TABLE II

VAPOR PRESSURE OF F_3NO

Temp, °K	Pressure, mm		Temp, °K	Pressure, mm	
	Obsd	Calcd		Obsd	Calcd
116.2	1.0	1.0	162.5	172.0	170.4
130.5	8.0	7.9	177.4	469.0	468.1
142.0	28.0	28.6	187.6	845.0	847.9
153.6	84.0	84.0	190.9	995.0	1013.4

6.0553102. The normal boiling point from the equation is −87.6°, Trouton's constant is 20.7, and the heat of vaporization is 3.85 kcal/mol.

The critical temperature of F_3NO was determined by the "disappearing meniscus" procedure. A heavy-walled Pyrex capillary tube was partially filled with F_3NO (98% purity) and sealed with a torch. The temperatures at which the meniscus disappeared on heating (29.8°) and reappeared on cooling (29.1°) were averaged to obtain the critical temperature, 29.5° (measured with a platinum resistance thermometer).

The critical density of F_3NO was determined by the method of Cailletet and Mathias.[16] Two heavy-walled Pyrex capillary tubes (calibrated for height *vs.* volume with weighed amounts of mercury) were partially filled with accurately weighed amounts of F_3NO and sealed off with a torch. The tubes were then immersed in a thermostatic bath controlled to ±0.1°, and the volumes of liquid and vapor at each temperature were obtained by measuring the heights of liquid in the tubes with a cathetometer (to 0.001 cm). The equations[16]

$$W^A = p_g^A V_g^A + p_l^A V_l^A$$
$$W^B = p_g^B V_g^B + p_l^B V_l^B$$

were then solved simultaneously to give gas and liquid density as a function of temperature. These data were used to obtain a plot of the rectilinear diameter (average density of the two phases). Extrapolation of the rectilinear diameter to the critical temperature (29.5°) gave the critical density (0.593 g/ml). A graphic representation of the data is given in Figure 2. Liquid densities measured at temperatures down to −120° (not shown on the graph) were also measured. From the data, the temperature dependence of liquid density over the range −80 to −120° was found to be $d_t = 1.237 - 0.003544t$, where t is in degrees centigrade and d_t is in grams per milliliter.

From the critical density and critical temperature values, the critical pressure was calculated using the van der Waals equation applied to the critical state. The pertinent data are summarized as follows: $T_c = 29.5°$, $d_c = 0.593$ g/ml, $a = 4.0965$ l.^{2} atm, $b = 0.0489$ l., and $P_c = 63.5$ atm. The critical pressure obtained by extrapolation of the vapor pressure equation was 64.0 atm, in excellent agreement with the value above.

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[16] Described in S. Glasstone, "Textbook of Physical Chemistry," 2nd ed D. Van Nostrand Co., Inc., Princeton, N. J., 1950, p 431.

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The Oxidation of Dimethylaminodifluorophosphine by Cyanogen Bromide

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Cyanogen bromide will interact with $(CH_3)_2NPF_2$ to give $(CH_3)_2NPF_3(CN)$ and $(CH_3)_2NPFBr$ as products. These new compounds have been completely characterized by chemical analysis and infrared, nmr, and mass spectroscopy. Cyanogen bromide does not interact with PF_3.

Discussion

A fairly large number of halofluorophosphoranes and substituted halofluorophosphoranes have been prepared.[1–5] Some of these such as $CCl_3PCl_2F_2$[4] and $(CH_3)_2NPF_2Cl_2$[5] can be obtained by oxidation of the corresponding phosphine by an appropriate halogen. Pseudohalogens such as cyanogen or thiocyanogen and pseudohalogen halides such as cyanogen chloride, cyanogen bromide, or thiocyanogen bromide have never been employed successfully as oxidizing agents with phosphines. Salthouse and Waddington[6] have recently reported that cyanogen chloride showed no oxidizing power toward phosphorus trichloride in liquid hydrogen chloride.

