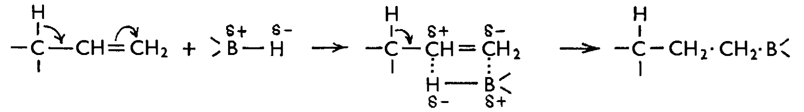
18. *Organoboron Halides. Part VI.*[1] *Hydroboration of 3,3,3-Trifluoropropene.*

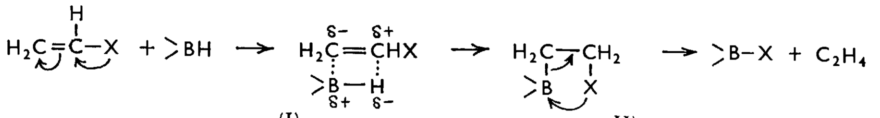
By J. R. Phillips and F. G. A. Stone.

A gas-phase reaction between diborane and 3,3,3-trifluoropropene is described. Products include 1,1-difluoropropene, 1-fluoropropene, boron trifluoride, n-propylboron difluoride, and the new compound 3,3,3-trifluoropropylboron difluoride. Product distribution shows that addition of B–H to 3,3,3-trifluoropropene is largely at the 2-position. Some properties of 3,3,3-trifluoropropylboron difluoride are described.

The direction of addition of diborane to simple straight-chain olefins is considered to depend on the hydridic character of hydrogen in a B–H bond, as well as the electronic shifts used to explain addition reactions of olefins:[2]



In contrast to these simple additions, treatment of certain substituted ethylenes $CH_2{:}CHX$ ($X = F$,[3,4] Cl,[5-7] or SiH_3 [7]) with diborane can result in cleavage of the C–X bond and formation of complex mixtures. With vinyl fluoride and diborane, no fluoroethylboron compounds are formed; ethylboron difluoride, diethylboron fluoride, boron trifluoride, and triethylboron are the sole boron-containing products obtained in amounts sufficient for characterization.* When X in $CH_2{:}CHX$ is halogen, formation of B–X bonds can be understood in terms of the reaction sequence:



(I) (II)

The final products may be accounted for in terms of possible disproportionation of the fragment $>$B–X or, if the latter possesses B–H bonds, by addition of these to $CH_2{:}CHX$ or to the ethylene formed by decomposition of compound (II). Several reactions are now known which involve transfer of halogen, usually fluorine, from carbon to boron. The compound $F{\cdot}CH_2{\cdot}BF_2$ forms boron trifluoride readily[9] and, although $CF_3{\cdot}BF_2$ has not been isolated in the free state, it is apparent that it easily produces boron trifluoride.[10]

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* When relatively high proportions of diborane are employed in reactions with fluoroethylenes at elevated temperatures, explosions sometimes occur. A statement to this effect in ref. 3 has been so emphasized in refs. 2 and 8, which contain no mention of the work described in ref. 4, that the incorrect impression is given that under all conditions treatment of a fluoro-olefin with diborane is hazardous. In fact, ref. 4 shows that, provided the correct proportions of diborane and fluoroethylene are employed, ethylboron fluorides can be obtained smoothly in good yield.

[1] Part V, Stafford and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6238.

[2] Brown, Amer. Chem. Soc. Monograph, " Organometallic Chemistry," ed. Zeiss, Reinhold Publ. Corp., New York, 1960, Ch. 4.

[3] Stone and Graham, *Chem. and Ind.*, 1955, 1181.

[4] Bartocha, Graham, and Stone, *J. Inorg. Nuclear Chem.*, 1958, **6**, 119.

[5] Hawthorne and DuPont, *J. Amer. Chem. Soc.*, 1958, **80**, 5830.

[6] Stafford, Ph.D. Thesis, Harvard University, 1961.

[7] Stone, " Advances in Inorganic Chemistry and Radiochemistry," ed. Emeléus and Sharpe, Academic Press, 1960, Vol. II, p. 279.

[8] Brown and Subba Rao, *J. Amer. Chem. Soc.*, 1959, **81**, 6428.

[9] Goubeau and Rohwedder, *Annalen*, 1957, **604**, 168.

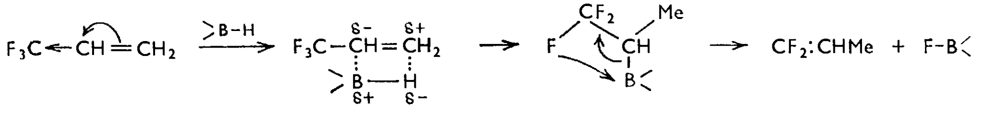
[10] Parsons, Baker, Burg, and Juvinall, *J. Amer. Chem. Soc.*, 1961, **83**, 250.

