acquire the tetrahedral configuration of a molecular addition compound. In the case of phenyl derivatives of the Group Vb atoms recent structural data on triphenylamine provide some support for Jaffé's suggestion.[31] The CNC angle is 116°,[32] considerably greater than that in trimethylamine.

[32] Y. Sasaki, K. Kimura and M. Kubo, *J. Chem. Phys.*, **31**, 477 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Organoboron Halides. II. The Vinylhaloboranes, A Preliminary Study of their Preparation and Properties[1,2]

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The new compound vinyldifluoroborane may be obtained by vinylation of boron trifluoride with divinylmercury, divinylzinc, tetravinyltin or di-*n*-butyldivinyltin. Vinyldichloro- and divinylchloroborane can be prepared by treating boron trichloride with tetravinyltin. Although vinyl groups are preferentially cleaved by boron halides from alkylvinyltin compounds, tetraalkyltin compounds react with boron halides to give a variety of alkylhaloboranes. Since many tetraorganotin compounds are commercially available, these reactions represent a useful route for the small-scale preparation of organohaloboranes. Vinyldifluoroborane is not further vinylated when heated with a variety of vinylmetallic reagents. For this reason divinylfluoroborane was prepared by treating divinylchloroborane with antimony trifluoride. A number of physical properties of the new vinylhaloboranes are reported, including the main features of their infrared spectra. Thermal stability of the vinylhaloboranes increases in the sequence $(CH_2{:}CH)_2BF < (CH_2{:}CH)_2BCl < CH_2{:}CHBCl_2 < CH_2{:}CHBF_2$. Modes of decomposition of the compounds are discussed. Vinyldifluoroborane has a high thermal stability, comparable with that of ethyldifluoroborane. The vinylhaloboranes react with water at elevated temperatures with either complete or partial removal of their vinyl groups as ethylene. With ammoniacal silver(I) ion the vinylhaloboranes react in a manner more similar to that of arylboron compounds than alkylboron compounds. Vinyldifluoroborane reacts with diethylzinc to give triethylborane and with trimethylaluminum to give trimethylborane.

In the century since the first report of an organoborane,[4] ever-increasing numbers of alkyl- and aryl-boron compounds have been prepared.[5] However, of the many characterized organoboron compounds only a few contain the $>C{=}CH{-}B$ configuration, *e.g.*, trivinylborane,[6] alkylvinyl-[6a] and alkylpropenylboranes,[6a] β-chlorovinylchloroboranes[7] and certain unsaturated boronic acids.[8] This scarcity of vinylboron compounds is disappointing since, as Ritter and his co-workers[6a,9] have pointed out, B–C π-bonding might occur if a vinyl group is one of three groups bonded to a boron atom. Such a mesomeric effect would be related to the stabilization of Lewis acids such as boron trifluoride by internal dative bonding and to the existence of certain boron compounds such as the dialkoxyboranes as monomers. It is thus clear that a study of vinylboron compounds might well allow a better understanding of the energetics of molecular addition compound formation and of the polymerization of some derivatives of the Group III elements.

Furthermore, from the purely preparative point of view compounds containing the $>C{=}CH{-}B$ grouping should be valuable intermediates in the synthesis of new boron compounds, provided cleavage of vinyl groups from boron is not too facile. With these ideas in mind, and in order to extend vinylboron chemistry, we were led to devise methods for preparing some unreported vinylhaloboranes. This paper describes these methods and also gives a preliminary account of the properties of the new compounds.

In our initial work it was found that vinyldifluoroborane could be prepared by treating boron trifluoride with divinylmercury[10a] or divinylzinc.[11] Later it was discovered that vinyldifluoroborane could be made in even better yield from the reaction between boron trifluoride and the recently described tetravinyltin.[12] Since divinylmercury is toxic and since divinylzinc is inflammable in air and thermally somewhat unstable, use of these reagents was largely abandoned in favor of tetravinyltin. Vinylation of boron trifluoride by the various vinylmetallics occurs slowly at ambient temperatures, but even at elevated temperatures. using a large excess of vinylmetallic, no di- or trivinylation of boron trifluoride occurs. Furthermore, vinyldifluoroborane resists vinylation by divinylmercury and tetravinyltin at temperatures from 100 to 200°.

In contrast to boron trifluoride's inertness to further vinylation both boron trichloride and

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[1] Previous paper, B. Bartocha, W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, **6**, 119 (1958).

[2] The work described in this paper was made possible by the award of a Grant (G5106) from the National Science Foundation and was first presented at the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[3] Public Health Predoctoral Fellow of the National Cancer Institute.

[4] E. Frankland and D. F. Duppa, *Ann.*, **115**, 319 (1860).

[5] M. F. Lappert, *Chem. Revs.*, **56**, 959 (1956).

[6] (a) T. D. Parsons, M. B. Silverman and D. M. Ritter, THIS JOURNAL, **79**, 5091 (1957). (b) A. V. Topchiev, A. M. Payshkin and A. A. Prokorova, *Doklady Akad. Nauk S.S.S.R.*, **129**, 598 (1959).

[7] (a) A. E. Borisov, *Isvest. Nauk S.S.S.R., Otdel. khim. Nauk*, 402 (1951); (b) H. R. Arnold, U. S. Patent 2,402,589 (1946); *C. A.* **40**, 5769 (1947).

[8] R. L. Letsinger and I. H. Skoog, *J. Org. Chem.*, **18**, 895 (1953).

