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REACTIONS OF DIBORON TETRAHALIDES WITH SOME UNSATURATED ORGANOMETALLIC COMPOUNDS

T. D. COYLE AND J. J. RITTER
Inorganic Chemistry Section, National Bureau of Standards, Washington, D.C., 20234 (U.S.A.)
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SUMMARY

Tetrachloro- and tetrafluorodiborane(4) add to the double bond in a number of vinyl derivatives of boron, carbon, silicon, germanium, and tin to form 1,2-bis(dihaloboryl)ethyl derivatives. Most of the compounds are stable *in vacuo* at temperatures in excess of 150°. Tetrachlorodiborane(4) undergoes addition considerably more readily than does tetrafluorodiborane(4). Relative rates of addition have been determined and shown to be markedly dependent on the nature of the substituent on the vinyl group.

INTRODUCTION

The earliest reported investigations of the reactions of diboron tetrahalides with organometallic reagents involved unsuccessful efforts to prepare organo-substituted derivatives of these subhalides. Attempts to alkylate tetrachlorodiborane(4) with dimethylzinc yielded only trimethylborane and unidentified black residues that were presumed to contain elemental boron[1]. It was suggested that methylated derivatives of the subhalides, once formed, were unstable with respect to irreversible decomposition, or that the organometallic reagents were acting as reducing agents.

The reaction of the subchloride with an excess of tetramethyllead has been reported[2] to yield trimethyllead chloride, trimethylborane, and polymeric $(BCl)_x$. The boron-containing products were presumed to arise from disproportionation of partially methylated tetrachlorodiborane(4).

Reactions of tetrafluorodiborane(4) with a number of organometallic compounds have also been reported[3]. Treatment of the subfluoride with diphenylmercury led to reduction of the organometallic compound to elemental mercury, with the formation of phenyldifluoroborane. Diethylmercury gave ethane, ethyldifluoroborane, and residues containing the metal.

With unsaturated organic derivatives of metals and metalloids, at least two types of reactions could be anticipated, in addition to the reduction already noted. Metathetical reactions might produce unsaturated organochlorodiborane(4) derivatives, possibly unstable with respect to disproportionation. Alternatively, addition of the diboron compound to the carbon-carbon multiple bond could occur[4a]. In the earliest investigations of the addition of tetrachlorodiborane(4) to acetylene[4], only the 1:1 addition product, 1,2-bis(dichloroboryl)ethylene, was obtained. It was suggested that the presence of the dichloroboryl groups decreased the reactivity of the double bond in this unsaturated organoboron compound. A subsequent study[5] showed, however, that further addition to the double bond can occur in the presence of excess subhalide to give the highly stable 2:1 product, 1,1,2,2-tetrakis(dichloroboryl)ethane. It is apparent, however, that the bis(dichloroboryl)ethylene is considerably less reactive toward the subhalide than is ethylene itself.

The reaction of tetrafluorodiborane(4) with tetravinyltin did not yield a simple addition product[3]. Instead, ethylene, vinyldifluoroborane, and colored involatile products were obtained.

Recent studies in this laboratory[6] have shown that tetrafluoro- and tetrachlorodiborane(4) can undergo both metathetical and addition reactions with a variety of organometallic reagents. In this paper we report the results of our investigations of the reactions of the subhalides with some vinyl derivatives of boron, carbon, silicon, germanium, and tin. Reactions with saturated organometallic compounds will be reported in a subsequent publication.

