of acetylene to the diborane-treated alumina suggests that the alumina plays a part in the cyclization reaction. If this is true, it would tend to substantiate the Danforth[3] concept of alumina atoms as the Lewis acid sites in silica–alumina. Substitution of BH_2 for hydrogen in Al–OH on the silica–alumina surface may result in an increase in acidity of the Lewis acid site due to the borane electron deficiency. In such a case induced polarization of the acetylene molecule would be sufficient to initiate the cyclization reaction. The results of other chemical reactions, which may further elucidate the structure of silica–alumina catalysts, will be reported later.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Fluorocarbon–Phosphinoborines and Related Chemistry[1]

BY ANTON B. BURG AND GOTTFRIED BRENDEL

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The new compound $(CF_3)_2PF$ (m.p. −150°; b.p. −12°) reacts with B_2H_6 at 0° or higher to produce H_2, $(CF_3)_2PH$, BF_3 (also at 0° a partially fluorinated borine), and the new $[(CF_3)_2PBH_2]_3$ (air-stable; m.p. 30.5°; b.p. est. 177°; slow decomp. at 200° converting all B to BF_3). The highly volatile complex $(CF_3)_2PF{\cdot}BH_3$ is present during the reaction. The reaction between $(CF_3)_2PH$ (m.p. −137°; b.p. 0.9°) and B_2H_6 also produces $[(CF_3)_2PBH_2]_3$; and it was possible to isolate also a trace of $[(CF_3)_2PBH_2]_4$ (m.p. 116°; slightly volatile). Dimethyl ether catalyzes this reaction, and also attacks the reactants to form $B(OCH_3)_3$ and the recently-discovered $CH_3P(CF_3)_2$ (m.p. −105°; b.p. 37.5°). Aqueous HCl attacks $[(CF_3)_2PBH_2]_3$ only very slowly at 150°; methanol–HCl is more effective at 85°, producing H_2, $(CF_3)_2PH$, $B(OCH_3)_3$ and CH_3Cl quantitatively. Aqueous NaOH at room temp. attacks $[(CF_3)_2PBH_2]_3$, forming $3HCF_3$. The ring-stability of $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$ probably is enhanced by delocalization of B–H electrons for supplementary B–P bonding.

The high stability and relatively inert chemical character of the compound $[(CH_3)_2PBH_2]_3$ (and higher polymers) would accord with the hypothesis that the P–B dative sigma bond is supplemented by an unusual type of pi bonding wherein B–H bonding electrons are partially assigned to phosphorus orbitals above the $3sp^3$ system.[2] This idea seems to gain support from the observation that the HBH and BPB bond angles are near 120° and the PBP angle near 112°,[3] all wider than the usual tetrahedral angle. Any such supplementary B–P bonding should gain importance if the groups on phosphorus were more electronegative: then the sigma bonding would be weaker because of the decreased electron-donor bonding power of phosphorus; but the inductive effect of an increased assignment of B–H electrons to phosphorus would partially compensate for such a weakening of the sigma bonds.

These ideas are supported by the stable existence of the new phosphinoborine low polymers $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$, which we have made by the reaction of diborane with either $(CF_3)_2PF$ or $(CF_3)_2PH$. They are slightly volatile solids which are observably decomposed as the temperature approaches 200°—in contrast to 400° for the incipient decomposition of $[(CH_3)_2PBH_2]_3$. However, even stability up to 200° would be surprising if the $(CF_3)_2PBH_2$ units were associated only by P–B sigma dative bonding, for the CF_3-substituted phosphines are very weak bases; for example, no evidence could be found for the existence of such borine adducts as $(CF_3)_3PBH_3$ or $(CF_3)_2PH{\cdot}BH_3$, and $(CF_3)_2PF{\cdot}BH_3$ apparently exists but is very unstable. The P–B dative bond in $(CF_3)_2PF{\cdot}BH_3$ doubtless gains strength through the inductive effect of a partial assignment of B–H electrons to weak B to P pi bonds. The same effect would account for the otherwise unexpected existence of $PF_3{\cdot}BH_3$.[4] A similar but wider-range delocalization of B–H electrons in the $(PB)_n$ rings would help to explain the stability of the trimer and tetramer of $(CF_3)_2PBH_2$.

The $(CF_3)_2PF$–B_2H_6 reaction converts some of the diborane to boron trifluoride; and at 0° there was evidence of the formation of a very unstable fluoroborine intermediate—probably HBF_2. The disproportionation of this fluoroborine at room temperature apparently is fast and irreversible, for there was no evidence for its presence in the $(CF_3)_2PF$–B_2H_6 reaction at 22°, and no reaction could be observed when diborane and boron trifluoride were left together for long periods of time.