[9] T. D. Parsons and D. M. Ritter, THIS JOURNAL, **76**, 1710 (1954).

[10] (a) B. Bartocha, F. E. Brinckman, H. D. Kaesz and F. G. A. Stone, *Proc. Chem. Soc.*, 116 (1958). (b) B. Bartocha and F. G. A. Stone, *Z. Naturforschg.*, **13b**, 347 (1958). (c) G. F. Reynolds, R. E. Dessy and H. H. Jaffe, *J. Org. Chem.*, **23**, 1217 (1958).

[11] B. Bartocha, H. D. Kaesz and F. G. A. Stone, *Z. Naturforsch.*, **14b**, 352 (1959).

[12] (a) D. Seyferth and F. G. A. Stone, THIS JOURNAL, **79**, 515 (1957). (b) S. D. Rosenberg, A. J. Gibbons and H. E. Ramsden, *ibid.*, **79**, 2137 (1957).

boron tribromide react with tetravinyltin at ambient temperatures or on mild heating to give a mixture of vinylboron compounds. In the case of boron trichloride, by suitably choosing the proportions of reactants, it is possible to obtain mainly vinyldichloroborane or mainly divinylchloroborane. The boiling points of the vinylchloroboranes are sufficiently far apart that the compounds may be effectively separated by fractional distillation at normal pressure, although gas chromatography was used for purification of samples for vapor pressure studies. Gas chromatography, elemental analysis for bromine and treatment with ammoniacal silver(I) ion (see below) also established that a mixture of vinylbromoboranes and trivinylborane is always obtained on treatment of tetravinyltin with boron tribromide, even with the boron halide in large excess. The boiling points of the boron-containing products of this reaction are so close that it proved impossible to separate them adequately by distillation. Furthermore, the boron-bromine bond is so reactive that we have not as yet found a chromatographic column material which is chemically inert to boron bromides yet separates the bromides satisfactorily. Because of these difficulties and because it is doubtful whether the vinylbromoboranes have chemical properties very different from the easily obtained vinylchloroboranes, we were led to abandon studies with the bromo-compounds.

During the course of our work it was found that the vinyl group is cleaved preferentially from alkylvinyltin compounds by boron halides. Therefore, compounds such as di-*n*-butyldivinyltin also may be used to prepare vinyldifluoro-, vinyldichloro- and divinylchloroborane. Similarly, it was observed that ethylvinylmercury and boron trifluoride react to give vinyldifluoroborane and that ethyldifluoroborane is not produced. Although boron halides cleave vinyl groups in preference to alkyl from alkylvinylmetallic compounds, it proved possible to prepare alkylhaloboranes by treating tetraalkyltin compounds with boron halides. Furthermore, tetraallyltin and tetraphenyltin react with boron trifluoride to afford allyldifluoro- and phenyldifluoroborane, respectively.[13a]

Since many tetraorganotin compounds are commercially available or can be prepared very easily, the tin compounds represent an easy laboratory route to a wide variety of organohaloboranes. In this Laboratory, besides obtaining many alkylhaloboranes such as dimethylbromo- and methyldichloroborane from the appropriate tetraalkyltin compound and boron halide, we have recently extended this type of reaction to prepare a series of perfluorovinylboron compounds, *e.g.*, $(CF_2{:}CF)_2BCl$[13b] from perfluorovinyltin compounds.

Although on treatment with excess of tetravinyltin at elevated temperatures neither boron trifluoride nor vinyldifluoroborane could be converted to divinylfluoroborane, the latter was obtained in good yields *via* the reaction

$$(CH_2{:}CH)_2BCl \xrightarrow{SbF_3} (CH_2{:}CH)_2BF$$

carried out well below 0°.

The vinylboron halides (Table I) vary in thermal stability. In the gas phase vinyldifluoroborane and its ethyl analog have comparable stabilities. These fluorides may be stored for months without decomposition. Samples of $CH_2{:}CHBF_2$ and $C_2H_5BF_2$ were recovered essentially quantitatively after being heated at 200° for 20 hr. at pressures of about 0.2 atm. In fractionation of vinyldichloroborane at normal pressures no significant decomposition occurred even though the still-pot temperature reached 80–100°. Pure samples of $CH_2{:}CHBCl_2$, however, after storage as liquid for several months deposited small quantities of a white solid. Since no boron trichloride was recovered, it appears that the usual disproportionation of organohaloboranes is not involved, but rather slight polymerization occurs. A liquid sample of divinylchloroborane after 24 hr. at ambient temperature underwent decomposition to the extent of about 3%, forming a small amount of air-sensitive solid, but again no boron trichloride was formed. Divinylfluoroborane, however, decomposes extensively in the gas phase in 24 hr. at room temperature, the decomposition products consisting primarily of vinyldifluoroborane and trivinylborane, together with some glassy solid, apparently polymeric in nature. These studies show that thermal stability increases in the sequence $(CH_2{:}CH)_2BF$, $(CH_2{:}CH)_2BCl$, $CH_2{:}CHBCl_2$, $CH_2{:}CHBF_2$. The compound allyldifluoroborane, which does not seem to have been described in the chemical literature before, is much less stable than vinyldifluoroborane, since it forms some boron trifluoride and polymer within a few minutes when stored at 0° in the liquid phase. In general allyl compounds of metals and metalloids appear to be thermally less stable than their vinyl analogs.[14]