RESULTS AND DISCUSSION

Preparation and characterization of addition products

Tetrachloro- and tetrafluorodiborane(4) reacted readily with a variety of

TABLE I

ANALYTICAL DATA FOR ADDITION PRODUCTS

	Compound		Mol. wt.[a]	Elemental analysis (%)[b]				
				C	H	B	Metal	Halogen
(I)	$CH_2(BCl_2)CH(BCl_2)_2$	Calcd.	272.2	8.82	1.10	11.93		78.16
		Found	269±1	9.04	1.13	11.87		79.33
(II)	$CH_2(BCl_2)CH(BCl_2)SiCl_3$	Calcd.	324.9	7.38	0.92	6.66	8.65	76.38
		Found	306±2	7.42	0.98	6.61	8.60	75.66
(III)	$CH_2(BCl_2)CH(BCl_2)GeCl_3$	Calcd.	369.4	6.49	1.01	5.86	19.65	67.18
		Found	350±2	6.44	0.82	5.76	19.58	67.46
(IV)	$CH_2(BCl_2)CH(BCl_2)SnCl_3$	Calcd.	415.5	5.77	0.72	5.20	28.57	59.33
		Found	390±2	5.57	0.72	4.95	28.28	59.77
(V)	$CH_2(BCl_2)CH(BCl_2)C(CH_3)_3$	Calcd.		29.09	4.85	8.74		57.31
		Found		29.33	5.61	9.14		56.88
(VI)	$CH_2(BCl_2)CH(BCl_2)Si(CH_3)_3$	Calcd.		22.76	4.55	8.21	10.66	53.74
		Found		22.62	4.61	8.14	10.75	54.32
(VII)	$CH_2(BF_2)CH(BF_2)_2$	Calcd.	173.5	13.85	1.74	18.69		65.72
		Found	172±2	13.57	1.82	17.83		66.22
(VIII)	$CH_2(BF_2)CH(BF_2)C(CH_3)_3$	Calcd.	181.8	39.64	6.66	11.90		41.80
		Found	182±2	39.41	6.74	11.60		41.65
(IX)	$CH_2(BF_2)CH(BF_2)Si(CH_3)_3$	Calcd.	197.6	30.35	6.07	10.94	14.21	38.42
		Found	203±1	31.09	6.32	11.19		38.09

[a] Molecular weights: chlorides determined cryoscopically on *ca.* 0.02 molal solutions in cyclohexane ($K_f = 20.0°$/kg mole); fluorides by vapor density. Indicated error limits are average deviations of two or more determinations.
[b] Elemental analyses by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

monovinyl derivatives of boron, carbon, silicon, germanium, and tin. The products, obtained in yields of up to 90%, were formulated as 1 : 1 addition products, *i.e.* substituted 1,2-bis(dihaloboryl)ethanes, on the basis of elemental analyses, molecular weights, and infrared and nuclear magnetic resonance spectra. The new compounds obtained are listed, with analytical data, in Table 1.

The principal bands in the infrared spectra of the addition products are given in Table 2. While complex, the spectra showed several common features: a shift of the C–H stretching modes to lower frequencies than in the unsaturated starting material, disappearance of the C=C stretching modes present in the vinyl compounds, and absorptions characteristic of the appropriate dihaloboryl groups.

Proton magnetic resonance data are summarized in Table 3. The resonances of the C_2H_3 protons are all in the region characteristic of hydrogen bonded to saturated carbon. Protons on carbon atoms bonded to difluoroboryl groups have resonances at higher field than those in the corresponding dichloroboryl compounds, as noted previously in simpler organoboron halides[7].

TABLE 2

INFRARED SPECTRA OF BIS(DIHALOBORYL)ETHANES

w, weak; m, medium; s, strong; br, broad; sh, shoulder; v, very.

