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REACTIONS OF TETRACHLORODIBORANE(4) WITH FLUOROOLEFINS

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SUMMARY

Tetrachlorodiborane(4) reacts with trifluoroethylene to give dichloro-2,2-difluorovinylborane and both isomers of dichloro-2-chloro-2-fluorovinylborane. These compounds can be converted to the corresponding difluoro(halovinyl)boranes by treatment with SbF_3. Reaction of B_2Cl_4 with vinyl fluoride gives 1,1,2-tris(dichloroboryl)ethane. A facile halogen exchange with B_2Cl_4 was observed for a number of fluoroolefins, including vinyl fluoride, 1,1-difluoroethylene, 2-fluoropropene, and 3,3,3-trifluoropropene. No reaction was observed with 2,3,3,3-tetrafluoropropene.

INTRODUCTION

The interaction of B_2Cl_4 with fluoroolefins has been discussed only briefly in the literature. In an early study[1] of the addition of B_2Cl_4 to a number of olefins, it was reported that no isolable addition product was obtained with vinyl fluoride, 1,1-difluoroethylene, or tetrafluoroethylene. In the same investigation, a complex reaction of the subhalide with excess allyl fluoride was reported to give, among other products, allyl chloride and B_2F_4.

A previous report from these laboratories[2] described the reactions of B_2Cl_4 and B_2F_4 with chloro- and bromoolefins to yield saturated poly(dihaloboryl)organo derivatives. In that work, evidence was obtained for a reaction sequence involving addition of the subhalide to the haloolefin followed by dehaloboration and subsequent addition of a second subhalide molecule to the resulting vinyldihaloborane. Accumulation of the various intermediate compounds in the sequence was observed to occur to different extents depending on the identity of the subhalide and the reactant olefin. This result suggested that significant variations are possible in the relative rates of the separate steps in the overall reaction. It was therefore of interest to extend the earlier investigations to an examination of the reactions of B_2Cl_4 with a number of structurally distinct fluoroolefins.

RESULTS AND DISCUSSION

Two new vinylboron derivatives—dichloro-2,2-difluorovinylborane and dichloro-2-chloro-2-fluorovinylborane (*cis* and *trans*)—have been obtained in preparatively useful yields from the reaction of B_2Cl_4 with trifluoroethylene. The corresponding difluoroboranes can readily be obtained from the chlorides by treatment with SbF_3. In contrast to the behavior with trifluoroethylene, reaction of the subhalide with vinyl fluoride gave the saturated addition product 1,1,2-tris(dichloroboryl)-ethane, previously prepared by the reactions of B_2Cl_4 with dichlorovinylborane[3] and with vinyl chloride[1]. In the reactions of both fluoroolefins, fluorine was recovered principally in the form of monoboron halides.

Formation of the tris-substituted ethane from vinyl fluoride is the result expected from the reaction sequence previously proposed[1] for the vinyl chloride – B_2Cl_4 reaction. For vinyl fluoride, this may be written* as:

$$CH_2{=}CHF + B_2Cl_4 \rightarrow (Cl_2B)CH_2CHF(BCl_2) \tag{1}$$

$$(Cl_2B)CH_2CHF(BCl_2) \rightarrow CH_2{=}CHBCl_2 + FBCl_2 \tag{2}$$

$$CH_2{=}CHBCl_2 + B_2Cl_4 \rightarrow (Cl_2B)CH_2CH(BCl_2)_2 \tag{3}$$

This sequence does not account, however, for the observed recovery of most of the unreacted olefin as vinyl chloride. Examination of reaction mixtures by NMR showed that the vinyl fluoride is in fact converted to chloride early in the reaction, and that formation of the tris(dichloroboryl)ethane occurs at the expense of the latter. Thus, while some reaction according to (1) cannot be excluded, it is apparent that the reaction involves a halogen exchange, preserving the B–B bond, *e.g.*:

$$CH_2{=}CHF + B_2Cl_4 \rightarrow CH_2{=}CHCl + B_2Cl_3F \tag{4}$$

followed by reaction of the vinyl chloride with diboron species in the manner previously described. The halogen exchange was also observed with BCl_3, albeit at a much slower rate.