TABLE I

PHYSICAL PROPERTIES OF SOME VINYLHALOBORANES

Compound	M.p.[a] (°C.)	Log $p_{(mm.)} = B - AT^{-1}$ B	Log $p_{(mm.)} = B - AT^{-1}$ A	B.p.[b] (°C.)	Trouton constant[b] (e.u.)	$\Delta H_{vap.}$ (kcal. mole^{-1})
$CH_2{:}CHBF_2$	−133.4	7.915	1180	−38.8	23.0	5.40
$CH_2{:}CHBCl_2$	−111.1	7.434	1449	45.1[c]	20.8	6.63
$(CH_2{:}CH)_2BF$[d]	.....	7.416	1347	23.8	20.7	6.16
$(CH_2{:}CH)_2BCl$	−109.6	7.885	1723	71.1	22.9	7.88

[a] Stock magnetic plunger method. [b] By extrapolation of the vapor pressure equation. [c] Observed 45.4°. [d] Forms glass, melting range −164 to −157°.

Vinyldifluoroborane reacts with water at 120° to form ethylene quantitatively. Under identical hydrolytic conditions ethyldifluoroborane produced no ethane,[15] and vinyldichloro- and divinylchloroborane yielded ethylene in about 85 and 30% yields, respectively. However, at room temperature hydrolysis of vinyldifluoroborane occurs

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(13) (a) When R_4Sn is a non-volatile or high melting material, it has been found useful to add small amounts (*ca.* 10%) of either BCl_3 or BBr_3 to the BF_3/R_4Sn reaction. The desired RBF_2 is isolated by vacuum fractionation. (b) H. D. Kaesz, S. L. Stafford and F. G. A. Stone, THIS JOURNAL, **81**, 6336 (1959). See also Abstracts of Papers presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960, p. 38-M.

(14) For a recent review of vinylmetal and -metalloid compounds see H. D. Kaesz and F. G. A. Stone, chapter 3, A.C.S. Monograph "Organometallics," Ed. H. Zeiss, Reinhold Publishing Co., New York, N. Y., 1960, chapter 3.

(15) S. L. Stafford and F. G. A. Stone, THIS JOURNAL, **82**, 6238 (1960).

without any cleavage of the vinyl group. Perfluorovinyldifluoroborane, on the other hand, immediately releases some trifluoroethylene on treatment with water at ambient temperatures.[15] Qualitatively the susceptibility of these various boron halides toward cleavage of their organo-groups by water thus increases in the order, $C_2H_5BF_2$ < $(CH_2:CH)_2BCl$ < $CH_2:CHBCl_2$ < $CH_2:CHBF_2$ < $CF_2:CFBF_2$.

In order to learn more about the nature of the reaction between organoboranes and ammoniacal silver(I) ion the vinylhaloboranes were reduced with ammoniacal silver oxide solution at 100°, and the resultant gases fractionated, measured and identified by comparing their infrared spectra with those of the pure compounds (Table II). It is interesting that only in the case of the divinylhaloboranes or trivinylborane is butadiene produced. Furthermore, during the hydrolysis studies, mentioned above, no butadiene formation was observed even from the divinylhaloboranes. Apparently for coupling of vinyl groups to take place at least two vinyl groups must be present on the same boron atom, and a reductive-type cleavage reagent must be used. Qualitatively the reduction of ammoniacal silver(I) ion by substances containing certain kinds of boron–carbon bond has been known for many years,[16] but it was not until 1938 that a systematic study of the reaction was reported.[17] In an investigation of the reaction between a wide variety of alkyl- and arylboronic acids with ammoniacal silver(I) ion, it was found that reductive cleavage, with formation of a silver mirror and coupling of organogroups, occurred only with alkylboron compounds. Although aryl groups on boron were cleaved by the reagent, no silver mirror was produced, nor was coupling of aryl groups observed. It is interesting, therefore, as shown by the work described here (Table II), as well as that described earlier on the alkylvinylboranes,[6a] that the behavior of a vinyl group on boron is intermediate between that of an aryl or an alkyl group toward ammoniacal silver(I) ion.[17] Since the earlier work[17] involved boronic acids, while the more recent studies involve alkylvinyl- and vinylhaloboranes, for comparison purposes the reaction between *n*-propyldifluoroborane and ammoniacal silver(I) ion was studied. *n*-Hexane was the principal hydrocarbon produced the reaction thus paralleling that of the alkylboronic acids. Allyldifluoroborane, on the other hand, yielded propylene only (Table II), and thus the allyl-boron linkage apparently is similar to that of the aryl-boron group in that although a reaction occurs it is principally a hydrolytic cleavage and does not involve reduction.