The $(CF_3)_2PH$–B_2H_6 reaction required an accelerator, and dimethyl ether proved to be effective. Very pure $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$ could be obtained by this method, because B–F bonds were absent. However, the yields were only moderate because the ether was split, with formation of methyl borate and methylation of some of the phosphine to form the interesting compound $CH_3P(CF_3)_2$. This substance has been reported also as a component of a mixture obtained by the reaction of methyl iodide with tris-trifluoromethylphosphine.[5] In the present work it was not difficult to obtain a nearly pure sample because similarly volatile impurities were absent.

Experimental Part

I. Preliminary Syntheses

The New Compound Bis-trifluoromethyl-fluorophosphine.—The iodophosphine $(CF_3)_2PI$ was made by known

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[1] This research was supported by the United States Air Force under Contract AF 33(616)-2743, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] A. B. Burg and R. I. Wagner, THIS JOURNAL, **75**, 3872 (1953).

[3] W. C. Hamilton, *Acta Cryst.*, **8**, 199 (1955).

[4] R. W. Parry and T. C. Bissot, THIS JOURNAL, **78**, 1524 (1956).

[5] R. N. Haszeldine and B. O. West, *J. Chem. Soc.*, 3880 (1957).

methods[6,7] and purified by fractional condensation in a special high-vacuum apparatus with halocarbon-greased stopcocks. An 8.46-g. sample reacted with 7.1 g. of resublimed SbF_3 during three days at room temperature to produce 4.83 g. of $(CF_3)_2PF$ (calcd., 5.38 g.). A minor by-product was 0.20 g. of $P_2(CF_3)_4$, which was identified by its molecular weight (found, 338; calcd., 338.0) and by comparison of its vapor tensions with those of a sample made by the original method.[6] Other minor by-products were not identified.

The $(CF_3)_2PF$ was purified by high-vacuum fractional condensation, passing a trap at −108° and condensing at −125°. Its melting range was observed as −149.9 to −149.6°, and its vapor phase molecular weight was 188.2 (calcd., 188.0). Its purity was checked by analysis: a 1.11 mmole sample was hydrolyzed by 5 ml. of 10% aqueous sodium hydroxide at room temperature, yielding after 24 hr. 2.20 mmoles of HCF_3 (calcd., 2.22). The hydrolysis of a 0.569-mmole sample with plain water (24 hr. at room temp.) yielded 0.568 mmole of HCF_3 and presumably an equivalent amount of CF_3PHOOH. A phosphorus analysis by the Simmons–Robertson method[8] gave 16.2% P (calcd., 16.5).

The vapor tensions of pure $(CF_3)_2PF$, shown in Table I, determined the equation $\log_{10} P_{mm} = 6.2919 - 0.007259T + 1.75 \log_{10}T - 1501/T$, according to which the normal b.p. is −11.85° and the Trouton constant 21.10 cal./deg. mole.

TABLE I

VAPOR TENSIONS OF LIQUID $(CF_3)_2PF$

t (°C.)	p_{mm}- (obsd.)	p_{mm}- (calcd.)	t (°C.)	p- (obsd.)	p- (calcd.)
−114.9	0.32	0.32	−59.0	64.10	64.17
− 93.6	3.75	3.75	−43.6	165.3	165.4
− 84.5	8.92	8.89	−24.1	447	447
− 74.7	20.34	20.37	−16.0	634	637
− 62.8	49.52	49.51	−11.8	765	763

Other Special Reagents.—Diborane was prepared by the action of lithium aluminum hydride upon BF_3 etherate,[9] with no contamination by ethane because the etherate was freshly prepared. Each sample of diborane was repurified before use, after storage in closed bulbs at room temperature had produced higher boranes. The phosphine $(CF_3)_2PH$ was made as recently described.[10] The phosphine $(CF_3)_3P$ was obtained as a by-product of the synthesis of $(CF_3)_2PI$.[6,7] It was used only in attempts to make an adduct such as $(CF_3)_3PBH_3$ but proved to be quite inert toward diborane at pressures up to 9 atm. and temperatures from 20 to 80°.

Other reagents were commercial products which were carefully purified by distillation in the high-vacuum system.

Physical Properties of Bis-trifluoromethyl-phosphine.—The melting range of pure $(CF_3)_2PH$ was observed as −137.4 to −137.0°. The vapor phase molecular weight was 170.2 (calcd., 170.0). The vapor tensions, shown in Table II, determined the equation $\log_{10} p_{mm} = 6.9740 - 0.008310T + 1.75 \log_{10} T - 1667/T$, conforming to the observed b.p. of 0.9° and giving the Trouton constant as 20.9 cal./deg. mole.