Unequivocal evidence for the halogen exchange reaction was found with several other fluoroolefins. Thus, 1,1-difluoroethylene gave 1-chloro-1-fluoroethylene almost quantitatively, boron being recovered as a mixture of the previously reported[4] diboron chlorofluorides (eqn. 5). Similarly, 2-fluoropropene was found to react rapidly to form 2-chloropropene (eqn. 6), while 3,3,3-trifluoropropene exchanged all of the carbon-bonded fluorine to yield the allylic rearrangement product, 1,1,3-trichloropropene** (eqn. 7).

$$CH_2{=}CF_2 + B_2Cl_4 \rightarrow CH_2{=}CFCl + B_2Cl_xF_{(4-x)} \tag{5}$$

$$CH_3CF{=}CH_2 + B_2Cl_4 \rightarrow CH_3CCl{=}CH_2 + B_2Cl_xF_{(4-x)} \tag{6}$$

$$CF_3CH{=}CH_2 + B_2Cl_4 \rightarrow CH_2ClCH{=}CCl_2 + B_2Cl_xF_{(4-x)} \tag{7}$$

---

* In these and some succeeding equations, specific boron–halogen species are indicated. It is well known, however, that halogen exchange occurs readily among boron trihalide, diboron tetrahalide, and organoboron halide species, and that a mixture of redistribution products will usually be present when more than one kind of halogen is available. Isolation of a particular haloboron species from systems containing more than one boron-bonded halogen may reflect particular stability of that species, but may also be an artifact of the separation.

** Rearrangement of $CCl_3CH{=}CH_2$ to $CClH_2CH{=}CCl_2$ in the presence of HCl and $FeCl_3$ has been reported previously[5].

Similar halogen exchange between boron halides and fluoroorganic derivatives has been observed previously. Olah and Kuhn[6] observed halogen exchange in a study of the boron halide-catalyzed haloalkylation of benzene:

$$F(CH_2)_nCl + BX_3 \rightarrow X(CH_2)_nCl + BF_3 \qquad (X = Cl, Br) \tag{8}$$

While this work was in progress, Chivers[7] reported halogen exchange between boron halides and trifluoromethylphenyl derivatives:

$$o\text{-}CF_3C_6H_4Y + BCl_3 \rightarrow o\text{-}CCl_3C_6H_4Y + BF_3 \tag{9}$$
$$(Y = H, SiMe_3)$$

As mentioned above, the reaction of allyl fluoride with B_2Cl_4 is also believed to involve halogen exchange[1]. To our knowledge, however, the present work provides the first example of such exchange involving fluorine on an unsaturated carbon atom. It is apparent that the reaction is sensitive to structural factors. Thus, $CF_3CF{=}CH_2$ was found to be unreactive with B_2Cl_4, and 1,2-difluoroethylenes were distinctly different in behavior from $CF_2{=}CH_2$.

Comparison experiments showed that B_2Cl_4 undergoes halogen exchange significantly more rapidly than BCl_3 with vinyl fluoride and 2-fluoropropene. It is also of interest that while 2-fluoropropene exchanges halogen much more rapidly with B_2Cl_4 than does vinyl fluoride, addition of subhalide to the resulting chloroolefins is much slower for the propene. The latter result is in accord with the generally reduced reactivity of alkyl-substituted ethylenes toward subhalides addition[8].

The substituted vinylboron compounds obtained in the reaction of B_2Cl_4 with trifluoroethylene may arise by several pathways, consistent with previous observations, that involve halogen exchange and addition-elimination steps. It is of interest that NMR studies gave no evidence for the accumulation of significant amounts of chlorofluoroethylenes in this reaction and indicated that dichloro-2-chloro-2-fluorovinylborane is not formed by reaction of CF_2CHBCl_2 with B_2Cl_4.

Although the trifluoroethylene–B_2Cl_4 system has some synthetic utility, it is apparent from this study that the chemistry of boron subhalide–fluoroolefin systems is dominated by the more general halogen exchange reactions. These may in fact offer some potential for specific substitution reactions in haloolefin chemistry. This aspect of the behavior of fluorocarbons with inorganic halides is currently under investigation.