In addition, no pentacoordinate pseudohalofluorophosphoranes have been reported, although a pseudohalofluorophosphine, PF_2CN, has recently been re-

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[1] R. Baumgartner, W. Sawalny, and J. Gobeau, *Z. Anorg. Allgem. Chem.*, **333**, 171 (1964).

[2] Zh. M. Ivanova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **31**, 3991 (1961).

[3] Zh. M. Ivanova and A. V. Kirsanov, *ibid.*, **32**, 2592 (1962).

[4] J. F. Nixon, *J. Inorg. Nucl. Chem.*, **27**, 1281 (1965).

[5] K. Cohn and R. W. Parry, *Inorg. Chem.*, **7**, 46 (1968).

[6] J. A. Salthouse and T. C. Waddington, *J. Chem. Soc.*, *A*, 1096 (1967).

ported by Rudolph, Taylor, and Parry.[7] We wish to report the preparation and characterization of the first pseudohalofluorophosphorane, $(CH_3)_2NPF_3(CN)$. This compound has been prepared by the oxidation of dimethylaminodifluorophosphine, $(CH_3)_2NPF_2$, by cyanogen bromide, BrCN.

Experimental Section

Apparatus.—Standard high-vacuum techniques were used throughout.

Materials and Analyses.—Cyanogen bromide (Aldrich Chemical Co.) was used without further purification. Dimethylaminodifluorophosphine was prepared by a previously described method.[8] The identity of the phosphine was established by comparison of its infrared spectrum with a previously reported spectrum[9] and by a vapor pressure of 93.7 mm at 0° (lit.[8] pressure 93.4 mm). Phosphorus trifluoride (Ozark Mahoning Co.) was bubbled through water at 0° and dried by passing the gas through 0 to −78 to −196° traps. The −78° fraction was discarded. The purity of the sample thus obtained was established by a vapor pressure of 114.4 mm at −126.0° (lit.[10] pressure 113.9 mm).

Infrared Spectra.—The infrared spectra were obtained on a Perkin-Elmer 237B grating spectrophotometer. For the region below 600 cm^{-1}, a Perkin-Elmer 301 spectrophotometer was employed. Liquid materials were examined as smears between KBr plates. For volatile materials a gas cell with a 7.5-cm path length and CsI windows was used.

Nuclear Magnetic Resonance Spectra.—Proton nmr spectra were observed on a Varian Model A-60 nuclear magnetic resonance spectrometer operating at the ambient temperature of the instrument. Fluorine nmr spectra were obtained on a Varian Model 56/60 nuclear magnetic spectrometer operating at 56.4 Mc. For the proton spectra tetramethylsilane and methylene chloride were used as external standards. For fluorine magnetic resonances, fluorotrichloromethane was used as an external reference, by the tube-interchange technique. Whenever possible, samples were run as neat liquids. For solids appropriate solvents were used, as indicated.

Mass Spectra.—All mass spectra were obtained on a Consolidated Electrodynamics Corp. Model 21-103C spectrometer operating with an ionizing voltage of 70 V.

Vapor-Phase Chromatography.—An F & M 810 research chromatograph was used, with helium as the carrier gas and a flame ionization detector. Glpc analyses of the products were performed on a 0.125 in. × 20 ft stainless steel column packed with 20% silicon gum rubber SE 30 on Chromosorb W. The column was operated at 70°. Collection of the product was accomplished by attaching an effluent splitter to the column. The desired fraction was collected at −45° with a Nuclear Magnetic Resonance Specialties gas-collecting kit, Catalog No. 12-000. The flow rate of He was 60 ml/min. The retention times were: $(CH_3)_2NPOF_2$, 15 min; $(CH_3)_2NPF_3(CN)$, 22 min; $(CH_3)_2NPFBr$, 26 min. The samples thus collected were maintained in an inert atmosphere until they were sealed. After the nmr spectra were obtained, the nmr tube used to collect the fractions was opened in an inert atmosphere and introduced into a tube equipped with a standard taper joint. This assembly was attached to a vacuum line, and the sample was distilled *in vacuo* to a −196° trap. This fraction was subsequently employed for ir and mass spectral analyses, as well as elemental analyses.