II. The $(CF_3)_2PF$–B_2H_6 Reaction

TABLE II

VAPOR TENSIONS OF LIQUID $(CF_3)_2PH$

t (°C.)	p_{mm}- (obsd.)	p_{mm}- (calcd.)	t (°C.)	p- (obsd.)	p- (calcd.)
−108.8	0.22	0.22	−56.1	38.08	38.10
− 96.5	1.01	1.01	−48.8	62.31	62.34
− 85.5	3.26	3.25	−41.3	99.42	99.45
− 71.5	11.67	11.65	+ 0.9	760.0	760.0

The five experiments summarized in Table III were run in sealed Pyrex tubes of such sizes that the initial pressure exceeded 4 atm. Each tube could be opened to the high-vacuum system for investigation of the volatile components—in three cases with arrangement for multiple sealing and opening to permit separation, measurement and return of the volatiles at more than one stage of the process. The production of hydrogen could be taken as the measure of the extent of the main reaction $3(CF_3)_2PF + B_2H_6 \rightarrow H_2 + BF_3 + 2(CF_3)_2PH + (CF_3)_2PBH_2$, deviations from which can be explained in terms of detailed observations which are described in the following text. The last product appeared largely as the trimer $[(CF_3)_2PBH_2]_3$ (formula-proof described in Section IV), the per cent. yields of which are given in Table III in terms of $3H_2$ per mole. This yield basis would remain valid even if some $(CF_3)_2PBH_2$ units were formed by the far slower secondary reaction $2(CF_3)_2PH + B_2H_6 \rightarrow 2H_2 + 2(CF_3)_2PBH_2$. The tetramer $[(CF_3)_2PBH_2]_4$ and higher polymers probably were formed but were not studied in relation to this group of experiments. The separate values for BF_3 and B_2H_6 (reported for the final stages of expts. 2 and 4) were obtained by removing the BF_3 as the etherate $(CH_3)_2OBF_3$ and analyzing the separated B_2H_6 by hydrolysis. The phosphines $(CF_3)_2PF$ and $(CF_3)_2PH$ are reported together (including the borine adduct of the former); but in some cases they were separately estimated as described in the summaries of the individual experiments.

Experiment 1.—In the preliminary experiment the diborane was virtually all consumed, for the BF_3 fraction was nearly pure (mol. wt. 67.6 *vs.* calcd. 67.8; m.p. −131° *vs.* known −128°; vapor tensions checked known values). The ratio of BF_3 to H_2 was twice that expected on the basis of the assumed main reaction; hence it might be supposed that the simple exchange reaction $6(CF_3)_2PF + B_2H_6 \rightarrow 2BF_3 + 6(CF_3)_2PH$ played an important part, under conditions such that much of the reaction mixture was liquid (tube volume, 24 ml.).

Experiment 2.—The next experiment was planned to give information about the early stages of the process, as well as the over-all reaction. It was only 19% along after 4 days, but 87% after 10 days, and 98% after 17 days, according to the H_2 measurement. The final fluorocarbon–phosphine fraction (obsd., 3.775 mmoles; calcd., 3.768) was exposed to pure water for 24 hr. at room temperature to remove the $(CF_3)_2PF$ (forming 0.495 mmole of HCF_3), and the yield of $(CF_3)_2PH$ (mol. wt. obsd. 170.0; calcd., 170.0; vapor tensions checked) was measured as 3.273 mmoles. The amount according to the main equation would have been 3.660 mmoles; hence 0.387 mmole of $(CF_3)_2PH$ may have been used up in the secondary reaction with diborane while 0.50 mmole of $(CF_3)_2PF$ remained unused.

Of special interest was the low value for the BF_3–B_2H_6 fraction at the 4-day point: found, 1.454 mmoles; calcd., 1.867. This discrepancy, amounting to more than the expected yield of BF_3 at this point, could be explained best by assuming that 0.413 mmole of B_2H_6 had been caught by the fluorocarbon–phosphine fraction, in the form of an inseparable adduct such as $(CF_3)_2PF \cdot BH_3$. Such an adduct would be analogous to the highly volatile and dissociable adducts $PF_3 \cdot BH_3$[4] and BH_3CO.[11] Then as the $(CF_3)_2PF$ and B_2H_6 were used up in the further course of the main reaction, the adduct also would disappear and be replaced by $(CF_3)_2PH$. Thus the discrepancy in the BF_3–B_2H_6 fraction had nearly corrected itself after ten days, at which point the partial pressures of $(CF_3)_2PF$ and B_2H_6 were too low to maintain any important equilibrium proportion of the adduct.