Perfluorovinylboron compounds such as $CF_2{:}CF\cdot BCl_2$ also slowly release boron trifluoride.[1] In order to obtain more information about reactions involving transfer of halogen from carbon to boron the effect of diborane on 3,3,3-trifluoropropene has been studied. By virtue of the increased negative character of the 2-carbon atom in $CF_3\cdot CH{:}CH_2$ relative to that in $CH_3\cdot CH{:}CH_2$, addition of unsymmetrical reagents to the two olefins often occurs with opposite orientations.[11,12] It seemed likely, therefore, that hydroboration of 3,3,3-trifluoropropene would lead to attack of relatively more boron atoms in the 2-position than is the case with propene. Such an occurrence would be of interest on account of the information that would be gained concerning the stability of a boron compound in which a trifluoromethyl group is separated from a boron atom by one carbon atom.

Reactions between diborane and 3,3,3-trifluoropropene were studied in the absence of ether, since it was expected that several Lewis acids would be formed which in the presence of ether would form ether complexes, making identification of the many products more difficult. It has been observed that the nature of the products from diborane and vinyl fluoride, or vinyl chloride, is independent of whether ether is used as a catalyst or not, and it is reasonable to assume that this is also probably true for the diborane–3,3,3-trifluoropropene reaction. It was found that 3,3,3-trifluoropropene and diborane in 4 : 1 molar ratio react at room temperature with consumption of all B–H-containing material in 1—2 weeks. The reaction is thus much faster than those between fluoroethylenes and diborane.[4] The products, volatile *in vacuo* at room temperature, were boron trifluoride, 1,1-difluoropropene, 1-fluoropropene, n-propylboron difluoride, and 3,3,3-trifluoropropylboron difluoride. In addition, a mixture of less volatile materials was obtained but was not separated into its components. This mixture contained compounds, presumably of the types R_2BF and R_3B, having $CF_3\cdot C_2H_4$ and C_3H_7 groups attached to boron. Consideration of the relative amounts of the various products showed that reaction between 3,3,3-trifluoropropene and B–H bonds involves preferential addition at the carbon atom attached to the CF_3 group. Of the 3,3,3-trifluoropropene used, about 17% was recovered unreacted, about 18% was involved in terminal addition to form substances containing $CF_3\cdot CH_2\cdot CH_2B{<}$ groups, about 56% was converted into 1,1-difluoropropene or its reduction products, and about 9% was unaccounted for. The relatively small amount of terminal addition of B–H bonds to 3,3,3-trifluoropropene should be compared with the 93% terminal addition to but-1-ene,[2] the 80% terminal addition to styrene,[2] and the 63% terminal addition to trimethylvinylsilane.[13]

The new compound 3,3,3-trifluoro-n-propylboron difluoride is only about 8% decomposed at 160° in several days and 1,1-difluoropropene is not a decomposition product. These conditions are far more vigorous than those employed in the formation of the boron compound by hydroboration of 3,3,3-trifluoropropene. It is thus apparent that the 1,1-difluoropropene found after treatment of 3,3,3-trifluoropropene with diborane is not formed by a decomposition, $CF_3\cdot CH_2\cdot CH_2B{<} \longrightarrow CF_2{:}CH\cdot CH_3 + FB{<}$, a process which if it occurred would obviate the necessity to invoke addition of boron to the β-carbon in the hydroboration of 3,3,3-trifluoropropene.

Formation of 1,1-difluoropropene from the diborane–3,3,3-trifluoropropene reaction can be accounted for by the processes:



The 1,1-difluoropropene would be expected to be converted by substances having B–H bonds into 1-fluoropropene, and ultimately into propene (by analogy with the effect of

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[11] Henne and Kaye, *J. Amer. Chem. Soc.*, 1950, **72**, 3369.
[12] Haszeldine, *J.*, 1952, 2504.
[13] Seyferth, *J. Amer. Chem. Soc.*, 1959, **81**, 1844.