Reaction of $(CH_3)_2NPF_2$ with BrCN.—In a typical experiment a sample of solid cyanogen bromide (7.07 g, 66.7 mmol) was transferred to a 200-cc glass reaction tube equipped with a standard taper joint and a ground-glass stopcock. Dimethylaminodifluorophosphine (14.4 g, 127 mmol) was then condensed *in vacuo* into the reaction tube which was held at −196°. The reaction mixture was warmed to −20° by placing the reaction tube in a bath of salt and ice. The mixture was allowed to warm to −8° over a period of 25 hr. The colorless reaction mixture turned pale yellow but still existed in two phases. There was, however, less solid present after the 25-hr period than the amount of solid cyanogen bromide initially added.

The volatile products were recovered by a 0.5-hr distillation *in vacuo* to a trap held at −196°. The reaction mixture was heated to 70° during this distillation.

The products, collected at −196°, were passed through traps held at −23, −78, and −196°. A 38-mmol sample of unreacted $(CH_3)_2NPF_2$, identified by its infrared spectrum and vapor pressure of 93.5 mm at 0°, was recovered from the −78° trap. The −23° trap held a 5.8-ml fraction containing a mixture of products. It was impossible to separate this mixture using trap to trap distillation. In a separate experiment, no effective separation was accomplished when the mixture was distilled at 20 mm pressure using a 16-in. column packed with glass helices. Separation could only be accomplished by vapor phase chromatography as previously described. After separation, it was possible to identify $(CH_3)_2NPF_3(CN)$, $(CH_3)_2NPFBr$, and $(CH_3)_2NPOF_2$ in the mixture of products. Identification of these products is described in the subsequent sections of this paper. A proton nmr spectrum obtained of a portion of the 5.8-ml fraction containing the mixture of products revealed that the mixture contained about 50% $(CH_3)_2NPF_3(CN)$, about 35% $(CH_3)_2NPFBr$, and about 15% $(CH_3)_2NPOF_2$ (identified by its infrared spectrum[11] and a vapor pressure at 0° identical with that previously reported[11]).

In similar experiments in which the reaction mixture was not heated during distillation, the yield of volatile products was about 20% of that reported above. In addition, $(CH_3)_2NPOF_2$ was not present as a product. The mixture of $(CH_3)_2NPF_3(CN)$ and $(CH_3)_2NPFBr$ subsequently obtained from mixtures which were not heated during distillation formed a yellow, viscous, nonvolatile liquid upon standing at 25° for 2 hr. In contrast to this behavior, the mixture of $(CH_3)_2NPF_3(CN)$ and $(CH_3)_2NPFBr$ obtained from a reaction mixture which was heated during distillation was stable for a period of several hours at 40°. It is possible that small amounts of water or BrCN which were not involved in the reaction at lower temperatures catalyzed a subsequent polymerization.

A deep red-brown, viscous, nonvolatile liquid always remained in the reaction tube. The proton nmr spectrum of this material is extremely broad and complex. No further characterization of this product has been attempted.

Characterization of $(CH_3)_2NPF_3(CN)$.—The infrared spectrum of $(CH_3)_2NPF_3(CN)$ shows absorptions at 2955 (ms), 2880, 2830 (m), 2207 (s), 1478 (m), 1306 (s), 1202 (m), 1039, 915, 866, 775 (vs), 710 (mw), 620 (w), 560, 500, and 442 (m) cm^{-1}.

The vapor pressure of $(CH_3)_2NPF_3(CN)$ is 5.5 mm at 25°. It can be distilled at 35° at 20 mm. The melting point is −44 ± 3°, determined with a thermometer and visual observation of the phase change.

