sub>N·BFEt<sub>2</sub> (Found: C, 55·9; H, 13·0; N, 9·9. C<sub>7</sub>H<sub>10</sub>BFN requires C, 57·2; H, 13·03; N, 9·53 per cent).

Vapour-pressures of Et<sub>2</sub>BF over the range  $-45^{\circ}$ C to  $-13^{\circ}$ C (Table 2) determine the relevant constants summarized in Table 4.

t, °C	-45·2	-35.6	-22·8	-16.0	-13.1
$P_{\rm mm}$ (found)	11.6	20.9	43.9	62.8	73.3
$P_{\rm mm}$ (calc.)	11.5	21.1	<b>43</b> ·9	62.9	72.9

TABLE 2.---VAPOUR TENSIONS OF LIQUID Et<sub>2</sub>BF

Stability of ethylboron difluoride, with respect to disproportionation into boron trifluoride and diethylboron fluoride, was examined by heating a 103.2 c.c. sample at  $80^{\circ}$ C for 48 hr. No decomposition occurred, and 102.8 c.c. EtBF<sub>2</sub> (identified from its molecular weight and infra-red spectrum) was recovered.

In a similar experiment, diethylboron fluoride was found to be thermally stable, showing no sign of disproportionation.

### 2. **DISCUSSION**

As described in the experimental section, the main boron-containing products formed on treating any of the fluoroethylenes with diborane are always boron trifluoride, ethylboron difluoride, diethylboron fluoride and triethylboron. Moreover, mass spectrometer analyses of tetra-, tri-, and 1-1-di: fluoroethylene residues recovered from the reactions of these olefins with diborane showed them to contain appreciable quantities of less fluorinated olefins.

These observations show that all the reactions follow an essentially similar course. Fluorine in the fluoroethylenes is first replaced by hydrogen derived from B—H-containing material. In this way ethylene is eventually formed, while at the same time B—F bonds are created. Once formed, the ethylene undergoes addition reactions with molecules containing B—H linkages, whereby B—C bonds are synthesized.

There are obviously a large number of possible reaction paths that can be followed during both replacement of fluorine by hydrogen from B—H, and addition of B—H to ethylene. Fortunately, the number of stable boron-containing molecules ultimately obtained is limited by the inherent tendency of unsymmetrical borine derivatives to disproportionate. A further limitation on the number of final products is imposed because several reaction intermediates react to give the same compounds. The probable reaction scheme is outlined on page 127.

Borine converts tetrafluoroethylene to trifluoroethylene, the  $BH_2F$  group being produced. The  $BH_2F$  molecule would be expected to exist as a dimer, and to be highly unstable, disproportionating to  $BH_3$  and  $BHF_2$ . Fluoroborine could also attack tetrafluoroethylene or other fluoroethylenes, exchanging H for F, or alternatively it could add to ethylene giving EtB(H)F. The  $BHF_2$  molecule would have similar properties, transferring hydride to carbon in the fluoroethylenes, and adding across the double bond in ethylene, giving  $EtBF_2$ . Disproportionation of  $BHF_2$ would give another final product, boron trifluoride.

Under the proposed reaction scheme, attack of B-H on trifluoroethylene, formed from tetrafluoroethylene, would yield either 1:1-difluoroethylene or 1:2-difluoroethylene. 1:1-Difluoroethylene was indeed identified, by infra-red and mass spectrometer analysis, in the excess of tetra- or tri-fluoroethylene recovered at  $-196^{\circ}$ C after reaction with diborane. 1:2-Difluoroethylene was not found in either the tetra- or the tri-fluoroethylene recovered from their respective reactions with diborane. Ethylboron difluoride condensing at  $-130^{\circ}$ C, however, showed contamination with small quantities of a fluorocarbon which in the mass spectrometer gave a principal peak at M/e = 64, and had an infra-red spectrum corresponding to that expected for CFH: CFH. The compound CFH : CFH, presumably as a mixture of *cis*- and *trans*-isomers, would be expected to be less volatile than the other fluoroethylenes, and its appearance in the  $-130^{\circ}$ C fractions rather than at  $-196^{\circ}$ C is not unexpected. It is to be noted that cis- and trans-1:2-dichloroethylene are considerably less volatile than all other chloroethylenes.<sup>(13)</sup> The compound 1:2-difluoroethylene is of particular interest, since although it is a relatively simple molecule it has never been reported in the chemical literature. Unfortunately, it is formed in such small amounts by the reactions reported here that it has not been characterized completely, although it may be possible to do so at a later date.

Much other, evidence for the proposed mechanism may be deduced from the work <sup>(13)</sup> E. H. HUNTRESS Organic Chlorine Compounds. John Wiley, New York (1948).



The effect of diborane on fluoroethylenes

described in the experimental section. Thus, whereas the presence of ethyldiboranes as products of the diborane-ethylene reaction was not demonstrated in previous work,<sup>(3)</sup> these compounds were found under milder reaction conditions used by us. Moreover, in reactions carried out between diborane and fluoroethylenes at room temperature a very complex mixture of products was obtained whenever the reaction was stopped before all B—H-containing material was used up. One product, tentatively identified\* as EtB(H)F·BH<sub>3</sub>, condensing in very small amounts at  $-96^{\circ}$ C, could not be separated from diethylboron fluoride. Especially complicated were the mixtures obtained by treating vinyl fluoride with diborane at room temperature when small quantities of ethyldiboranes were detected. When reactions with vinyl fluoride were carried out

<sup>\*</sup> Treatment of diethylboron fluoride and the impurity (infra-red showed B—H) believed to be  $EtB(H)F \cdot BH_3$  with trimethylamine gave a liquid. Addition of boron trifluoride yielded  $Et_2BF$ , as expected, but also  $B_2H_6$ , and ethylboron difluoride. The latter would form by disproportionation of the EtB(H)F group.

above 50°C, however, boron trifluoride, ethyl- and diethyl-boron fluoride, and triethylboron were the only boron-containing compounds observed.