Experiment 3. Bis-trifluoromethyl-fluorophosphine Borine.—The third experiment of Table III was undertaken for the specific purpose of studying the capture of diborane by the fluorocarbon–phosphine fraction. Separate experiments showed no appreciable tendency for adduct formation between $(CF_3)_2PH$ and B_2H_6; hence the diborane must have been held by the $(CF_3)_2PF$. The adduct could not be isolated by high-vacuum fractional condensation at −111°, but there was enrichment of boron-hydride content in the less volatile fractions. One such fraction was allowed to dissociate at room temperature, hypothetically according to the equation $2\ (CF_3)_2PF \cdot BH_3 \rightarrow B_2H_6 + 2(CF_3)_2PF$. The rate could be followed roughly by the increase of pressure and was distinctly higher than for the analogous dissociation of BH_3CO under similar conditions. When the dissociation

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[6] F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

[7] A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber and D. L. Herring, THIS JOURNAL, **79**, 247 (1957).

[8] W. R. Simmons and J. H. Robertson, *Anal. Chem.*, **22**, 294, 1177 (1950).

[9] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

[10] A. B. Burg and W. Mahler, *ibid.*, **79**, 4242 (1957).

[11] A. B. Burg and H. I. Schlesinger, *ibid.*, **59**, 780 (1937).

TABLE III

THE B_2H_6–$(CF_3)_2PF$ REACTION

Expt. no.	Reactants (mmoles) B_2H_6	Reactants (mmoles) $(CF_3)_2PF$	Temp. (°C.)	Total reaction time (days)	Products and recovered reactants (mmoles) H_2	$[(CF_3)_2PBH_2]_3$	BF_3	B_2H_6	$(CF_3)_2PH$ + $(CF_3)_2PF$
1	1.241	7.924	25	10	0.705	0.160 (68%)	1.423	...	6.794
2	1.867	5.598	22	4	0.355	.092 (78%)	1.454		5.246
			22	10	1.628	.434 (80%)	1.864		3.986
			22	17	1.830	.491 (81%)	1.819	0.030	3.775
3	2.403	4.127	22	3	0.139	.029 (63%)	1.937		(See text)
4	2.177	4.995	50	2	1.118	.294 (79%)	2.003		3.818
			50	5	2.277	.614 (81%)	1.839	0.075	2.680
5	1.920	5.742	0	13	1.083	.255 (71%)	1.881		4.675
			0	33	1.701	.431 (76%)	2.027[a]		4.016

[a] Decreasing with time.

was nearly complete, 0.209 mmole of B_2H_6 was isolated and checked by hydrolytic analysis; and the plain-water hydrolysis of the rest of the sample yielded 0.059 mmole of H_2, bringing the total estimate of BH_3 groups to 0.438 mmole. The same hydrolysis yielded 0.540 mmole of HCF_3 and 0.137 mmole of $(CF_3)_2PH$ was isolated. Since the plain-water hydrolysis of $(CF_3)_2PF$ normally yields one HCF_3 per mole, while $(CF_3)_2PH$ is unaffected, these results correspond to a mixture of 0.137 $(CF_3)_2PH$, 0.102 $(CF_3)_2PF$ and 0.438 $(CF_3)_2PF \cdot BH_3$. Considering that the adduct is nearly as volatile as the fluorocarbon-phosphines, no larger-molecule interpretation seems possible.

Experiment 4.—The increase of reaction rate with temperature was about as usually expected; and at the midpoint a deficiency in the BF_3–B_2H_6 fraction again indicated the presence of $(CF_3)_2PF \cdot BH_3$ in the reaction mixture. At the final stage, this experiment also gave a sure indication of the previously-mentioned slow secondary reaction $2(CF_3)_2PH + B_2H_6 \rightarrow 2H_2 + 2(CF_3)_2PBH_2$: the H_2-production and the consumption of B_2H_6 (2.102 mmoles) both considerably exceeded main-equation calculations based upon the available $(CF_3)_2PF$; and even the 81% yield of $[(CF_3)_2PBH_2]_3$ would require some use of $(CF_3)_2PH$. The final fluorocarbon-phosphine fraction was pure $(CF_3)_2PH$, for it was not affected by pure water. Its molecular weight was 170.6 (calcd., 170.0).

Experiment 5.—The reaction at 0° required much more time but was of special interest on account of the unusual character of the BF_3–B_2H_6 fraction. At the point of 57% completion of the main reaction, the deficiency of this fraction was not so evident as might have been expected if a reasonable part of the otherwise unused B_2H_6 had gone to make $(CF_3)_2PF \cdot BH_3$; and at the 89% stage there actually was 5% more gas in this fraction than could be expected if BF_3 were the only reaction-product accompanying the unused B_2H_6. It also was noted that the amount of gas in this fraction decreased as it stood at room temperature (without forming any condensed phase)—as though a reaction such as $3H_2BF \rightarrow BF_3 + B_2H_6$ or more probably $6HBF_2 \rightarrow 4BF_3 + B_2H_6$ were taking place. Any such reaction apparently is quite irreversible, for a mixture of 5.140 mmoles of BF_3 and 0.580 mmole of B_2H_6 showed no appreciable increase of standard gas volume after 23 days in a sealed tube at 0°. Hence the fluoroborine would have been a transitory reaction-intermediate, not all decomposed when the $(CF_3)_2PF$–B_2H_6 reaction occurred at 0°.