The mass spectrum shows peaks attributed to the following species (with mass number and relative abundance, respectively): $(CH_3)_2NPF_3(CN)^+$, 158, 11; $[(CH_3)(CH_2)N]PF_3(CN)^+$, 157, 1; $(CH_3)_2NPF_4^+$, 150, 1; $CH_3NPF_3(CN)^+$, 142, 1; $(CH_3)_2NPF_2(CN)^+$, 139, 7; $(CH_3)_2NPF_3^+$, 132, 38; (?), 129, 1; (?), 128, 1; (?), 116, 7; $PF_3(CN)^+$, 114, 100; $(CH_3)_2NPF_2^+$, 113, 2; (?), 112, 4; PF_4^+, 107, 4; POF_3^+ or SiF_4^+, 104, 4; PF_3^+, 88, 7; PF_2O^+, 85, 5; PF_2H^+, 70, 17; PF_2^+, 69, 27; PF^+, 50, <1; PC^+, 43, 4; POF_2^{2+} (?) or $(CH_2)_2N^+$, 42, 9; CH_3CN^+, 41, 2; P^+, 31, 1; N_2^+, 28, 2; HCN^+, 27, 7; CN^+, 26, 7; H_2O^+, 18, 1; CH_3^+, 15, 7.

Anal. Calcd for $(CH_3)_2NPF_3(CN)$: C, 22.78; H, 3.82; N, 17.72. Found: C, 22.80; H, 4.23; N, 17.86; Br, <0.5. These data are discussed in a subsequent portion of this article.

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(7) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966).

(8) J. G. Morse, K. Cohn, R. W. Rudolph, and R. W. Parry, *Inorg. Syn.*, **10**, 147 (1967).

(9) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).

(10) H. S. Booth and A. R. Bozarth, *J. Am. Chem. Soc.*, **61**, 2927 (1939).

(11) R. G. Cavell, *Can. J. Chem.*, **45**, 1309 (1967).

Characterization of $(CH_3)_2NPFBr$.—The infrared data for $(CH_3)_2NPFBr$ may be summarized by: 2950 (m), 2905 (mw), 2855, 2810 (w), 1475, 1460, 1445 (m), 1290, 1185 (ms), 1175 (sh), 1060 (mw), 985 (s), 815 (ms), 707 (sh), 698, 458 (m), and 387 (ms) cm^{-1}.

The vapor pressure of $(CH_3)_2NPFBr$ is 6.5 mm at 25°. It can be distilled at 37°, at 20 mm; mp −73 ± 5°, determined with a thermometer and visual observation.

The mass spectrum shows peaks attributed to the following species (with mass number and relative abundance, respectively): $(CH_3)_2NPF^{81}Br^+$, 175, 6; $(CH_3)_2NPF^{79}Br^+$, 173, 6; $(CH_3)_2NPF_3^+$, 132, 4; $PF^{81}Br^+$, 131, 6; $PF^{79}Br^+$, 129, 6; $(CH_3)_2NPF_2^+$, 113, 1; $[(CH_3)(CH_2)]NPF_2^+$, 112, 1; $(CH_3)_2NPFH^+$, 95, 3; $(CH_3)_2NPF^+$, 94, 100; $[(CH_3)(CH_2)]NPF^+$, 93, 4; PF_2O^+, 85, 1; $^{81}Br^+$, 81, 3; $^{79}Br^+$, 79, 3; (?), 78, 6; PF_2^+, 69, 3; (?), 65, 10; (?), 51, 9; PF^+, 50, 11; $(CH_3)_2NPF_2^+$ (?), 47, 11; $(CH_3)_2N^+$, 44, 11; $[(CH_3)(CH_2)]N^+$ or PC^+, 43, 10; POF_2^{2+} or $(CH_2)_2N^+$ (?), 42, 43; P^+, 31, 17; N_2^+, 28, 14; H_2O^+, 18, 1.