	Compound	Frequencies and relative intensities
(I)	$CH_2(BCl_2)CH(BCl_2)_2$	445vw, 461w, 565m, 598w, 666m, 770s, 925vs, br, 1032vs, br, 1116vs, br, 1145vs, br, 1272s, br, 1310vs, 1580w, 2850w, br
(II)	$CH_2(BCl_2)CH(BCl_2)SiCl_3$	430w, 455w, sh, 512m, 559s, 573s, 610s, 652w, 697w, 759s, 778s, 925vs, br, 1038m, 1058m, 1103s, 1136s, 1166m, sh, 1207vw, 1260m, 1304m, 1380m, 2860m
(III)	$CH_2(BCl_2)CH(BCl_2)GeCl_3$	422s, 568w, 580vw, 622w, 698m, 776m, 925vs, 946s, sh, 975m, sh, 1038m, 1060m, 1110m, 1140m, 1165w, 1214vw, 1262m, 1308m, 1370m, 2860m, 2880w
(IV)	$CH_2(BCl_2)CH(BCl_2)SnCl_3$	495w, 559m, 575m, 636m, 654m, 669m, 776s, 922vs, br, 950s, sh, 1035m, br, triplet, 1105m, 1142m, 1165m, sh, 1233m, 1268m, 1312m, 1380m, 2860m, 2900w
(V)	$CH_2(BCl_2)CH(BCl_2)C(CH_3)_3$	495w, 525vw, 595m, 618m, 671w, 695w, 750m, 772s, 865m, 890–980vs, br, absorp., 1011m, 1022m, 1052s, br, 1100s, 1138s, 1160s, 1212s, 1270vs, 1293s, 1325m, 1380s, 1470s, 2730w, 2750w, 2870m, 2960s
(VI)	$CH_2(BCl_2)CH(BCl_2)Si(CH_3)_3$	456m, doublet, 568m, 622w, 635w, sh, 665w, 697s, 750s, 767s, 842vs, 880–970vs, br, band, 1051vs, br, 1125vs, br, 1219m, 1260vs, 1320s, 1380m, 1420m, 2860m, 2890m, 2960s
(VII)	$CH_2(BF_2)CH(BF_2)_2$	486s, br, 522m, 665w, 692w, 742m, 778s, 812s, 848m, 900s, 1040s, 1090m, 1120s, 1200vs, 1255vs, sh, 1370vvs, 2840w, 2910m, 2960w
(VIII)	$CH_2(BF_2)CH(BF_2)C(CH_3)_3$	460m, 521m, 638m, 693w, 752m, 809w, 837w, 875m, 920w, 940w, sh, 1045m, 1120m, 1150m, 1188s, 1240s, 1380vvs, 1480s, 2880s, 2970vs
(IX)	$CH_2(BF_2)CH(BF_2)Si(CH_3)_3$	488m, 522w, 621vw, 637vw, 694m, 705m, 758m, sh, 772m, 853vs, 886s, sh, 1012s, 1045s, 1118m, 1195s, 1246s, 1275s, 1360vvs, 2900m, 2960s

TABLE 3

PROTON MAGNETIC RESONANCE DATA FOR BIS(DIHALOBORYL)ETHANES

Chemical shifts in ppm relative to external tetramethylsilane (TMS). Positive shifts indicate resonance at lower field than TMS.

Compound	Chemical shift	Description	Assignment
(I)	2.25	Doublet (J 6 Hz)	CH_2
	2.90	Broad triplet	CH
(II)	2.02 to 2.97	Complex, 9 lines resolved	C_2H_3
(III)	2.48 to 3.43	Complex, 9 lines resolved	C_2H_3
(IV)	2.71	Doublet (J 7 Hz)	CH_2
	3.65	Triplet (J 7 Hz)	CH
(V)	1.05	Singlet	CH_3
	1.75 to 2.11	Complex	C_2H_3
(VI)	0.15	Singlet	CH_3
	1.18 to 2.22	Complex	C_2H_3
(VII)	1.1	Broad line (half width 16 Hz)	C_2H_3
(VIII)	0.75	Singlet	CH_3
	0.5 to 1.1	Broad multiplet, poorly resolved	C_2H_3
(IX)	−0.33	Triplet ($J \sim 0.5$ Hz)	CH_3
	0.2 to 1.1	Broad absorption	C_2H_3

Except for the tris(dihaloboryl) derivatives, all of the compounds reported here are of the type CH_2XCHXY. Despite this structural similarity, the magnetic resonance spectra of the C_2H_3-group protons in the various compounds show significant differences. The appearance of the spectrum for this type of three-spin system will, of course, be affected by the chemical shift differences between the CH_2 and CH protons. In addition, the methylene group protons are geometrically non-equivalent and may, if the environmental differences are sufficiently great, be chemically shifted from one another. The spectra expected for the bis(dihaloboryl)ethyl groups might thus be expected to range from AX_2 to ABC types, depending on the magnitudes of the chemical shifts and coupling constants.

The extremes encountered are shown by the proton spectra of the addition products of B_2Cl_4 with the vinyltrichloro derivatives of tin, germanium, and silicon (Fig. 1). In 1,2-bis(dichloroboryl)ethyltin trichloride, (IV), the potential non-equivalence of the methylene protons is not observed at 60 MHz. The CH_2 and CH proton resonances are separated by 0.94 ppm, and the spectrum consists of a doublet and triplet of relative intensities 2.02 : 1.00. The silicon and germanium analogues, (II) and (III), have considerably more complex spectra. The spectrum of (III) has been analyzed as a system of three non-equivalent spins by Dr. R. B. Johannesen of this laboratory. This indicates that the complexity of the spectrum is attributable to the geometric non-equivalence of the methylene protons and not to the presence of slowly interconverting rotational isomers. Inspection of models suggests that steric interactions between substituent groups in this series of compounds will be smallest for the larger Group IV atoms.