diborane on fluoroethylenes [4]). In these reactions, the species BF_3, $CF_3\cdot CH_2\cdot CH_2\cdot BF_2$, $n\text{-}C_3H_7\cdot BF_2$ and R_2BF ($R = Pr^n$ and/or $CF_3\cdot CH_2\cdot CH_2$), BH_2F, BHF_2, $CF_3\cdot CH_2\cdot CH_2\cdot BHF$, and $n\text{-}C_3H_7\cdot BHF$ could be produced from the appropriate B–H containing substances. A second type of reaction involving terminal addition of boron–hydrogen bonds to carbon–carbon double bonds of propene and 3,3,3-trifluoropropene must also occur, with production of the substances RBF_2, R_2BF, R_3B, R_2BH ($R = CF_3\cdot CH_2\cdot CH_2$ and/or Pr^n), $CF_3\cdot CH_2\cdot CH_2\cdot BH_2$, $n\text{-}C_3H_7\cdot BH_2$, $CF_3\cdot CH_2\cdot CH_2\cdot BHF$, and $n\text{-}C_3H_7\cdot BHF$. No isopropylboron compounds were isolated from the reaction mixture, nor was an organoboron compound obtained containing such groups as $CF_3\cdot CHMe\cdot B<$, $CHF_2\cdot CHMe\cdot B<$, or $CH_2F\cdot CHMe\cdot B<$. It is interesting that no compound containing fluoroethyl groups bonded to boron, *e.g.*, $CH_2F\cdot CH_2\cdot B<$, was isolated in the earlier work.[4]

The properties of 3,3,3-trifluoropropylboron difluoride were found to be little affected by the presence of the trifluoromethyl group. As mentioned above, the thermal stability of the compound is relatively high. A further indication of stability is the failure of basic hydrolysis to yield a cyclopropane derivative, as is the case with γ-chloropropylboron compounds.[14]

EXPERIMENTAL

Reactants.—Diborane, graciously presented by the Callery Chemical Company, was distilled before use from a vessel cooled to −150°. 3,3,3-Trifluoropropene was obtained as previously described.[12]

Apparatus and Instruments.—Experiments were conducted in a vacuum system of conventional design. Vapour-pressure measurements were made by using a tensimeter.[15] Infrared spectra were obtained by using a Perkin–Elmer model 21 double-beam spectrophotometer equipped with a sodium chloride prism, and a 4 cm. gas cell with sodium chloride windows. Nuclear magnetic resonance spectra were measured with a Varian V4300B spectrometer equipped with superstabilizer. ^{19}F measurements were made at 56·4 Mc./sec., ^{1}H measurements at 60 Mc./sec.

Reaction between Diborane and 3,3,3-*Trifluoropropene.*—In a typical reaction, a 1-l. Pyrex bulb, fitted with a cold-finger and side-arm, was charged with 196 c.c.* of diborane and 784 c.c. of 3,3,3-trifluoropropene (molar ratio 1 : 4·0). After a few hours at room temperature, clear liquid began to appear in the bulb, but the latter was not opened until two weeks later, previous experience having shown that, by that time, all material containing B–H bonds would have been consumed. The bulb was cooled to −196°, attached to the vacuum system through a tube-opener, and opened. A trace of non-condensible gas was pumped away. The temperature of the cold finger of the bulb was then allowed to rise to −15° (ice–salt), and material volatile at this temperature was taken into the vacuum system and separated into fractions retained at −196° (*A*), −140° (*B*), −112° (*C*), and −63° (*D*).

Fraction *A* (156 c.c.) was shown by its infrared spectrum to consist mainly of boron trifluoride with a small quantity of an olefin. When treated with an excess of distilled water all but 9·2 c.c. of material *A* was absorbed, corresponding to 147 c.c. of boron trifluoride. The residual olefin was added to fraction *B* after passage through a trap at −78°.

Fraction *B* (421·6 c.c.) was shown by its infrared spectrum to be composed mainly of olefins with a small amount of n-propylboron difluoride.[16] The latter was removed by treatment of the gas with trimethylamine to afford Me_3N,BF_2Pr^n. The olefins were then freed from the amine by dilute sulphuric acid to give 395·4 c.c. of boron-free gas. The infrared spectrum of this gas showed that it was largely 1,1-difluoropropene,† with some 3,3,3-trifluoropropene and a trace of 1-fluoropropene.‡ If the latter is assumed to have been present to only a small extent, the approximate composition of the gas as calculated from the average molecular weight was 1,1-difluoropropene, 66%, and 3,3,3-trifluoropropene, 34%.

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* Here and elsewhere in this paper the term " c.c." refers to gas volumes at N.T.P.

† We are indebted to Professor R. N. Haszeldine for a copy of the spectrum of the authentic olefin.

‡ A spectrum of 1-fluoropropene was kindly supplied by Mr. R. Beaudet of this laboratory.

[14] Hawthorne, *J. Amer. Chem. Soc.*, 1960, **82**, 1886.

[15] Burg and Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780.

[16] Brinckman and Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 6218.