The compound trivinylborane mentioned in Table II is formed in the thermal decomposition of divinylfluoroborane. Alternatively, it may be produced in small quantities by treating boron trichloride with tetravinyltin in a 1:1 ratio, although with this ratio of reactants divinylchloroborane is the main product. The data in Table II concerning trivinylborane indicate the presence of three vinyl groups per boron atom. The gas density of the material also conformed with the formulation $(CH_2:CH)_3B$.[18] However, trivinylborane has been previously described,[6a] but the vapor pressures reported earlier do not agree with those obtained in this Laboratory. Thus at 0° we observed vapor pressures of from 35–40 mm., whereas Ritter and co-workers[6a] report 63 mm. It is interesting that the earlier workers report that their trivinylborane decomposes to a "daughter" compound of unspecified composition with a vapor pressure at 0° of about 37 mm.[6a] Perhaps trivinylborane is able to exist in several different forms, for example monomeric as a gas but slowly changing from monomer to dimer or to more highly polymerized species in the liquid phase. Such behavior is not unknown in boron chemistry. As a solid $(CH_3)_2BNH_2$ is dimeric, but as a gas at 30° it is monomeric.[19] Similarly, dimethylaminodichloroborane $[(CH_3)_2NBCl_2]$ when initially formed is a liquid whose vapor is monomeric, but in a few days the liquid changes into a solid which is dimeric in benzene.[20]

TABLE II

PRODUCTS OF REACTION OF VINYLHALOBORANES AND RELATED COMPOUNDS WITH SILVER AMMONIUM HYDROXIDE

Compound	Vol. taken for reaction (cc.)[a]	Time of heating at 100° (hr.)	C_2H_4 (cc.)[a]	$CH_2:CHCH:CH_2$ (cc.)[a]	Vinyl groups cleaved per boron atom
$CH_2:CHBF_2$	19.4	3	17.1	..	0.88
$CH_2:CHBCl_2$	18.7	18	17.1	..	0.92
$(CH_2:CH)_2BF$	51.5	3	83.5	8.0	1.93
$(CH_2:CH)_2BCl$	27.3	1	36.1	5.2	1.70
$(CH_2:CH)_3B$	35.6	3	69.5	10.7	2.56[b]
$CH_2:CHCH_2BF_2$	15.9	3	..	..	..[c]
n-$C_3H_7BF_2$	47.3	2	..	..	..[d]

[a] Throughout this paper the abbreviation "cc." refers to gases at standard conditions. [b] In a previous study[6a] of reductive cleavage of trivinylborane 0.79 vinyl group per boron atom was cleaved as ethylene and butadiene. [c] Propylene equivalent to 0.93 allyl group per boron atom was obtained. [d] The hydrocarbon products were 10.8 cc. of *n*-C_6H_{14} and 9.6 cc. of $CH_3CH:CH_2$.

During the course of our work the infrared spectra of the new vinylhaloboranes were recorded.[14,21] Some of these spectra will be the subject of detailed analyses later, *e.g.*, $CH_2:CHBF_2$,[22] but brief comment is made here since the spectra were used extensively in following successive steps in purification of the vinylhaloboranes. The characteristic infrared bands of the compounds listed in Table I are given in the Experimental Section. All the vinylhaloboranes show C–H stretching modes between 2975 and 3100 cm.$^{-1}$. These absorptions are relatively more intense in the divinylhaloboranes than in the vinyldihaloboranes. The vinylboron halides, as well as trivinylborane, all have a band from medium to strong intensity

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[16] A. Michaelis and P. Becker, *Ber.*, **15**, 181 (1882).

[17] (a) H. R. Snyder, J. A. Kuck and J. R. Johnson, THIS JOURNAL, **60**, 105 (1938). (b) J. R. Johnson, M. G. Van Campen and O. Grummitt, *ibid.*, **60**, 111 (1938). (c) J. R. Johnson, H. R. Snyder and M. G. Van Campen, *ibid.*, **60**, 115 (1938).

[18] A molecular weight of 92.7 was observed; C_6H_9B requires mol wt. of 92.0.

[19] J. Goubeau and R. Link, *Z. anorg. Chem.*, **267**, 27 (1951).

[20] E. Wiberg and K. Schuster, *ibid.*, **213**, 77 (1933).

[21] F. E. Brinckman, Ph.D. Thesis, Harvard University.

[22] The infrared spectra of vinyldifluoroborane is being studied by Professor M. K. Wilson and his co workers.

between 1610 and 1640 cm.$^{-1}$ which may be assigned to the C=C stretching vibration. In the preparation of vinyldifluoroborane it is necessary to free the vinyl compound from unreacted boron trifluoride by distillation in the vacuum line. Since boron trifluoride has an intense band at 691 cm.$^{-1}$,[23] whereas vinyldifluoroborane has no band at this frequency, distillation is repeated until the band at 691 cm.$^{-1}$ vanishes from the spectrum of the vinyl compound. In this manner we have found that as little as 0.2 mole% of boron trifluoride in vinyldifluoroborane is detectable. Similarly, the strong band at 954 cm.$^{-1}$ in the spectrum of boron trichloride[24] does not coincide with any band in the spectrum of vinyldichloroborane. Therefore, this band at 954 cm.$^{-1}$ may be used to ensure that vinyldichloroborane is free from boron trichloride. As would be expected, the infrared spectra of divinylchloro- and divinylfluoroborane are more complex than those of their monovinyl analogs. However, divinylfluoroborane has no band at 728 cm.$^{-1}$ where vinyldifluoroborane has a band of medium intensity and, therefore, this band can be used to follow the removal of vinyldifluoroborane from the divinylfluoro-compound. In the preparation of divinylchloroborane common impurities are vinyldichloroborane and trivinylborane. Although these compounds are readily separable by chromatography, infrared spectroscopy also can be used to check on purity since bands at 751 cm.$^{-1}$ in the spectrum of trivinylborane and at 640 cm.$^{-1}$ in the spectrum of vinyldichloroborane do not coincide with any bands in the spectrum of divinylchloroborane.