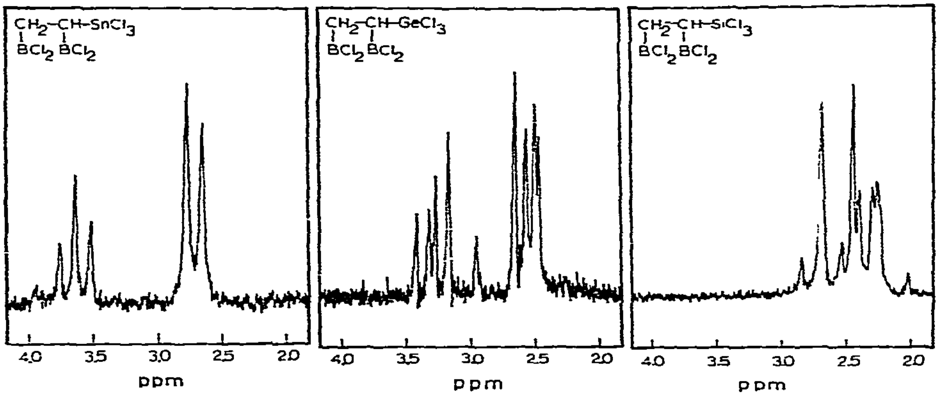


Fig. 1. Proton magnetic resonance spectra (60 MHz) of (IV), (III), and (II). Spectra were recorded at 35° using pure liquid samples and an external tetramethylsilane reference.

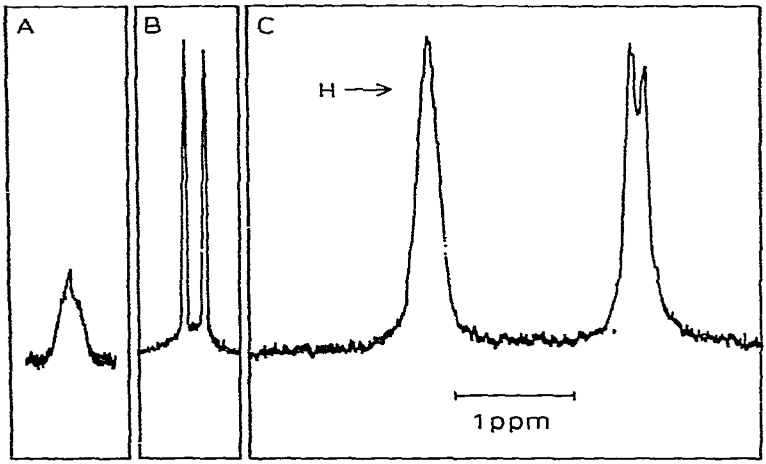


Fig. 2. A. Fluorine magnetic resonance spectrum of $F_2BCH_2CH(BF_2)Si(CH_3)_3$ (IX) at 56.4 MHz. B. Fluorine spectrum recorded with simultaneous irradiation at 19.25 MHz to decouple the ^{11}B nuclei. Scale and instrument parameters identical to A. C. Expanded ^{19}F–^{11}B double resonance spectrum.

Fluorine magnetic resonance spectra of B_2F_4 addition products showed broad single peaks with chemical shifts in the range from 71–77 ppm on the CCl_3F scale. This region is characteristic of fluorine resonances in organodifluoroboranes[8,9]. By the use of ^{11}B spin-decoupling, the spectrum of [1,2-bis(difluoroboryl)ethyl]trimethylsilane, (VI), was shown to consist of two fluorine peaks of equal intensity separated by 1.8 ppm, confirming the presence of two non-equivalent difluoroboryl groups (Fig. 2).

Reactions of tetrachlorodiborane(4) with certain other vinylmetallic derivatives gave results somewhat different from those already described. As indicated in the *Experimental* section, addition to the double bond in vinylsilane and vinyltrifluorosilane evidently took place. The identity of the more volatile products indicated, however, that transfer of hydride and fluoride to boron occurred during the reactions. The "adducts" obtained may thus be mixtures of products resulting from such redistribution reactions. Transfer of fluorine from carbon to boron has been observed in the reaction of B_2Cl_4 with allyl fluoride, which produces allyl chloride and B_2F_4, among other products[4]. Halide–hydride interchange has been noted in reactions of saturated organosilanes with both B_2Cl_4 and B_2F_4[10].