Further Evidence Confirming a Fluoroborine.—The BF_3–B_2H_6 fraction was treated at −78° with dimethyl ether in excess, in order to form stable complexes of BF_3 and any fluoroborines, while the complex $(CH_3)_2O \cdot BH_3$ would be appreciably unstable.[12] After thorough removal of the non-fluorinated material by high-vacuum fractional condensation at −78°, the mixture of ether complexes was further fractionated to remove the BF_3 etherate as the least volatile fraction. Finally the more volatile part was treated with $(CH_3)_3N$ to displace the ether and form a very stable complex. The vapor tensions of this complex, shown in Table IV, determined the equation $\log_{10} P_{mm} = 9.545 - 3163/T$ with such good conformity as to indicate a uniform substance. This equation represents volatility between $(CH_3)_3NBH_3$ and $(CH_3)_3NBF_3$, but the material could not well have been a solid solution of these complexes for two reasons: (1) the −78° fractionation would have eliminated the BH_3 groups as diborane; and (2) the sample developed some slightly more volatile material on heating, suggesting a disproportionation such as a mixture of the end products could not undergo. However, when the whole amine-complex sample was hydrolyzed by heating with hydrochloric acid the resulting hydrogen ran lower than expected: from the 6.1 mg. sample, 0.042 mmole of H_2; calcd. for $(CH_3)_3NBHF_2$, 0.056. Probably the material was chiefly $(CH_3)_3NBHF_2$ with a little $(CH_3)_3NBF_3$, but a solid solution of $(CH_3)_3NBH_2F$ with more $(CH_3)_3NBF_3$ cannot be excluded from consideration.

TABLE IV

VAPOR TENSIONS OF THE SUPPOSED $(CH_3)_3NBHF_2$ (SOLID)

t (°C.)	23.8	40.4	51.1	58.6	65.8	74.2
p_{mm}(obsd.)	0.09	0.28	0.61	1.01	1.68	2.75
p_{mm}(calcd.)	0.09	0.29	0.62	1.03	1.64	2.75

III. The $(CF_3)_2PH$–B_2H_6 Reaction

Some of the samples of $[(CF_3)_2PBH_2]_3$ from the $(CF_3)_2PF$–B_2H_6 reaction were pure enough for proof of the formula, but it was difficult to eliminate B-F bonds. In order to be sure of a product suitable for final characterization and for a fruitful search for the tetramer, it seemed better to employ the reaction between $(CF_3)_2PH$ and B_2H_6. This very slow process probably requires a slight formation of the exceedingly unstable $(CF_3)_2PH \cdot BH_3$, wherein the P–B dative bond would induce an increase of protic activity of the P–H bond and improve the hydridic reactivity of the B–H bond. Thus the rarity of formation of the complex intermediate would account for the slowness of the reaction. It was not feasible to accelerate the process by heat, for the decomposition of the diborane seemed to be accelerated more, and the presence of the resulting decaborane would interfere seriously when the similarly volatile tetramer $[(CF_3)_2PBH_2]_4$ was sought. Hence a suitable catalyst was needed to promote the desired reaction.

For this purpose it was considered useful to improve the hydridic reactivity of the B–H bond by forming a BH_3 complex with a weak base, which would not interfere with the polymerization of the $(CF_3)_2PBH_2$ units. Dimethyl ether served fairly well, although a more suitable catalyst probably can be found. The complex $(CH_3)_2OBH_3$ is partially dissociated even at −78°[12] but probably exists in solution or in adsorbed films at much higher temperatures. Thus it could provide a larger proportion of complex-bonded BH_3 groups than would occur through formation of the hypothetical $(CF_3)_2PH \cdot BH_3$. The main disadvantage of the ether as a catalyst was its side reactions with both $(CF_3)_2PH$ and B_2H_6; however, the resulting loss of yield of the desired trimer and tetramer was offset by their high purity.

The Uncatalyzed Reaction.—Table V summarizes two experiments in which mixtures of $(CF_3)_2PH$ and B_2H_6 were

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[12] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 296 (1938).