Anal. Calcd for $(CH_3)_2NPFBr$: C, 13.80; H, 3.48; N, 8.05; Br, 45.94. Found: C, 13.65; H, 3.24; N, 8.29; Br, 46.18. These data are discussed in a subsequent portion of this article.

Interaction of PF_3 with BrCN.—BrCN (1.02 mmol) was condensed at −196° *in vacuo* into a 300-cc reaction tube equipped with a stopcock and a standard taper joint. While the tube was maintained at −196°, 3.21 mmol of PF_3 was distilled *in vacuo* onto the solid BrCN. The mixture was allowed to warm to 25° for 1 hr. After this time, the gaseous mixture was heated to 75° for 5 hr by immersion of the reaction tube into a heated oil bath. After heating, the reaction mixture was passed through traps held at 0, −78, and −196°. A 3.20-mmol sample of unreacted PF_3 was recovered from the −196° trap, indicating no reaction occurred. The PF_3 thus recovered was identified by its infrared and mass spectra, which were identical with those of a sample of authentic PF_3.

Results and Discussion

$(CH_3)_2NPF_3(CN)$.—The formula $(CH_3)_2NPF_3(CN)$ is supported by the proton and fluorine nmr spectra. The proton spectrum shows a 1:1 doublet (δ −2.8 ppm), due to H–P coupling (J_{HP} = 12.8 cps). Each member of the doublet is split into a 1:3:3:1 quartet by HF coupling (J_{HF} = 2.8 cps).

Muetterties and co-workers[12] have established that most five-coordinate phosphorus(V) derivatives have a trigonal-bipyramidal coordination about the phosphorus atom, with the most electronegative groups at the axial sites of the trigonal bipyramid. On the basis of this work, the structure for $(CH_3)_2NPF_3(CN)$ may be designated as a trigonal bipyramid in which the two fluorine atoms are located at the axial positions. The nonequivalence of fluorine atoms is clearly indicated by the fluorine nmr spectra at 35° shown in Figure 1. The low-field doublet (δ +26 ppm) arises from the axial fluorine atoms which interact with the phosphorus (J_{PF_a} = 780 cps). Each member of this doublet is further split into a doublet owing to interaction with the equatorial fluorine atom ($J_{F_aF_e}$ = 63 cps). This low-field pair of doublets has twice the intensity of the higher field pair of triplets (δ +60 ppm). The pair of triplets arises from the equatorial fluorines which interact with the phosphorus (J_{PF} = 950 cps) and the two equivalent axial fluorines ($J_{F_aF_e}$ = 63 cps). The values of the chemical shifts and coupling constants are in complete accord with the proposed formulation.[13]

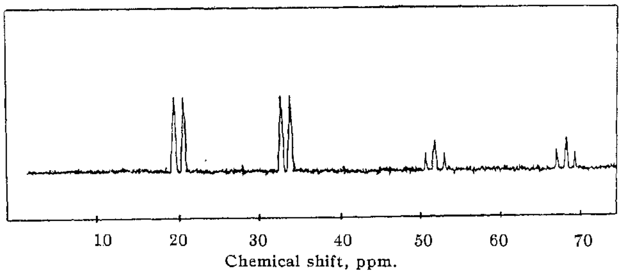

Figure 1.—The fluorine-19 nmr spectrum of $(CH_3)_2NPF_3(CN)$.