With divinyltin dichloride, the product fraction appeared to consist of at least two distinct materials. Infrared evidence suggests that these may be produced by addition of the boron subhalide either to one or both vinyl groups. The products were quite unstable, depositing tin(II) chloride at room temperature.

Thermal stabilities

Most of the compounds listed in Table 1 are stable *in vacuo* at room temperature and undergo only slight decomposition when heated in sealed bulbs at 150° for 17 hours (Table 4).

The product of addition of B_2Cl_4 to ethylene, 1,2-bis(dichloroboryl)ethane, is partly decomposed[11] in several days at 200°. This compound is thus roughly similar in stability to the vicinal bis(dihaloboryl) compounds studied in this work.

TABLE 4

VOLATILE PRODUCTS OF THERMAL DECOMPOSITION REACTIONS

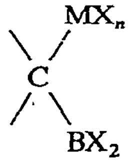
Quantities in millimoles. Samples heated at indicated temperatures for 17 hour periods unless otherwise specified.

Compound		Products obtained at indicated temperature							
		100°		150°		230°		290°	
(I)	(0.37)	HCl	(0.05)	HCl	(0.06)			HCl	(0.08)
				BCl_3	tr.			BCl_3	(0.45)
								CH_3BCl_2	(0.08)
								H_2	(0.02)
(II)	(1.08)	Unident.	tr.	Unident.	tr.	BCl_3	(0.04)		
						(125 h)			
(III)	(0.42)	Unident.	tr.	$C_2H_3GeCl_3$	(0.01)	BCl_3	(0.65)		
						$GeCl_4$	(0.14)		
						HCl	(0.09)		
						(67 h)			
(IV)	(0.57)	BCl_3	(0.55)						
		$C_2H_3BCl_2$	(0.52)						
		$SnCl_2$	(0.55)						
		HCl	(0.09)						
(VII)	(0.34)	BF_3	(0.03)	BF_3	(0.05)			BF_3	(0.54)
		SiF_4		SiF_4				SiF_4	(0.02)
								H_2	(0.03)
(VIII)	(0.53)	BF_3	tr.	BF_3	(0.02)			BF_3	(0.18)
		SiF_4	tr.	SiF_4				SiF_4	(0.18)
								H_2	(0.08)
								Unident.	(0.19)
								Unident.	(0.05)
(IX)	(0.88)	BF_3	(0.02)	BF_3	(0.05)			BF_3	(0.25)
		SiF_4		SiF_4	(0.03)			SiF_4	(0.12)
								CH_3BF_2	(0.16)
								$(CH_3)_3SiF$	(0.29)
								$(CH_3)_3SiF_2$	(0.08)
								Unident.	(0.07)

The stabilities of the addition products of the vinyltrichloro derivatives of silicon, germanium, and tin decrease in that order. Traces of boron trichloride were obtained from [1,2-bis(dichloroboryl)ethyl] trichlorosilane, (II), after 125 hours at 230°. The corresponding germanium compound, (III), was decomposed to boron trichloride, germanium tetrachloride, hydrogen chloride, and unidentified black solids after 67 hours at that temperature. The decomposition of the tin derivative, (IV), is unique among the compounds studied. The compound slowly deposits tin(II) chloride at room temperature. Heating overnight at 100° results in essentially quantitative decomposition to three well-defined products:

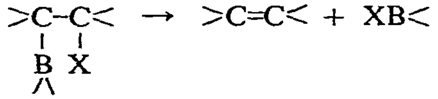
$$Cl_2BCH_2CH(BCl_2)SnCl_3 \rightarrow CH_2{=}CHBCl_2 + BCl_3 + SnCl_2$$

The addition products derived from vinylhalometallic compounds, (I), (II), (III), (IV), and (VII), have, as a common structural feature, a geminal arrangement of dihaloboryl and halometal groupings:



(I): $M=B, X=Cl, n=2$
(II): $M=Si, X=Cl, n=3$
(III): $M=Ge, X=Cl, n=3$
(IV): $M=Sn, X=Cl, n=3$
(VII): $M=B, X=F, n=2$