TABLE V

THE UNCATALYZED $(CF_3)_2PH–B_2H_6$ REACTION

Expt. no.	Reactants (mmoles) $(CF_3)_2PH$	Reactants (mmoles) B_2H_6	Temp. (°C.)	Time (hr.)	Recovered reactants (mmoles) $(CF_3)_2PH$	Recovered reactants (mmoles) B_2H_6	Products (total mmoles) H_2	Products (total mmoles) $[(CF_3)_2PBH_2]_3$
1	2.672	1.187	0	144	2.673	1.187	0.003	Nil
			22	144	2.648	1.162	.040	0.012
			47	120	2.573	1.109	.135	.036
2	2.663	1.132	75	40	2.384	0.861	.484	.067

TABLE VI

THE $(CF_3)_2PH–B_2H_6$ REACTION, WITH DIMETHYL ETHER

Expt. no.	Reactants (mmoles) $(CF_3)_2PH$	Reactants (mmoles) B_2H_6	Reactants (mmoles) $(CH_3)_2O$ (total)	Temp. (°C.)	Time (days)	Recovered reactants (mmoles) B_2H_6	Recovered reactants (mmoles) $(CF_3)_2$-PH	Recovered reactants (mmoles) $(CH_3)_2O$	Products (total mmoles) H_2	Products (total mmoles) CH_4	Products (total mmoles) CH_3P-$(CF_3)_2$	Products (total mmoles) $B(OCH_3)_3$	Products (total mmoles) $[(CF_3)_2$-$PBH_2]_3$	Products (total mmoles) $[(CF_3)_2$-$PBH_2]_4$
1	2.732	0.529	0.161	22	7	0.334	2.470		0.539	...	...	...	0.059	...
			2.092	0	28	0.010	1.263	1.017	1.640	0.191	0.944	0.260	.153	...
2	1.875	2.577	1.922	22	5	1.250	0.497	...	1.362	3.810	.064	...	.255	0.039
3	1.749	0.335	5.845	24	2	0.005	0.720	5.07	0.953	0.264	.717	.189	.0942	.007

allowed to react in sealed Pyrex tubes, of volume 22 and 39 ml., respectively. The relatively small temperature coefficient of the reaction rate would correlate with a decrease of equilibrium concentration of the postulated $(CF_3)_2PH\cdot BH_3$ with rise of temperature.

The Ether-catalyzed Reaction.—Table VI summarizes three experiments on the synthesis of the trimer and tetramer of $(CF_3)_2PBH_2$ by the $(CH_3)_2O$-catalyzed $(CF_3)_2PH–B_2H_6$ reaction. The first part of expt. 1 showed that the ether caused a very useful increase over the rates indicated in Table V, even though the reactants mostly were in the vapor phase (initial pressure near 2.8 atm.) throughout the process. In the second part, more ether was added for further effect, and the by-products methane, methyl borate and $CH_3P(CF_3)_2$ were observed. In the second experiment of Table VI the reaction was pushed so far as to use up all of the catalyst; and the relatively low yield of $CH_3P(CF_3)_2$ suggests that this may also have been brought into the reaction in some way. In expt. 3 the containing tube was small enough to keep the components mostly in the liquid phase, and the over-all rate was considerably improved. In this case it is noted that the reaction balance is quantitative with respect to $(CF_3)_2P$ and CH_3 groups, if we assume the identity of the material designated as $CH_3P(CF_3)_2$. The non-volatile residue would account for minor losses of the other elements: 0.160 mg.-atom of B, 0.208 mg.-atom of O, 0.076 mg.-atom of H^+ and 0.142 mg.-atom of H^-.

Methyl-bis-trifluoromethyl-phosphine: Characterization and Proof.—A refractionated sample of the supposed $CH_3P(CF_3)_2$ melted in the range −104.9 to −104.6°. Its vapor-phase molecular weight was 183.4 (calcd., 184.0). Its vapor tensions, shown in Table VII, determined the equation $\log_{10} P_{mm} = 6.7834 - 0.007258T + 1.75 \log_{10} T - 1867/T$, according to which the normal b.p. is 37.5° and the Trouton constant 20.7 cal./deg. mole.

TABLE VII

VAPOR TENSIONS OF $CH_3P(CF_3)_2$

t(°C.)	p_{mm} (obsd.)	p_{mm} (calcd.)	t(°C.)	p(obsd.)	p(calcd.)
−60.4	3.45	3.45	0.00	169.2	169.7
−46.0	11.01	10.95	11.0	277	278
−38.3	18.99	18.98	27.5	531	535
−34.6	24.41	24.36	37.7	764	764
−28.7	35.8	35.6			

The formula $CH_3P(CF_3)_2$, already indicated by the reaction balance (expt. 3, Table VI) and by the molecular weight, was confirmed by alkaline hydrolysis to yield $2HCF_3$.[5] A 14.1 cc. (standard gas) sample yielded 27.6 cc. of HCF_3 (calcd., 28.2 cc.) after 19 hr. with dilute KOH at 94°.