EXPERIMENTAL

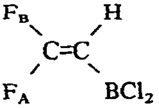
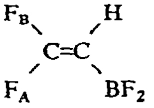
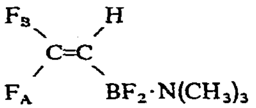
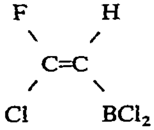
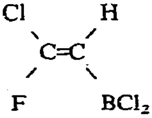
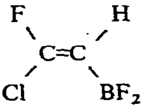
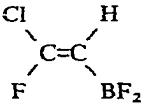
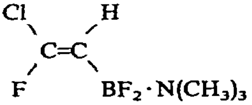
General procedures used in this work have been described in previous publications[2,3]. Fluorocarbons were obtained from commercial sources and were subjected to trap-to-trap distillation prior to use to eliminate possible traces of moisture. Purity was checked by infrared and/or NMR examination. Analyses were performed by a commercial laboratory (Schwarzkopf Microanalytical Laboratories, Woodside, New York).

Reaction of B_2Cl_4 with trifluoroethylene

A mixture consisting of 1.47 mmol of each reagent was allowed to react for 18 days at room temperature in a sealed NMR sample tube. Separation of the product mixture gave BF_3 (0.40), BCl_3 (0.83), HCl (0.36), unreacted trifluoroethylene (0.13), together with two new materials, I (0.71) and II (0.43). A small quantity of brown, air-sensitive, involatile oil remained in the reaction tube.

TABLE I

NMR PARAMETERS FOR DIHALO(DIHALOVINYL)BORANES

Compound	*Chemical shifts*[a]	*Coupling constants*
	H, −4.63 F_A, 55.4 F_B, 52.7	HF_A, 30 HF_B, 7.2 F_AF_B, 41
	H, −3.70 F_A, 62.5 F_B, 56.7 BF_2, 86.0	HF_A, 32.4 $HF_B \sim H\text{-}BF_2$, 6.0 $F_AF_B \sim F_A\text{-}BF_2$, 19.6
	H, −3.98 CH_3, −2.74	HF_A, 37.5 $HF_B \sim \underline{H}\text{-}B\underline{F}_2$, 8.5
	H, −5.74 F, 25.8	HF, 18
	H, −5.42 F, 34.9	HF, 35
	H, −4.95 F, 31	HF, 12.0 $H\text{-}BF_2$, 2.9
	H, −4.87 F, 41.3 BF_2, 83.9	HF, 38.2 $H\text{-}BF_2$, 6.7 $F\text{-}BF_2$, 21.7
	H, −5.01 CH_3, −2.79	HF, 45.3 $H\text{-}BF_2$, 8.2

[a] In ppm. Proton shifts relative to external TMS. Fluorine-19 shifts reported relative to external CCl_3F. Fluorine shifts of the dichloroboryl compounds were measured relative to external CH_3SiF_3 and converted to the CCl_3F scale using the relation $\delta(CH_3SiF_3) = 136.7$. Positive sign indicates shift to high field of reference line.

Compound I was identified as dichloro-2,2-difluorovinylborane. Molecular weight (vapor density): found, 142; calcd., 145. IR (gas): 3350 w, 3080 w, 2630 w, 2580 m, 2460 m, 2250 w, 2175 w, 2090 w, 2030 w, 1925 w, 1820 m, 1690 vs, 1490 w, 1410 s, 1370 vs, 1310 m, 1233 s, 1126 vs, 1028 w, 966 s, 945 s, 898 vs, 831 s, 726 w, 676 s, 618 m, 588 m, 551 w, 516 w, cm^{-1}. Protonolysis (CH_3COOH, 100°, 16 h) gave 1,1-difluoroethylene.

The NMR parameters obtained from first-order analysis of the spectra are given in Table 1, together with corresponding data for other compounds studied in this work. The NMR signals from fluorine atoms *trans* to boron in these fluorovinylboron derivatives were found to be significantly broader than *cis*-fluorine resonances, as has been noted previously[9] for perfluorovinylboranes. In the case of I, this broadening, presumably arising from ^{11}B quadrupole relaxation, was so severe that ^{11}B decoupling was required to reveal the structure of the *trans*-fluorine resonance[10].