These compounds may thus be considered to be hetero-atom analogues of β-halo-organoboranes. It is well known that organoboron compounds containing β-halogen substituents may undergo elimination reactions involving transfer of halogen to boron:



$$>\underset{\underset{/\backslash}{B}}{C}-\underset{X}{C}< \rightarrow >C{=}C< + XB<$$

Eliminations of this sort have been invoked to account for the instability of the hydroboration products of vinyl chloride[12] and 3-chlorocyclohexene[13] and for the transfer of fluorine from carbon to boron in reactions of fluoroolefins with diborane[14,15], tetramethyldiborane[16], and difluoroborane[17]. Similar eliminations have been studied[18] in β-substituted organoboranes containing other, non-halogen, substituents*.

Studies in this laboratory[19] of the reaction of difluoroborane with vinyldifluoroborane suggest that 1,1-bis(difluoroboryl)ethane undergoes rapid elimination of boron trifluoride with the formation of polymeric products:

$$HBF_2 + CH_2{=}CHBF_2 \rightarrow [CH_3CH(BF_2)_2] \xrightarrow{-BF_3} (CH_3CHBF)_n$$

This reaction would be formally similar to the eliminations postulated in the hydroboration of 3,3,3-trifluoropropene with diborane[15] and to the decomposition of dimethyl(1,1,1-trifluoro-2-propyl)borane[16]:

$$CF_3CH(CH_3)B(CH_3)_2 \rightarrow CF_2{=}CHCH_3 + (CH_3)_2BF\,.$$

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* Transfer reactions not involving elimination may play a part in some of the systems mentioned (see ref. 18b).

Evidence has also been obtained for the room-temperature elimination of boron trifluoride in the reaction of difluoroborane with vinyltrifluorosilane. It is noteworthy, therefore, that (I), (II), (III), and (VII), all of which have halogen substituents on a hetero-atom in a β-position relative to boron, are all stable to at least 150°. The geminal boron compound, 1,1,2,2-tetrakis(dichloroboryl)ethane[5] is also reportedly stable to 200°.

Relative reactivities of the vinylmetallics

Rates of addition of the subhalides to the various vinyl derivatives were investigated semi-quantitatively by observing the change with time of the proton magnetic resonance spectra of equimolar mixtures of the reactants. The resonance due to the saturated addition product is in each case well separated from that of the unsaturated organometallic compound; the relative amounts of each material can thus be determined readily by integration of the spectrum. Times required for conversion of half of the vinyl compound to addition product at 35°, which provide an approximate measure of the reaction rate, are given in Table 5.

TABLE 5

HALF-TIMES FOR ADDITION REACTIONS AT 35°

Reaction	$t_{0.5}$	Reaction	$t_{0.5}$
$C_2H_3Si(CH_3)_3+B_2Cl_4$	< 5 min	*trans*-$Cl_2BCH{=}CHBCl_2+B_2Cl_4$	5 days
$C_2H_3BCl_2+B_2Cl_4$	~ 5 min	*cis*-$Cl_2BCH{=}CHBCl_2+B_2Cl_4$	7 days
$C_2H_3SnCl_3+B_2Cl_4$	~ 5 min	$C_2H_3Si(CH_3)_3+B_2F_4$	< 20 h
$C_2H_3C(CH_3)_3+B_2Cl_4$	30 min	$C_2H_3BF_2+B_2F_4$	100 h
$C_2H_3SiCl_3+B_2Cl_4$	55 min	$C_2H_3C(CH_3)_3+B_2F_4$	> 100 h
$C_2H_3GeCl_3+B_2Cl_4$	160 min	$C_2H_3SiF_3+B_2F_4$	∞

It is apparent from the results in Table 5 that B_2Cl_4 reacts much more readily with a given vinyl compound than does B_2F_4. This result is in agreement with the observations of others on the addition of the subhalides to simple olefins[4] and may reflect the reduced electrophilic character of boron fluorides as compared to the corresponding chlorides.