Distribution of boron among the products of diborane-fluoroethylene reactions varies with the ethylene used and is summarized in Table 3. With each olefin from experiment to experiment the boron distribution changes slightly even with a constant ratio of reactants. Nevertheless, this variation is small compared with the change in boron distribution brought about by substituting one fluoroethylene by another. Thus, with tetrafluoroethylene, molar ratio olefin : diborane of 4:1, yield is in the order  $BF_3 > EtBF_2 \gg Et_2BF > Et_3B$ . With vinyl fluoride it is  $EtBF_2 > Et_2BF \gg$  $BF_2 \sim Et_3B$ . These changes in proportions of boron-containing products are to be expected under the reaction scheme suggested. Substitution of one fluoroethylene by another with a lower fluorine content should favour those reactions leading to B-C bond formation over those leading to B-F bond synthesis. Similarly, as indicated in Table 3, a change in ratio of reactants brings a slight but expected shift in boron distribution.

	Ratio of	% Boron in the products as				
Olefin	reactants olefin: $B_2H_6$	BF <sub>3</sub>	EtBF <sub>2</sub>	Et <sub>2</sub> BF	Et₃B	
C <sub>2</sub> F <sub>4</sub>	4.2:1	58.0	30.0	0(р) і	0(b, c)	
C <sub>2</sub> F <sub>3</sub> H	4.1:1	51.7	32.6	О(р)	0(b, d)	
1:1-C <sub>2</sub> F <sub>2</sub> H <sub>2</sub>	4.1:1	43.6	36-5	19.7	0 <sup>(e)</sup>	
C₂FH₃	4.1:1	7.0	55.0	32.6	3.5	
C <sub>2</sub> F <sub>4</sub>	3.1:1	54.2	35.3	0	0 <sup>(b, c)</sup>	
C <sub>2</sub> FH <sub>3</sub>	4.6 : 1	9.3	51.2	33.9	0	

TABLE 3.—BORON DISTRIBUTION IN DIBORANE-FLUOROETHYLENE REACTIONS<sup>(a)</sup>

(a) Results presented in this Table refer to representative reactions conducted under conditions such that all B-H-containing material was consumed.

<sup>(b)</sup> Trace amounts of  $Et_{a}BF$  and  $Et_{a}B$  were sometimes obtained. <sup>(c)</sup> In the  $B_{a}H_{b}/C_{a}F_{a}$  reactions about 8 per cent boron taken as diborane for reaction is incorporated in the polymer, and a trace appears in the form of Lewis acids stronger than BF2.

<sup>(d)</sup> Small amount of boron appears as acids stronger than BF<sub>3</sub>.

(e) Small quantities Et<sub>a</sub>B sometimes obtained.

A very large change in the proportions of products may be accomplished by a preliminary addition of triethylboron to the diborane-olefin mixture. Thus as described in the experimental section mixtures of diborane, triethylboron and tetrafluoroethylene give mainly ethyl- and diethyl-boron fluoride. Only a relatively small amount of boron appears as boron trifluoride. It is well known that addition of triethylboron to diborane quickly gives equilibrium mixtures of ethyldiboranes.<sup>(12)</sup> These can function as sources of ethylborines, EtBH<sub>2</sub> and Et<sub>2</sub>BH. Obviously the latter are then fluorinated by the fluoroethylenes, giving EtBF<sub>2</sub> and Et<sub>2</sub>BF as the main products.

During the course of this work there was very little evidence for addition of borines to fluoroethylenes, e.g.

$$CH_2:CHF + BH_3 \rightarrow (C_2H_4F)BH_2.$$

However, when tetrafluoroethylene or trifluoroethylene was treated with diborane,

boron-containing Lewis acids stronger than  $BF_3$  were occasionally found, but in amounts far too small for identification. They may have been compounds with fluorine in the alkyl group. In any event, formation of these compounds was insignificant in comparison with the main reaction: conversion of fluoroethylenes to ethylene, followed by addition reactions of various borines occurring with ethylene only.

Whereas fluoroethylenes undergo complete reaction with diborane even at room temperature over a period of months, no reaction occurred between diborane and ethyl fluoride under the same conditions. This suggests that interaction of the borine group with the  $\pi$ -electrons of the double bond is a necessary part of the fluoroethylene-diborane reaction mechanism. It is possible, however, that ethyl fluoride and diborane would react at elevated temperatures under pressure, just as diborane and the paraffins react under such conditions.<sup>(3)</sup>

The compounds ethylboron difluoride and diethylboron fluoride are new. Some of their physical properties are summarized in Table 4. Like the methylboron fluorides<sup>(14)</sup> they do not disproportionate.

m.p. <sup>(a)</sup>		b.p. <sup>(b)</sup>	Log P mm =	= -A/T + B	$\Delta H_{(\rm VAD)}$	Trouton's constant (cal deg <sup>-1</sup> mole <sup>-1</sup> )
(°C)	(°C)	A	В	(kcal mole <sup>-1</sup> )		
$C_2H_5BF_2$	101 • 0	-25.4	1325	<b>8</b> ∙229	6.06	24.5
$(C_2H_5)_2BF$	-121.5	43·6	1479	7.550	6.77	21.4

TABLE 4.—PHYSICAL PROPERTIES OF THE ETHYLBORON FLUORIDES

<sup>(a)</sup> Stock magnetic plunger method.

(b) By extrapolation of vapour-pressure equation.

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<sup>(14)</sup> A. B. BURG J. Amer. chem. Soc. 62, 2228 (1940).