The inertness of vinyldifluoroborane toward tetravinyltin was mentioned earlier in this paper. Similarly, no reaction occurred between tetraethyltin and vinyldifluoroborane at 120° for 17 hr. However, vinyldifluoroborane does react with diethylzinc and trimethylaluminum. In an experiment with diethylzinc at room temperature triethylborane (43%) and unreacted vinyldifluoroborane (52%) were the major products. Trimethylaluminum and vinyldifluoroborane react exothermically at the melting point (*ca.* 15°) of the aluminum compound, with about a 70% conversion of the vinylboron compound to trimethylborane. Although no formation of mixed alkylvinylfluoroboranes was detected in these experiments, preliminary studies with vinyldichloroborane, which will be reported later, indicate that vinylchloroborane can be partially alkylated.

The vinyldihaloboranes partake in equilibria of the type

$$3CH_2{:}CHBF_2 + 2BCl_3 \rightleftharpoons 2BF_3 + 3CH_2{:}CHBCl_2$$

A subsequent paper will describe a mass spectrometric study of these equilibria showing that in these reactions only halogen atom exchange is involved, *i.e.*, the B–C bond is uniquely preserved in the exchange.

Experimental[25]

1. **Apparatus and Starting Materials.**—Divinylmercury, divinylzinc and di-*n*-butyldivinyltin were prepared as described previously.[10b,11,12a] Tetraallyl- and tetra-*n*-propyltin were obtained by treating tin tetrachloride with the appropriate Grignard reagent. Diethylzinc also was made by the Grignard method. We are indebted to the Metal and Thermit Corporation for gifts of tetravinyl- and tetraethyltin, and to the Ethyl Corporation for a gift of trimethylaluminum.

Much of the work described was carried out with the aid of a conventional-type high-vacuum system. Infrared spectra were recorded employing a Model 21 Perkin–Elmer double-beam spectrometer with sodium chloride optics. Chromatography was accomplished using a Perkin–Elmer Model 154-C vapor fractometer, suitably modified for introduction and collection of air-sensitive materials.

2. **Preparation of the Vinylhaloboranes. Vinyldifluoroborane.** (a) **From Divinylmercury.**—A dry one-liter Pyrex bulb was charged with 565 cc.[26] of boron trifluoride and 3.14 g. (12.3 mmoles) of divinylmercury. The bulb was sealed off and allowed to stand for 0.5 hr. at room temperature, during which time much white solid, which turned black in sunlight, was observed to form. The reaction bulb then was attached to the vacuum line, opened with a tube-opening device and its contents fractionally distilled through traps held at −80, −130 and −196°. In this manner vinyldifluoroborane (51.3 cc., 19% yield) was collected at −130°. In another experiment in which the reaction time at room temperature was 14 hr. the yield of vinyldifluoroborane was 30%. The compound was characterized by hydrolysis (a 31.2 cc. sample afforded 30.5 cc. of ethylene after treatment with water at 120° for 20 hr.), by molecular weight (found, 75.7; calcd. for $C_2H_3BF_2$, 75.9) and by analysis of the trimethylamine adduct, $Me_3N{\cdot}BF_2CH{:}CH_2$.

Anal. Calcd. for $C_5H_{12}NBF_2$: C, 44.5; H, 9.0; N, 10.4. Found: C, 44.6; H, 8.9; N, 10.3.

(b) **From Divinylzinc.**—A mixture of divinylzinc (0.547 g., 4.58 mmoles) and boron trifluoride (117.1 cc.) reacted on warming to −78°. Reaction was continued for 2 hr. at room temperature, after which fractionation afforded vinyldifluoroborane (28.0 cc., 27% yield) and boron trifluoride (75.4 cc.). The vinyldifluoroborane was characterized by comparing its infrared spectrum with that of the vinyldifluoroborane obtained from divinylmercury and boron trifluoride.

(c) **From Tetravinyltin.**—A carefully dried one-liter Pyrex bulb fitted with a break-off side arm was loaded with a 3.99 g. (17.6 mmoles) sample of tetravinyltin and 813 cc. (36.2 mmoles) of boron trifluoride. The bulb was sealed off and heated at 60° for 24 hr. The bulb then was opened to the vacuum line and its contents fractionated to give at −130° 410 cc. (52.0% yield) of vinyldifluoroborane (identified by comparing the infrared spectrum with a chemically analyzed sample) and at −196° 158 cc. of boron trifluoride.

In a similar manner 0.865 g. (3.01 mmoles) of di-*n*-butyldivinyltin and 135.2 cc. of boron trifluoride after 1 hr. at 100° gave 46.5 cc. of vinyldifluoroborane. No *n*-butyldifluoroborane, which is much less volatile than the vinyl compound, was obtained.

Vinyldichloroborane.—Tetravinyltin (7.03 g., 31.0 mmoles) was treated with boron trichloride (1481 cc., 66.1 mmoles) in a one-liter Pyrex bulb for 128 days at room temperature. The reaction vessel was then opened to the vacuum line and its volatile contents distilled through traps held at −45, −80 and −196°. The material retained at −80° then was fractionated under nitrogen through a small distillation column and thereby afforded 904 cc. (yield 65%) of vinyldichloroborane at 45.4° (760 mm.). Vinyldichloroborane was characterized by its molecular weight (found: 109.4; $C_2H_3BCl_2$ requires 108.8) and by analysis of its trimethylamine adduct.

Anal. Calcd. for $C_5H_{12}NBCl_2$: C, 35.8; H, 7.2; N, 8.3. Found: C, 35.5; H, 7.1; N, 8.2.