Additional support for the proposed formulation of the compound as $(CH_3)_2NPF_3(CN)$ is obtained from examination of the ir spectrum. The spectrum exhibits a sharp, strong absorption at 2207 cm^{-1} which is easily correlated with a C≡N stretching mode. A similar absorption is observed in the spectrum of $P(CN)_3$[14] at 2204 cm^{-1} and of PF_2CN[7] at 2194 cm^{-1}. Because the cyanide and isocyanide stretching frequencies fall close together,[15] it is difficult to differentiate between these linkages on the basis of the infrared spectrum. Other infrared absorptions, reported previously in this article, are similar in position and intensity to absorptions reported for $(CH_3)_2NPF_4$.[16]

Mass spectra of a sample of $(CH_3)_2NPF_3(CN)$ show traces of POF_3 or SiF_4. The parent ion was noted in a relatively high abundance. The most abundant peak is easily attributed to the $PF_3(CN)^+$ ion, suggesting that this ion is thermodynamically stable and that the P–N bond may be easily cleaved. Supporting this contention is the fact that the syntheses of PF_2X,[8] OPF_2X,[17] and PF_4X[18] (where X = Cl or Br) recently have been accomplished by cleaving the $(CH_3)_2N$ group from the appropriate fluorophosphine or -phosphorane with an anhydrous hydrogen halide. It may well be possible that stable species such as PF_4CN, $PF_3Cl(CN)$, and $PF_3Br(CN)$ may be obtained by treatment of $(CH_3)_2NPF_3(CN)$ with HF, HCl, and HBr, respectively. An investigation is currently being directed toward this end in these laboratories.

$(CH_3)_2NPFBr$.—As in the previous case, all data support the proposed formulation. The proton spectrum exhibits a 1:1 doublet (−2.6 ppm), due to H–P coupling (J_{HP} = 12.7 cps). Each member of the doublet is split into a 1:1 doublet by H–F coupling (J_{HF} = 3.1 cps). The fluorine spectrum exhibits a 1:1 doublet (+76.1 ppm), due to P–F coupling (J_{PF} = 1172 cps). Although the P–F coupling constant cannot be used to rule out pentavalent phosphorus com-

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[12] (a) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1290 (1964); (b) E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963).

[13] (a) R. Schmutzler, *Advan. Fluorine Chem.*, **5**, 252 (1965); (b) R. Schmutzler in "Halogen Chemistry," Vol. 2, V. Gutman, Ed., Academic Press Inc., New York, N. Y., 1967, p 31.

[14] J. Goubeau, H. Haeberle, and H. Ulmer, *Z. Anorg. Allgem. Chem.*, **311**, 110 (1961).

[15] J. L. Bellamy, "The Infrared-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1961.

[16] D. H. Brown, G. W. Fraser, and D. W. A. Sharp, *J. Chem. Soc., A*, 171 (1966).

[17] R. G. Cavell, *Can. J. Chem.*, **45**, 1309 (1967); (b) A. Muller, H. G. Horn, and O. Glemser, *Z. Naturforsch.*, **20b**, 1150 (1965).

[18] R. Rogowski and K. Cohn, unpublished results, Michigan State University, 1968.

pounds, it should be mentioned that no alkylaminofluorophosphorane exhibits a P–F coupling constant of more than 900 cps[12] although the P–F coupling constant of $(CH_3)_2NPF_2$ is 1194 cps.[19] This strongly suggests that the compound is a phosphine, not a phosphorane. Under higher resolution it can be seen that each member of the fluorine resonance doublet is split into a 1:6:15:20:15:6:1 septet owing to coupling with the six equivalent protons ($J_{HF} = 3.1$ cps).

The bands observed in the ir spectrum of $(CH_3)_2NPFBr$ may be fairly easily assigned by analogy with the ir assignments based on normal-coordinate calculations for $(CH_3)_2NPF_2$ and $(CH_3)_2NPBr_2$ recently made by Farran.[20] The complete spectrum may be summarized by the following absorptions (in cm^{-1}, with intensity and tentative assignments, respectively): 2950 (m), 2905 (mw), 2855 (w), and 2810 (w) (symmetric C–H stretch); 1475, 1460, and 1445 (m) (methyl deformation); 1290 (ms) (C–N stretch); 1185 (ms), 1175 (sh), and 1060 (mw) (methyl rock); 815 (ms) (P–F stretch); 458 (m) (?); 387 (ms) (C–N–C deformation or P–Br stretch).