The relative reactivities of the vinyl compounds toward a given subhalide are difficult to rationalize in a straightforward way. The apparent rates of addition to the double bond indicated by the reaction half-times in Table 5 do not appear to be simply related to either the size or the group electronegativities[20] of the organometal and halometal substituents. It is particularly interesting that replacing one of the hydrogen atoms in vinyldichloroborane with a second dichloroboryl group causes a marked decrease in reactivity. Other workers[4] have found that both alkyl and halogen substituents on olefinic carbon reduce the reactivity of the unsaturated compound toward B_2Cl_4. Thus, propene reacts less readily than does ethylene, and 2-butene is still less reactive. With haloethylenes, addition reportedly is completely inhibited.

The mechanism of the addition reaction has not been established, nor is it certain that all additions of B_2Cl_4 to olefins or acetylenes involve the same mechanism. It has been suggested[21,22] that the addition reactions involve a four-center association of the π-electron system of the unsaturated compound with the vacant p-orbitals of the diboron derivative, followed by B–B bond cleavage to give the final product. No unequivocal experimental evidence has been given for the existence of intermediate complexes in these systems, although such complexes could be involved in the apparent stabilization of B_2Cl_4 by haloolefins*.

Other suggested mechanisms for the addition reaction involve initial homolytic or heterolytic B–B cleavage. It has been reported[23] that addition of B_2Cl_4 to cyclopentene, followed by hydrolysis and oxidation, gives exclusively *trans*-1,2-cyclopentanediol. This suggests that the reaction is stereospecific, and, if the configuration of the diol is that of the bis(dichloroboryl) precursor, argues against the four-center mechanism, which would be expected to lead to *cis*-addition. Other studies[24,25,26] have shown, however, that *cis*-addition predominates in the reaction of B_2Cl_4 with olefins and acetylenes.

EXPERIMENTAL

Apparatus and experimental methods

Manipulations of volatile materials were carried out in a grease-free, borosilicate glass vacuum apparatus fitted with valves constructed of glass and fluorocarbon polymer and with joints sealed with fluorocarbon polymer O-rings. Other materials were handled in a dry, oxygen-free nitrogen atmosphere in an efficient recirculating dry box. Pressure measurements in work with B_2Cl_4 were made using a glass spiral gauge.

Infrared spectra in the 4000–400 cm^{-1} range were recorded with a commerical double-beam grating spectrophotometer (Perkin–Elmer 337). Gaseous samples were contained in 5 cm pathlength cells fitted with grease-free valves, using KBr windows sealed to the cell body with fluorocarbon polymer O-rings; liquid samples were contained between KBr plates separated by a 0.005 inch lead spacer.

Proton magnetic resonance spectra were obtained with a standard commercial 60 MHz high-resolution proton spectrometer. Fluorine NMR measurements and double resonance experiments were performed on the modified spectrometer described in a previous publication from this laboratory[27].

Elemental analyses were performed by a commercial laboratory.

Molecular weights of the B_2Cl_4 addition products were determined cryoscopically, using solutions approximately 0.02 molal in cyclohexane ($K_f = 20.0°$/kg mole)[28]. The solvent was dried by distillation from lithium aluminum hydride. For the B_2F_4 addition products, molecular weights were determined by vapor density measurements at pressures significantly below the saturation pressures of the compounds.

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* Tetrachlorodiborane(4) decomposes at about 0° with the formation of red solids[1]. In agreement with the results of other workers[4] we find that mixtures of B_2Cl_4 with various chloroethylenes remain colorless for periods of up to one year at room temperature. The proton magnetic resonance spectra of C_2HCl_3/B_2Cl_4 mixtures show only the principal and satellite peaks due to the olefin, even after long standing. We have been unable to observe the additional resonances in the high-field region that have been reported[21]. We have, however, obtained evidence for slow reactions of B_2Cl_4 with (2-chlorovinyl)dichloroborane and vinyl halides. The nature of the products and of the B_2Cl_4-haloolefin interaction will be discussed in a subsequent publication.

Reagents

Tetrachlorodiborane(4) was prepared by reduction of boron trichloride in an electric discharge, using copper wool electrodes[29]. Tetrafluorodiborane(4) was obtained by fluorination of the chloride with a large excess of SbF_3 at −80°.