In another preparation of vinyldichloroborane 4.14 g. (18.25 mmoles) of tetravinyltin was treated with 834 cc. (37.23 mmoles) of boron trichloride at ambient temperature for 24 hr. The mixture was then fractionated in the vacuum line through traps held at −80 and −196°. In this manner 672 cc. of gas was retained at −80°, but the infrared spec-

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[23] J. Vanderryn, *J. Chem. Phys.*, **30**, 331 (1959), and references cited therein.

[24] L. P. Lindeman and M. K. Wilson, *ibid.*, **24**, 242 (1956), and references cited therein.

[25] Microanalyses were performed by Dr. Carol K. Fitz, Needham Heights, Mass.

[26] See Table II, footnote *a*.

TABLE III

VAPOR TENSIONS OF LIQUID n-$C_3H_7BF_2$

t, °C.	−78.4	−63.8	−50.8	−45.0	−36.1	−24.7
$p_{mm.}$ (obsd.)	3.9	14.1	37.1	56.2	101.5	198.8
$p_{mm.}$ (calcd.)	4.0	14.1	37.7	56.4	100.9	200.0

TABLE IV

VAPOR TENSIONS OF LIQUID $CH_2{:}CHCH_2BF_2$

t, °C.	−78.8	−63.3	−52.6	−45.0	−36.2	−24.3
$p_{mm.}$ (obsd.)	4.3	15.9	34.0	55.9	98.5	193.4
$p_{mm.}$ (calcd.)	4.4	15.7	34.1	56.6	98.0	193.2

TABLE V

VAPOR TENSIONS OF THE VINYLHALOBORANES

t, °C.	$p_{mm.}$ (obsd.)	$p_{mm.}$ (calcd.)	t, °C.	$p_{mm.}$ (obsd.)	$p_{mm.}$ (calcd.)
		(a) $CH_2{:}CHBF_2$			
−95.5	18.5	18.8	−74.3	96.2	95.9
−83.6	50.2	49.1	−63.3	196.3	196.3
−77.4	75.0	77.3	−51.9	381.3	382.8
			−45.0	553.1	554.6
		(b) $CH_2{:}CHBCl_2$			
−36.2	20.5	20.9	− 0.4	134.3	132.4
−23.9	41.7	41.9	5.0	167.5	168.3
−13.8	69.9	70.5	8.7	196.6	196.8
		(c) $(CH_2{:}CH)_2BF$			
−79.8	3.1	2.8	−36.2	53.2	54.0
−67.4	7.6	7.4	−23.7	104.0	104.0
−54.4	18.2	18.2	−10.6	198.1	193.5
−45.0	32.2	32.6	− 0.3	303.8	302.0
		(d) $(CH_2{:}CH)_2BCl$			
1.9	41.7	42.0	15.6	83.4	83.0
4.9	48.8	48.9	17.6	91.2	91.2
7.1	54.6	54.7	20.1	102.3	102.3
9.6	61.9	61.9	22.6	114.5	114.8
13.6	75.2	75.3	24.9	126.7	127.3

TABLE VI[a,b]

INFRARED SPECTRA OF THE ORGANOHALOBORANES (cm.$^{-1}$)

(a) Vinyldifluoroborane: 3095(w); 3040(sh); 2995(d,w); 1980, 1965(d,vw); 1640, 1629, 1620(m); 1431(f,s); 1383, 1369(d,s); 1327, 1319, 1309(s); 1256, 1248, 1241(s); 1023(sh,w); 1013(m); 988(sh,m); 730(sh,-m); 728(m)

(b) Vinyldichloroborane: 3095(w); 3060(w); 3025, 2985-(d,w); 1980(d,vw); 1610(m); 1424(s); 1379(m); 1290(w); 1149(sh,s); 1125, 1116(d,vs); 1032(sh,m); 1007(vs); 987(sh,m); 913(b,vvs); ca. 640(b,m)

(c) Divinylfluoroborane: 3100(mw); 3009(mw); 1976, 1963, 1946(w); 1632, 1620(d,m); 1443, 1433(d?,s); 1339(sh,w); 1312, 1300(d?,m); 1261, 1250(d,m); 1185(sh,w); 1157, 1149(ms); 1126(sh,w); 1094, 1088, 1082(m); 1015(sh,m); 981(ms); 973(sh,m); 848(b,vw); 749(b,m)

(d) Divinylchloroborane: 3080(mw); 3050(w); 3000, 2975(d,mw); 1965(w); 1612(m); 1435, 1427(s); 1294(b,w); 1190(sh,w); 1166, 1155(m); 1138(sh,w); 1078(ms); 1013, 1000, 994, 983, 973(f,m); 935(b,m); 703(b,w)

(e) Trivinylborane: 3080(ms); 3050(sh,m); 3003, 2972-(d,ms); 1947(w); 1619, 1605(d,s); 1422(vs); 1297-(w); 1183(sh,ms); 1151(s); 1086(s); 1014(sh,f,s); 969(b,f,vs); 751(b,m)

(f) n-Propyldifluoroborane: 2980(m); 2950(sh,m); 2900-(sh,m); 2170(vw); 2113(vw); 1377(f,vs); 1273(m); 1195(m); 1027(w); 894(b,vw); 838, 802(vb,w); 728(b,w)

(g) Allyldifluoroborane: 3135(w); 3100(sh,vw); 3055-(sh,vw); 3020(w); 2930(b,sh,w); 1843, 1836(d,vw); 1654, 1647(d,m); 1375, 1344(vs); 1180(s); 989(m); 913(b,f,s); 844(b,f,m)

[a] w = weak; m = medium; s = strong; d = doublet; v = very; b = broad; f = unresolved fine structure; sh = shoulder. [b] Spectra were calibrated against standard atmospheric peaks.

trum indicated it was a mixture of vinyldichloro- and divinylchloroborane. Complete separation of the two components then was accomplished by repeated slow distillation through a trap held at −65°. In this manner 294 cc. (36% yield) of vinyldichloroborane was obtained.