The mass spectra of a sample of $(CH_3)_2NPFBr$ show ions which correspond to the anticipated fragmentation pattern. Two peaks of about equal intensity at m/e 175 and 173 correspond to parent ions $(CH_3)_2NPF^{79}Br^+$ and $(CH_3)_2NPF^{81}Br^+$. The most abundant peak appears at m/e 94 and corresponds to the loss of a bromine atom from $(CH_3)_2NPFBr$. The mass spectra of other dialkylaminofluorophosphines and dialkylaminofluorophosphoranes generally exhibit a fragmentation pattern which suggests that the P–N is most easily cleaved.[21] This does not appear to be the case with dialkylaminohalofluorophosphines and -phosphoranes.[22]

It has been mentioned in the Experimental Section that the principal volatile products of the reaction between BrCN and $(CH_3)_2NPF_2$ are $(CH_3)_2NPF_3(CN)$ and $(CH_3)_2NPFBr$. It is possible to suggest that the reaction proceeds according to the equation

$$2(CH_3)_2NPF_2 + BrCN \longrightarrow (CH_3)_2NPF_3(CN) + (CH_3)_2NPFBr$$

The nonvolatile solid also obtained in this reaction may be accounted for by postulating the presence of a polymeric cyanophosphine or further reaction of the alkylamino moiety with BrCN. Such reactions are well known.[23] It is of interest to note that PF_3, in contrast to $(CH_3)_2NPF_2$, does not interact with BrCN, even at 75°. This may suggest that the electron-donating ability of the $(CH_3)_2N$ group (which increases the negativity of the phosphorus atom) allows attack of BrCN.

Acknowledgment.—Generous support of this work by the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. It is also a pleasure to thank Dr. J. Heeschen of the Dow Chemical Co., Midland, Mich., for help in obtaining the ^{19}F nmr spectra.

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(19) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

(20) C. F. Farran, Ph.D. Thesis, The University of Michigan, Ann Arbor, Mich., 1967.

(21) R. G. Cavell, *Can. J. Chem.*, **45**, 1309 (1967).

(22) W. Z. Borer and K. Cohn, unpublished results, Michigan State University, 1968.

(23) H. A. Hagerman in "Organic Reactions," Vol. 7, John Wiley and Sons, Inc., New York, N. Y., 1953, pp 198–262.

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Synthesis of the Hydrides of Germanium, Phosphorus, Arsenic, and Antimony by the Solid-Phase Reaction of the Corresponding Oxide with Lithium Aluminum Hydride[1]

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When SiO_2, GeO_2, P_2O_5, As_2O_3, or Sb_2O_3 was heated with a deficit of $LiAlH_4$ in the absence of solvent at 148–170°, a rapid reaction took place to give SiH_4, a mixture of GeH_4, Ge_2H_6, and Ge_3H_8, PH_3, AsH_3, and SbH_3, respectively. No volatile tin, boron, or titanium hydrides were formed when SnO_2, B_2O_3, or TiO_2 was heated with $LiAlH_4$.

It has been demonstrated by Weiss and Fisher[2] that when lithium aluminum hydride is heated to approximately 200° with excess powdered silicon dioxide in the absence of solvent, silane, SiH_4, is formed. Approximately 7.1% of the hydrogen present in the lithium aluminum hydride appeared in the SiH_4 produced. This is a most convenient method for the small-scale synthesis of SiH_4 since no volatile reagents or solvents, from which the SiH_4 must be subsequently separated, are employed; the apparatus and experimental procedure are also extremely simple. The present study was undertaken in order to ascertain whether this procedure could be used for the convenient synthesis of other volatile hydrides.

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[1] This report is based on portions of a thesis submitted by J. M. Bellama to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work was supported in part by the Advanced Research Projects Agency, Office of the Secretary of Defense.

(2) H. G. Weiss and H. D. Fisher, *Inorg. Chem.*, **2**, 880 (1963).