Vinyltrichlorosilane, vinyltrimethylsilane, tert-butylethylene, and tetravinyltin were obtained from commercial sources. Other reagents were prepared as follows: vinyldihaloboranes from tetravinyltin and the appropriate boron trihalide[30]; vinyltin trichloride and divinyltin dichloride by the Kocheshkov procedure as modified by Seyferth and Stone[31]; vinyltrichlorogermane from divinylmercury and germanium tetrachloride; vinyltrifluorosilane by fluorination of the chloride with SbF_3; vinylsilane by reduction of the chloride with lithium aluminum hydride. The *cis*-isomer of 1,2-bis(dichloroboryl)ethylene was prepared from B_2Cl_4 and acetylene; the *trans*-isomer was produced by the photochemical procedure described previously[26]. With the exception of tetravinyltin, which was used as received, all materials were given a final purification by vacuum-line fractionation just prior to use. Purity was checked by comparison of infrared spectra with those of authentic samples and was also indicated, in appropriate cases, by the absence of extraneous peaks in the proton magnetic resonance spectrum.

Reactions of tetrachlorodiborane(4) with vinyl derivatives

Addition of tetrachlorodiborane(4) to monovinylated metal derivatives occurred readily in the liquid phase at room temperature or below. In a typical reaction, a mixture of vinyldichloroborane (1.15 mmole) and the subchloride (1.26 mmole) was kept at room temperature for 24 h in a 10 ml bulb equipped with a glass–fluorocarbon polymer valve. The reaction mixture was distilled through a U tube maintained at −63°, in which the product, 1,1,2-tris(dichloroboryl)ethane, was obtained. Material passing −63° consisted of boron trichloride (0.07 mmole) and unreacted tetrachlorodiborane(4) (0.13 mmole). Small amounts of involatile residue remained in the reaction bulb.

By similar procedures, the expected 1,2-bis(dichloroboryl)ethyl derivatives were obtained from vinyltrichlorosilane, vinyltrichlorogermane, tert-butylethylene, vinyltrimethylsilane, and vinyltin trichloride. With the latter, a white solid residue, apparently tin(II) chloride (see below), remained after removal of the 1,2-bis(dichloroboryl)ethyltin trichloride.

A mixture of tetrachlorodiborane(4) (1.62 mmole) and vinylsilane (1.53 mmole) was kept at −80° for 22 h and then warmed slowly to −10° over a period of 10 h. The mixture was fractionated through a −45° trap. The product retained at −45° was a clear, colorless liquid whose infrared spectrum indicated the presence of Si–H (2190 cm^{-1}) and B–Cl (918 cm^{-1}) bonds. The proton magnetic resonance spectrum showed absorptions in the high-field region. Analyses were unsatisfactory, however. Examination of the volatiles showed these to consist of boron trichloride (0.20 mmole) and a mixture (0.30 mmole) of diborane and dichloroborane, estimated to contain about 5% of the latter. Similarly, reaction of the subchloride (1.74 mmole) with vinyltrifluorosilane (1.74 mmole) gave a product of low volatility together with a mixture of volatiles containing boron trifluoride (0.22 mmole) and small amounts of chlorodifluoroborane, silicon tetrachloride, and boron trichloride.

Reactions of tetrafluorodiborane(4) with vinyl derivatives

A gaseous mixture of vinyldifluoroborane and tetrafluorodiborane(4) underwent no reaction at 100° in 24 h or at room temperature in one year. However, when the reactants were sealed in a glass vessel of such dimensions that the reactants were at an initial pressure of 5–6 atm, droplets of liquid product became apparent within a few days at room temperature. It was found convenient, therefore, to carry out the reactions in NMR sample tubes and to monitor the reaction by observing the growth of the resonances due to the products. The substituted 1,2-bis(difluoroboryl)ethanes were considerably more volatile than the corresponding chlorides and could be readily manipulated by vacuum-line procedures. Vapor pressures of the products at 0° were: $CH_2(BF_2)CH(BF_2)_2$, 23 mm; $CH_2BF_2CH(BF_2)C(CH_3)_3$, 9 mm; $CH_2BF_2CH(BF_2)Si(CH_3)_3$, 5.5 mm. No product was obtained with vinyltrifluorosilane.

Thermal stability of the addition products

The stabilities of the purified addition compounds were investigated by heating in sealed glass bulbs under vacuum. All samples were heated initially at 100° for 17 h and the volatile products examined. Where appropriate, the products were returned to the bulb, which was resealed and subjected to further heating. Table 4 summarizes the results of the thermal decomposition experiments and lists the volatile products obtained. The degradation of the samples at the higher temperatures also produced involatile solid residues which were not investigated further.

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