Divinylchloroborane.—Using procedures similar to those described above, 8.00 g. (35.26 mmoles) of tetravinyltin and 794 cc. (35.43 mmole) of boron trichloride were heated at 60° for 1.5 hr. Volatile products then were fractionated through traps held at −45° (to remove tetravinyltin), −80° and −196°. Only 45.8 cc. of gas collected at −196° and infrared spectroscopy established it to be a mixture of ethylene, 1,3-butadiene and phosgene, the last a common contaminant of commercial boron trichloride. The −80° fraction (1.34 g.) was chromatogrammed on a column of paraffin on firebrick, establishing it as a mixture of vinyldichloroborane (5.2%), divinylchloroborane (91.7%) and trivinylborane (3.1%). Elution times were 9.0, 15.4 and 21.4 minutes, respectively, at 60° and using a helium flow of 98 cc./min.

Yield of chromatographically[27] pure divinylchloroborane based on starting tetravinyltin was 35%.

Anal. Calcd. for C_4H_6BCl: Cl, 35.3; mol. wt., 100.4. Found: Cl, 35.4, 35.3; mol. wt., 100.7.

Divinylfluoroborane.—A 42.6 g. (238 mmoles) sample of antimony trifluoride was dried at 120° for several days and placed in a trap attached to the vacuum line. Freshly prepared divinylchloroborane (242.5 cc., 10.8 mmoles) was then distilled on the antimony trifluoride and held at −80° for 35 hr. This treatment yielded 42.5 cc. of gas volatile at −80° which was removed. The reaction vessel was maintained at −25° for another 5 hr. and in this manner a further 112.3 cc. of gas volatile at −80° was recovered. Further reaction at 0° for 1 hr. afforded only 4.2 cc. of gas passing −80° so the fluorination was stopped. An examination of the infrared spectra of all the gas recovered and which passed −80° showed it to be a mixture of vinyldifluoroborane and material with a spectrum expected for divinylfluoroborane; this expectation was confirmed by mass spectral analysis. Fractionation through traps at −96, −116 and −196° afforded 7 cc. of gas at −96°, which was discarded, 45.4 cc. of vinyldifluoroborane at −196° and 100.4 cc. (41% yield) of divinylfluoroborane retained at −116°. The divinylfluoroborane was characterized by its molecular weight (found: 85.1; C_4H_6BF requires 83.9) and by reaction with ammoniacal silver(I) ion (Table II).

3. Preparation of Organohaloboranes from Tetraorganotin Compounds.—To illustrate this type of reaction the preparation of the new compound n-propyldifluoroborane is described. Tetra-n-propyltin (4.61 g., 15.8 mmoles) was heated with boron trifluoride (706 cc., 31.5 mmoles) at 110° for 20 hr. in a one-liter Pyrex bulb. Fractionation of the reaction products in the vacuum line through traps held at −45, −80, −125, and −196° yielded the bulk of the n-propyldifluoroborane at −80°, a little of the propyl compound together with a trace of boron trifluoride (detected by its infrared spectrum) at −125° and unreacted boron trifluoride at −196°. Further distillation using a bath at −120° gave 308 cc. (43.5% yield) of n-propyldifluoroborane characterized by its molecular weight and analysis of the adduct $(CH_3)_3N{\cdot}BF_2C_3H_7$.

Anal. Calcd. for $C_3H_7BF_2$: mol. wt., 91.9. Found: mol. wt., 92.5. Calcd. for $C_6H_{16}NBF_2$: C, 47.7; H, 10.7; N, 9.3. Found: C, 47.9; H, 10.8; N, 9.5.

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(27) Divinylchloroborane of at least 95% minimum purity may be obtained by vacuum line distillation, without the aid of vapor phase chromatography.

The vapor tensions of *n*-propyldifluoroborane (Table III) determined the equation $\log p_{mm.} = 8.478 - 1535\ T^{-1}$, from which is calculated a boiling point of 1.1°, and the Trouton constant of 25.6 e.u. The compound melts at −106°.

The new compound allyldifluoroborane was prepared by heating boron trifluoride with tetraallyltin. The vapor tensions (Table IV) of allyldifluoroborane (m.p. −154.7°) determined the equation $\log p_{mm.} = 8.160 - 1462\ T^{-1}$, implying a boiling point of 3.7° and a Trouton constant of 24.2 e.u.

4. Vapor Tensions of the Vinylhaloboranes.—Vapor tensions given in Table V imply the relevant physical constants summarized in Table I.