IV. Characterization and Formula Proofs of $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$

Physical Properties of the Trimer.—The more volatile of the two phosphinoborine products had an observed mol. wt. of 547 (calcd. for the trimer of bis-trifluoromethylphosphinoborine, 545.5), in the vapor phase at 17 mm. and 89°. The vapor tensions are shown in Table VIII. The values for the solid determined the equation $\log_{10} P_{mm} = 13.806 - 4135/T$; for the liquid, $\log_{10} P_{mm} = 9.2405 - 0.00800T + 1.75 \log_{10} T - 3330/T$. Thus the normal b.p. is estimated as 176.6° and the Trouton constant as 21.0 cal./deg. mole. The two equations together give the heat of fusion as 9.50 kcal./mole and the m.p. as 30.5°; obsd. m.p. 30.3–30.4°. Under microscopic examination the trimer crystals seemed to be orthorhombic. They were not appreciably affected by the open air during 10 days at 25°.

TABLE VIII

VAPOR TENSIONS OF SOLID AND LIQUID $[(CF_3)_2PBH_2]_3$

Solid t (°C.)	Solid p_{mm} (obsd.)	Solid p_{mm} (calcd.)	Liquid t (°C.)	Liquid p(obsd.)	Liquid p(calcd.)
6.1	0.10	0.10	32.6	1.79	1.79
14.7	.26	.28	37.0	2.40	2.42
19.6	.50	.48	44.2	3.90	3.86
21.4	.60	.59	51.9	6.18	6.19
23.6	.76	.75	55.7	7.79	7.74
25.4	.92	.91	62.4	11.25	11.28
27.1	1.14	1.08	67.9	15.10	15.16
30.2	1.50	1.50	82.3	31.10	31.09

Chemical Behavior and Analyses of the Trimer.—A sample of the trimer $[(CF_3)_2PBH_2]_3$ remained unchanged after 18 hr. in a sealed tube at 155°. However, during 10 days in a sealed tube at 200°, an 88.5-mg. sample (0.487 mmole monomer) formed 0.344 mmole of BF_3, 0.117 mmole of H_2, 0.052 mmole of HCF_3 and 0.037 mmole of unidentified gas. The recovery of trimer amounted to 25.5 mg., 71% having been destroyed. All of the boron in the destroyed part went to BF_3; and the brown wall-coating would be empirically formulated as $P_6C_{11}F_{15}H_7$.

The acid hydrolysis of a 58.9-mg. sample of the trimer (from expt. 1, Table III), with 4 ml. of concd. hydrochloric acid, was only 95% complete after 8 days in a sealed tube at 150° but finally was brought to completion by further action upon the recovered trimer. The initial 95% hydrolysis yielded 0.276 mmole of $(CF_3)_2PH$, representing 2.69 $(CF_3)_2P$ groups per mole of trimer consumed. The presence of 0.018 mmole of HCF_3 would partially explain the deviation from $3(CF_3)_2P$ groups per mole. The final yield of H_2 was 0.646 mmole, representing 5.98 B–H bonds per molecule of trimer. Thus the formula $[(CF_3)_2PBH_2]_3$ was indicated by these results, taken with a preliminary molecular weight value of 541.

The considerably easier alkaline hydrolysis also gave evidence bearing upon the formula of the trimer. The 58.6-mg. sample, left with 5 ml. of 10% aqueous sodium hydroxide for 24 hr. at room temperature, yielded 0.316 mmole of HCF_3 (checked by mol. wt. and vapor tensions), or 2.94 HCF_3 per $[(CF_3)_2PBH_2]_3$. This result corresponds to the knowledge that $(CF_3)_2PH$ produces only one HCF_3 by alkaline hydrolysis.[13] The acidified solution gave no hydrogen; whether the B–H bonds remained in a protected situation or had served to reduce half of the CF_3 groups was not determined. A phosphorus analysis[8] gave 17.7% P; calcd., 17.0%.

A final analysis for all components of the trimer was done by a reaction with HCl and methanol—far easier to complete than the acid hydrolysis. The 58.0 mg. sample was heated with 1.112 mmole of HCl and 0.2 ml. of CH_3OH in a soda-lime glass tube for 15 hr. at 86°. The resulting H_2 was measured as 0.643 mmole (calcd., 0.638). The boric acid titration gave 0.318 mmole (calcd., 0.319). All of the HCl had been converted to CH_3Cl, so that the excess gas volume of the CH_3Cl-$(CF_3)_2PH$ fraction could be ascribed to $(CF_3)_2PH$: 0.326 mmole (calcd., 0.319). In a parallel experiment, 83.5 mg. of the trimer had been heated with aqueous methanol-HCl (8 days at 85°), and the $(CF_3)_2PH$ was isolated and fully identified: 0.459 mmole (calcd., 0.459). In this case the H_2 amounted to 0.916 mmole (calcd., 0.918).