Fraction *C* consisted entirely of boron-containing material which on repeated fractionation through a trap at −96° resulted in the isolation of 32 c.c. of the known n-propylboron difluoride (identified by its infrared spectrum [16]) and 46·4 c.c. of the less volatile 3,3,3-*trifluoropropylboron difluoride*, characterized by molecular weight (Found: *M*, 148·6. $C_3H_4BF_5$ requires *M*, 145·8), cleavage with propionic acid [17,18] to give 1,1,1-trifluoropropane quantitatively, and by analysis of the 1 : 1 *trimethylamine addition compound* (Found: C, 35·4; H, 6·5; N, 7·0. $C_6H_{13}BF_5N$ requires C, 35·1; H, 6·4; N, 6·8%). The ^{19}F and ^{1}H nuclear magnetic resonance spectra of the new organoboron fluoride established that it contained a $CF_3\cdot CH_2\cdot CH_2\cdot B-$ rather than a $CF_3\cdot CHMe\cdot B\!<$ group. The ^{1}H spectrum consisted of two groups of peaks of equal intensity separated by 54 c./sec. The high-field group was considerably broadened, which is characteristic behaviour for protons of a CH_2 group bonded to boron. The low-field group consisted of a complex multiplet containing at least six peaks, presumably arising from spin–spin coupling of β-CH_2 group protons with fluorine atoms of the CF_3 group and with the α-CH_2 group protons. The ^{19}F spectrum consisted of a low- and high-field absorption assigned to the CF_3 and the BF_2 group fluorine, respectively. The low-field absorption was a triplet with a splitting of 10·7 c./sec. These results are consistent with the presence of the group $CF_3\cdot CH_2-$ but not with that of the group $CF_3\cdot CH\!<$, which would be present in an isopropylboron structure.

Fraction *D*, a liquid at room temperature, was very difficult to separate into components, and by cleavage with propionic acid was shown to contain both propyl and trifluoropropyl groups bonded to boron. The material non-volatile at −15° was also treated with propionic acid at 160° for 7 days, giving with the gas obtained by cleavage of *D* a total volume of 199 c.c. of propane and 1,1,1-trifluoropropane. On the basis of gas density and infrared spectra this mixture was estimated to consist of roughly 60% of 1,1,1-trifluoropropane and 40% of propane. It is reasonable to assume that these gases were derived from boron by cleavage of n- rather than iso-groups in view of the fact that the $R\cdot BF_2$ compounds obtained from fraction *C* were shown to be the n-isomers.

In further reactions between diborane and 3,3,3-trifluoropropene similar results were obtained.

Properties of 3,3,3-*Trifluoropropylboron Difluoride*.—3,3,3-Trifluoropropylboron difluoride of purity suitable for physical studies was obtained by repeated distillation into a trap at −96°, a temperature at which it is a solid. n-Propylboron difluoride, the most persistent impurity, is a liquid at −96° and this factor, coupled with its greater volatility, contributes to the relatively greater effectiveness of collection at −96° rather than at −112°.

The vapour pressures of liquid 3,3,3-trifluoro-n-propylboron difluoride were measured over a 30° range:

Temp.	−31·5°	−25·0°	−16·3°	−15·8°	0·3°
Pressure (mm.)	22·9	25·0	61·2	62·3	147·4

These results conform to the equation $\log_{10} p$ (mm.) $= 8{\cdot}446 - 1712T^{-1}$, implying a normal b. p. of 34·5°, a heat of vaporization of 7·83 kcal./mole, and a Trouton's constant of 25·5 e.u. The m. p. of the compound is −89·5°.

The infrared spectrum, recorded at 17 and 105 mm. pressure, showed bands at 2967w, 2907w, 2198vw, 2132vw, 1445s, 1406s, 1368s, 1337s, 1269s, 1206d,s, 1135s, 1098s, 1031m, 941m, 883m, 854w, 798w, 759w.

A 14·1 c.c. sample of 3,3,3-trifluoropropylboron difluoride was sealed in a Pyrex tube and heated at 160° for 7 days. After this treatment 12·9 c.c. (91·5%) of the fluoride (identified by its infrared spectrum) were recovered, together with a trace of boron trifluoride. No 1,1-difluoropropene could be detected spectroscopically.

We are indebted to the United States Air Force for support of this work.

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Harvard University, Cambridge, Massachusetts.

[*Received, June 29th*, 1961.]

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[17] Brown and Murray, *J. Amer. Chem. Soc.*, 1959, **81**, 4108.
[18] Massey, *J.*, 1960, 5264.