5. Infrared Spectra of the New Organohaloboranes.—These were recorded as gases using a 4 cm. cell fitted with NaCl plates. Initially a pressure of 100 mm. was used, but in order to establish the centers of the strong bands, further spectra at 20 mm. pressure were taken.[14,21]

6. Reactions between Vinyldifluoroborane and Certain Organometallic Compounds.—Vinyldifluoroborane (101 cc., 4.5 mmoles) and *tetravinyltin* (0.643 g., 2.83 mmoles) were heated in a one-liter bulb at 120° for 15 hr., after which time 99.7 cc. of vinyldifluoroborane (identified by its infrared spectrum) and a trace of boron trifluoride (identified by its spectrum) were recovered. The vinyldifluoroborane then was returned to the reaction vessel and heated at 150° for 17 hr., but even under these conditions 98% of the vinylboron fluoride was recovered, although the tin compound had begun to decompose, yielding ethylene and a trace of butadiene (identified by their infrared spectra).

Vinyldifluoroborane was unaffected on heating for 18 hr. with *divinylmercury* (at 120°) and *tetraethyltin* (at 120°). Similarly, the vinylboron fluoride was 96% recovered after treatment with *divinylzinc* at room temperature for 18 hr.

A 0.611 g. (4.95 mmoles) sample of *diethylzinc* was treated with 101 cc. (4.51 mmoles) of vinyldifluoroborane for 1 hr. at ambient temperature. Fractionation of the products, with identification by comparing spectra with those of the pure compounds, yielded 43.4 cc. of triethylborane held at −80°, and 52.7 cc. of vinyldifluoroborane condensed at −196°. This represents a 95% recovery of boron.

Trimethylaluminum (1.59 g., 22.1 mmoles) reacted rapidly with vinyldifluoroborane (150 cc., 6.70 mmoles) near 0° to afford 104 cc. of trimethylborane (identified by comparing its infrared spectrum with an authentic sample of Me_3B) condensing at −120° and 3.5 cc. of a trimethylborane–ethylene mixture at −196°. This corresponds to a 71% conversion of vinyldifluoroborane to trimethylborane.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Organoboron Halides. III. Lewis Acidity and F^{19} Nuclear Magnetic Resonance Spectra of Some Organodifluoroboranes[1,2]

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The trimethylamine addition compounds of methyl-, ethyl-, *n*-propyl- and vinyldifluoroborane have been prepared and their liquid saturation pressures and gas-phase dissociations measured. The enthalpies of dissociation are markedly similar. F^{19} nuclear magnetic resonance chemical shifts indicate that the substituent group X in $X{-}BF_2$ molecules exerts an effect on the BF_2 moiety which is different from that predicted on the basis of simple electronegativity considerations. The possible significance of these observations is discussed.

Introduction

The study of gas-phase dissociation equilibria of molecular addition compounds[4] has demonstrated that a variety of factors may play a part in determining the relative stabilities of a series of similar adducts. The substituents bonded to any given pair of donor and acceptor atoms, *e.g.*, nitrogen and boron, are of great importance in determining their coördination behavior, and it has been amply shown that substituent effects may be inductive, steric, mesomeric or a combination of these and other factors. Unfortunately, most of the existing data which demonstrate substituent effects have been concerned with the donor. With but two exceptions, mentioned below, quantitative gas-phase dissociation studies of molecular addition compounds of boron with donor atoms of Groups V and VI have involved either boron trifluoride, borane or trimethylborane as the Lewis acid.

The earliest systematic investigation of the effect of varying substituents on the boron atom was performed by Burg and Green[5] who showed that successive substitution of methyl groups for the more highly electronegative fluorine led to decreasing acidity toward trimethylamine in the sequence BF_3, CH_3BF_2, $(CH_3)_2BF$, $(CH_3)_3B$. More recently, Miller[6] has shown a similar order of acidity in the methylchloroboranes.

The relative effect of different alkyl groups on the acceptor power of boron has not been investigated heretofore. In contrast, Brown and his co-workers[7] have shown that methyl, ethyl and *n*-propyl groups on nitrogen increase the Lewis basicity of the amines in the order $NH_3 < CH_3NH_2 < C_2H_5NH_2 < n\text{-}C_3H_7NH_2$, as would be expected on the basis of the accepted order of electron-releasing power of the substituent groups. A complementary study of the relative Lewis acidities of a series of organoboron compounds seemed, therefore, to offer an interesting area of investigation.

The possible effect on Lewis acidity of a vinyl group bonded to boron is particularly interesting, both intrinsically and for the sake of comparison

(1) (a) Previous paper, F. E. Brinckman and F. G. A. Stone, THIS JOURNAL, **82**, 6218 (1960). (b) Also Part IV of the series "Molecular Addition Compounds of Boron"; for Part III see H. D. Kaesz and F. G. A. Stone, *ibid.*, **82**, 6213 (1960).

(2) The work described in this paper was made possible by the award of a grant (G5106) from the National Science Foundation and was first presented at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

(3) Edwin W. Rice, Jr., Fellow of the General Electric Educational and Charitable Fund, 1959–1960.

(4) For a review of molecular addition compounds of the Group III elements, see F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958).

(5) A. B. Burg and A. A. Green, THIS JOURNAL, **65**, 1838 (1943).

(6) N. E. Miller, *Diss. Abstr.*, **18**, 1972 (1958).

(7) (a) H. C. Brown, H. Bartholomay and M. D. Taylor, THIS JOURNAL, **66**, 435 (1944); (b) H. C. Brown and M. D. Taylor, *ibid.*, **69**, 1332 (1947); (c) H. C. Brown, M. D. Taylor and S. Sujishi, *ibid.*, **73**, 2464 (1951).