A 1.70 mmol sample of I was treated for 18 hours at −78° with excess SbF_3. The crude product mixture was fractionated through traps held at −96, −130, −196°. Material held at −130° consisted of 1.39 mmol of the purified fluorination product, difluoro-2,2-difluorovinylborane. Molecular weight: found, 112; calcd., 111.8. NMR: see Table 1. IR: 3390 w, 3090 w, 2850 w, 2890 w, 2760 m, 2580 vw, 2540 w, 2440 m, 2240 m, 2090 w, 1920 w, 1850 w, 1780 m, 1720 vs, 1650 m, 1430 m, 1400 vs, 1305 s, 1225 w, 1151 vs, 1100 w, 1045 w, 988 m, 921 m, 827 s, 695 m, 671 s, 645 m, 620 m, 555 s cm^{-1}.

On treatment with excess trimethylamine, 0.89 mmol of the fluoroborane reacted with 0.92 mmol of the base to give a colorless addition product, liquid at 25°. (Found: C, 35.22; H, 5.65; B, 6.10; F, 44.54; N, 8.22. $C_5H_{10}NBF_4$ calcd.: C, 35.13; H, 5.89; B, 6.32; F, 44.45; N, 8.19 %).

Compound II was formulated as a mixture of *cis*- and *trans*-isomers of dichloro-2-chloro-2-fluorovinylborane. Molecular weight: found, 162; calcd., 161. NMR: see Table 1. IR: 3220 w, 3070 w, 2780 w, 2410 w, 1680 s, 1630 vs, 1320 s, 1288 m, 1150 s, 1127 vs, 1103 m(sh), 1066 s, 943 vs, 916 vs, 836 m, 797 vs, 730 s, 776 w, 633 s cm^{-1}. Protonolysis (CH_3COOH, 100 °, 16 h) gave CH_2CClF. The most abundant species was formulated as the isomer in which the fluorine atom is *cis* to boron on the basis of the relative magnitude of the H–F coupling constants.

The isomer mixture (1.29) was treated with SbF_3 for 18 hours at −78° and fractionated (−115, −130, −196°), yielding 0.89 mmol of purified difluoro-2-chloro-2-fluorovinylborane (*cis* and *trans*) in the −115° trap. Molecular weight: found, 127; calcd., 128.3. NMR: see Table 1. IR: 3915 vw, 3670 vw, 3260 w, 3080 w, 3020 vw, 2990 vw, 2850 vw, 2750 w, 2680 w, 2620 w, 2500 w, 2460 w, 2280 w, 2230 w, 2190 m, 2105 w, 2060 w, 1930 w, 1880 w, 1640 vs, 1500 m, 1438 m, 1378 vs, 1348 vs, 1228 vs, 1115 s, 1055 s, 997 w, 958 w, 868 m, 835 vs, 778 w(sh), 664 s, 617 w, 578 m, 548 s, 438 w cm^{-1}. A 0.58 mmol sample reacted with 0.56 mmol of trimethylamine, yielding a colorless addition product, liquid at 25°. (Found: C, 32.12; H, 5.34; B, 6.11; Cl, 18.80; F, 30.14; N, 7.35. $C_5H_{10}NBF_3Cl$ calcd.: C, 32.04; H, 5.37; B, 5.76; Cl, 18.91; F, 30.41; N, 7.47 %).

Reactions with vinyl fluoride

Examination of the proton NMR spectrum of a 1/1 mixture of B_2Cl_4 with C_2H_3F showed that the fluoride had been totally consumed after 5 days at room temperature while the spectrum of vinyl chloride appeared, along with weak, broad resonances at high field typical of poly(dihaloboryl) addition products. On further standing, the latter increased, and the C_2H_3Cl resonance diminished. Under somewhat different conditions (25°, 31 days, 70 ml vessel), 2.98 mmol C_2H_3F and 2.95 mmol B_2Cl_4 gave 0.25 and 0.43 mmol, respectively, of unreacted starting materials, together with 0.92 mmol BF_3, 0.70 mmol BCl_3, 1.23 mmol C_2H_3Cl and 329 mg (1.17 mmol) of a clear liquid with an NMR spectrum identical to that of the previously reported 1,1,2-tris(dichloroboryl)ethane.

Observation of a 1/1 mixture of vinyl fluoride with BCl_3 by proton NMR showed that 60% of the former had been converted to vinyl chloride after 9 weeks at room temperature.