Physical Properties of the Tetramer.—The less volatile phosphinoborine material, from the $(CF_3)_2PH$-B_2H_6 reaction with $(CH_3)_2O$, had a mol. wt. of 742 (calcd. for bis-trifluoromethyl-phosphinoborine tetramer, 727). The crystals, which melted sharply at 116°, were observed under a microscope and seemed to be orthorhombic. The vapor tensions of the solid, shown in Table IX, determined the equation $\log_{10} p_{mm} = 12.683 - 4489.2/T$.

TABLE IX

VAPOR TENSIONS OF SOLID $[(CF_3)_2PBH_2]_4$

t (°C.)	45.5	54.4	75.7	82.0	89.9	98.4	104.9
p_{mm}(obsd.)	0.04	0.10	0.66	1.10	2.11	4.00	6.44
p_{mm}(calcd.)	0.04	0.10	0.66	1.11	2.09	4.00	6.46

Analysis of the Tetramer.—A sample of the tetramer, roughly estimated as 23 mg., was sublimed into a soda-lime glass seal-off tube, into which 0.609 mmole of HCl and 0.3 ml. of methanol were condensed. The sealed tube was heated for 7 days at 93° and then yielded 0.268 mmole of H_2, 0.131 mmole of $(CF_3)_2PH$ (fully identified by its 6.5 mm. vapor tension at −78°) and methyl borate titrating as 0.136 mmole. These results would correspond to 24.3 mg. of $[(CF_3)_2PBH_2]_4$; calcd. values, 0.267, 0.134 and 0.134, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY* AND THE KNOLLS ATOMIC POWER LABORATORY, GENERAL ELECTRIC COMPANY†]

A Mass Spectrometric Appearance Potential Study of Isotopically Labeled Diboranes[1]

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The appearance potentials of the molecule ions formed by electron impact from B_2H_6, $B^{10}{}_2H_6$, B_2D_6 and $B^{10}{}_2D_6$ have been measured mass spectrometrically. A set of apparently self-consistent ionization potentials for these molecule ions has been estimated from the appearance potentials of the B^{10} enriched compounds. The resulting calculated ionization potentials for the fragments from $B^{10}{}_2H_6$ are compared with the ionization potentials the authors estimate for fragments from $B^{10}{}_2D_6$ and are also compared with the results obtained from C_2H_6. The mass spectra of B_2H_6, $B^{10}{}_2H_6$, B_2D_6 and $B^{10}{}_2D_6$ were also run at 70 e.v. ionizing voltage in order to obtain a set of fragmentation patterns of the isotopically labeled diboranes under identical conditions; from these the monoisotopic spectrum of each type of diborane was calculated.

The method of obtaining bond dissociation energies by ionization and dissociation of molecules by electron impact has been used with considerable success in a number of types of compounds. If one represents the process taking place as

$$R_1 - R_2 + e^- \longrightarrow R_1^+ + R_2 + 2e^-$$

then by the equation

$$A(R_1^+) = I(R_1) + D(R_1 - R_2)$$

(where $A(R_1^+)$ is the mass spectrometrically measured appearance potential of R_1^+, $I(R_1)$ is the ionization potential of R_1 and $D(R_1 - R_2)$ is the dissociation energy of $R_1 - R_2$, either the ionization potential of R_1 or the bond dissociation energy $R_1 - R_2$ may be calculated directly from the measured $A(R_1^+)$, *provided* that one knows the value for the other unknown in the equation. A necessary condition for the above equation to hold true is $I(R_1) < I(R_2)$.[2] If $I(R_1) > I(R_2)$, then $A(R_1^+) > I(R_1) + D(R_1 - R_2)$. In order to interpret correctly the appearance potentials of fragment ions, it is necessary to know what neutral fragments are simultaneously formed and the states of electronic excitation of the neutral fragments and the molecule ion. However, it has been shown that in a number of cases the simplest set of assumptions suffices for the interpretation of the data.

There have been two recent papers[3] in which the investigators have reported the appearance potentials of some boron compounds, but with the exception of assigning 10.9 e.v. as the $I(BH_3)$ by employing the relation

$$A(BH_3^+) = I(BH_3) + D(BH_3 - BH_3)$$

and using $D(BH_3 - BH_3)$ the dissociation energy of a B_2H_6 into two BH_3 fragments (28.4 ± 2 kcal./mole),[4] no calculations have been published in this field.

We have measured mass spectrometrically the appearance potentials of the molecule ions formed by electron impact from B_2H_6, $B^{10}{}_2H_6$, B_2D_6 and $B^{10}{}_2D_6$. Unfortunately, no ionization potentials had ever been reported for any of the ions except B and an estimate for BH_3. We have attempted to calculate a self-consistent set of ionization potentials for these molecule ions formed from diborane using what thermochemical data were available, and have compared these results for fragments from B_2H_6 with those from C_2H_6 and B_2D_6.

The progress on the electron impact induced dis-

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