Reaction of B_2Cl_4 with 1,1-difluoroethylene

In a typical experiment, 1.47 mmol CH_2CF_2, treated with 1.48 mmol B_2Cl_4 for 7 days at room temperature in the absence of solvent, gave 1.42 mmol (96.6%) of CH_2CFCl, identified by its molecular weight (found, 82.4; calcd., 80.4), infrared spectrum, and agreement between the proton NMR spectrum and that calculated from published[11] parameters. Other volatile products consisted of unreacted CH_2CF_2 (0.04 mmol), BF_3 (0.13 mmol), and a mixture of diboron chlorofluorides (1.09 mmol). Small amounts were also obtained of a clear, air-sensitive oil with volatility characteristics suggesting it was an olefin-subhalide addition product.

Reactions with 2-fluoropropene

A 2.21 mmol sample of BCl_3 was combined with 2.19 mmol of 2-fluoropropene in an NMR tube which was sealed off, warmed to room temperature, and inserted into the probe of an A-60 NMR spectrometer. Over a 40 minute period, the spectrum of the fluoroolefin disappeared, and a simpler spectrum, identified as that of 2-chloropropene, appeared. The reaction was essentially complete in 40 minutes. The product mixture was removed from the sample tube and fractionated through traps at −80, −130, and −196°. The −80° fraction contained traces of BCl_3. The −196° fraction was shown by IR spectroscopy to consist of a mixture of boron chlorofluorides. The IR spectrum of the −130° fraction indicated the presence of 2-chloropropene and boron chlorofluorides. After treatment of the −130° fraction with water at room temperature for 30 minutes, fractionation of the hydrolysis mixture gave 1.88 mmol of a gas identified as 2-chloropropene by molecular weight (found, 77.5; calcd., 76.5) and IR spectrum.

In a similar experiment, equimolar amounts of 2-fluoropropene and B_2Cl_4 were found to react completely in less than 10 minutes to give a product whose proton NMR spectrum was identical with that obtained in the BCl_3 reaction. After a similar fractionation and hydrolysis to remove diboron chlorofluorides, 2-chloropropene was isolated from the reaction mixture. The identity of this product was further established by observation of the NMR spectrum in benzene solution, which showed the characteristic features previously observed for this olefin in that solvent[12]. In contrast to the brief hydrolysis employed in the previous work-up, the product fraction in this experiment was treated with water overnight at room temperature. Fractionation of the hydrolysate gave significant quantities of a second product, identified by molecular weight (found, 114; calcd., 113.0), NMR, and IR spectra as 2,2-dichloropropane. Since the IR spectrum of the crude product mixture clearly indicated the absence of this compound in the sample taken for hydrolysis, it is clear that the dichloropropane was produced by addition of HCl to the olefin during the prolonged hydrolysis step. In other experiments, slow formation of broad peaks in the proton NMR spectrum over periods of several months indicated further reaction of the 2-chloropropene with the diboron species in the mixture.

Reaction of B_2Cl_4 with 3,3,3-trifluoropropene

The olefin (2.20 mmol) and B_2Cl_4 (2.34 mmol) were combined and the room temperature reaction monitored by proton NMR. After 6 days, the spectrum of the fluoropropene had been replaced by a simpler spectrum (weakly coupled AB_2: "triplet", rel. int. 1 at -6.33 ppm; "doublet", rel. int. 2 at -4.37 ppm; nominal splittings, 7.8 Hz). Fractionation of the reaction mixture gave 2.09 mmol 1,1,3-trichloropropene, with an NMR spectrum identical to that of the crude reaction mixture. Identification was confirmed from the infrared spectrum[5]. The other reaction products were principally a mixture of diboron chlorofluorides.

Other Reactions

The NMR spectra of mixtures of B_2Cl_4 with *cis*- and *trans*-difluoroethylene gave no evidence of formation of significant quantities of chlorofluoroethylenes or of the dichloroethylenes over a period of several months at room temperature. During this interval, however, a slow growth of broad resonances at 3.5–4 ppm below TMS was observed. These had the typical appearance of the spectra of olefin addition products[2], and it is concluded that formation of organoboron compounds is occurring in these systems at an exceedingly slow rate.

In contrast to 3,3,3-trifluoropropene and 2-fluoropropene, no reaction was observed between B_2Cl_4 and 2,3,3,3-tetrafluoropropene in periods of up to 6 months at room temperature.

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