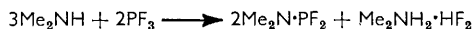


382. *Preparation and Properties of Dimethylaminodifluorophosphine.*

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Phosphorus trifluoride reacts with dimethylamine to form dimethylaminodifluorophosphine, which has been fully characterized. It forms a 1 : 1 complex with boron trifluoride, which is completely dissociated in the vapour. It reacts with hydrogen chloride to form chlorodifluorophosphine and with hydrogen iodide to form difluoroiodophosphine, the latter being very unstable.

DIMETHYLAMINODIFLUOROPHOSPHINE has been prepared recently¹ by two indirect routes involving the fluorination of dimethylaminodichlorophosphine with zinc fluoride and reaction of boron trifluoride with trisdiaminophosphine in xylene solution. The latter method, however, may under certain conditions yield only phosphorus trifluoride.² The difluorophosphine has now been prepared by direct interaction of phosphorus trifluoride with dimethylamine; a general method^{3,4} which has hitherto been applied mainly to other phosphorus halides. Dimethylamine reacts immediately in the gas phase in a 3 : 2 molar ratio with phosphorus trifluoride according to the equation:



Reaction was not complete at room temperature or at 40° and a small excess of dimethylamine remained, though no unchanged phosphorus trifluoride was detected. Excess of dimethylamine was best removed from the crude product by treatment with additional phosphorus trifluoride. Chlorodifluorophosphine reacts with dimethylamine under similar conditions to yield dimethylaminodifluorophosphine and the alkylammonium salt showing that the P-Cl bond is more susceptible to aminolysis than P-F.

Dimethylaminodifluorophosphine is a colourless liquid, b. p. 50.3°, with a normal Trouton constant of 21.6. Its i.r. spectrum is very similar to that of dimethylaminodichlorophosphine⁵ with additional strong peaks at 772 and 812 cm.⁻¹ due to P-F vibrations. The fluorine n.m.r. consists of a pair of septets arising from the splitting of the fluorine resonance into a doublet by the phosphorus, combined with a splitting of each line in the doublet into a septet by six methyl protons. The phosphorus resonance is a triplet with an intensity ratio 1 : 2 : 1, attributable to the action of two equivalent fluorine nuclei on the phosphorus spin. The p.m.r. consists of a pair of triplets of intensity 1 : 2 : 1 arising from splitting of the proton resonance into a doublet by the phosphorus: the doublet is further split into a 1 : 2 : 1 triplet by the two equivalent fluorines. Values of

¹ Noth and Vetter, *Ber.*, 1963, **96**, 1298.

² Holmes and Wagner, *J. Amer. Chem. Soc.*, 1962, **84**, 357.

³ Kosolapoff, "Organophosphorus Compounds," Wiley, New York, 1950.

⁴ Van Wazer, "Phosphorus and its Compounds," Vol. I, Interscience, London, 1958.

⁵ Harvey and Maygood, *Canad. J. Chem.*, 1955, **33**, 1552.

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the coupling constants and chemical shifts are given in Table 1. The data also shows that coupling constants calculated from different resonance spectra are in good agreement, thus confirming the assignment.

Chemical shift	Me ₂ NPF ₂	(Me ₂ N) ₂ PF	Coupling constants		Me ₂ NPF ₂	(Me ₂ N) ₂ PF
¹⁹ F (compared with CCl ₃ F)	+65.5	+100.4	<i>J</i> _{F-F}	<i>a</i>	1197	1023
³¹ P (compared with 85% H ₃ PO ₄)	-145	—		<i>b</i>	1194	—
			<i>J</i> _{F-H}	<i>c</i>	9.25	9.0
¹ H (compared with cyclohexane)	-1.225	-1.089	<i>J</i> _{F-H}	<i>a</i>	3.64	—
				<i>c</i>	3.67	3.2

(a) Derived from ¹⁹F spectra; (b) derived from ³¹P spectra; (c) derived from ¹H spectra.

Dimethylaminodifluorophosphine is somewhat less reactive to dimethylamine than is phosphorus trifluoride and an appreciable reaction occurs only at 50°. The product, bisdimethylaminofluorophosphine could not be adequately separated from the reactants by vacuum fractionation and it was identified in the impure reaction product by the fluorine and proton nuclear resonance spectra. The fluorine spectrum was a doublet, arising from splitting by the phosphorus. No proton-fluorine coupling was observed, probably because of the low concentration of the sample. The p.m.r. spectrum was a pair of doublets with all the lines of equal intensity, arising from the single phosphorus and fluorine nuclei with the twelve equivalent methyl protons. Data are included in the Table.

The reduced susceptibility of dimethylaminodifluorophosphine to aminolysis can be attributed to its increased basicity relative to the trifluoride. The first step in the reaction of dimethylamine with phosphorus trifluoride probably involves the formation of a weak complex similar to those studied by Holmes and Wagner,⁶ *e.g.*, PF₃.Me₂NH. Elimination of hydrogen halide leads to the aminophosphine. In the similar reaction of the aminophosphine with the amine, the presence of the dimethylamino-group will enhance the basic properties and so reduce the tendency to complex formation with a base. The increased basicity of dimethylaminodifluorophosphine is illustrated by the formation of a 1:1 complex with boron trifluoride, whereas phosphorus trifluoride does not form such a complex.⁷ The 1:1 dimethylaminodifluorophosphine-boron trifluoride complex is a volatile solid with a normal sublimation temperature of 61° and a heat of sublimation of 23,620 cal./mole. Molecular weight and i.r. data suggest that the complex is completely dissociated in the vapour. A 1:1 complex between dimethylaminodifluorophosphine and B₄H₈ has also been reported recently.⁸

Hydrogen chloride cleaves the P-N bond in dimethylaminodifluorophosphine to give the dimethylammonium salt and chlorodifluorophosphine. This is a unique preparative method for the mixed halogenofluorides, previously made by the method of Booth and Bozarth.⁹ Hydrogen iodide reacts in the same way to give the iodo-compound, PF₂I. This is unstable and difficult to characterize but the decomposition products are the tri-iodide and the trifluoride. Its reactions are being further studied.

EXPERIMENTAL

Phosphorus trifluoride was prepared by fluorinating the trichloride with antimony trifluoride at 80°; dichlorofluorophosphine was prepared by the method of Booth and Bozarth.⁹ These and other reagents were purified by standard procedures. Infrared spectra were recorded with a Perkin-Elmer Infracord instrument (NaCl and KBr optics) and occasionally with a Perkin-Elmer 21 instrument (with NaCl or CsBr optics). Ultraviolet spectra were measured

⁶ Holmes and Wagner, *Inorg. Chem.*, 1963, **2**, 384; Holmes, *J. Phys. Chem.*, 1960, **64**, 1295; *J. Amer. Chem. Soc.*, 1960, **82**, 5285.

⁷ Booth and Walkup, *J. Amer. Chem. Soc.*, 1943, **65**, 2334.

⁸ Ter Haar, Fleming, and Parry, *J. Amer. Chem. Soc.*, 1962, **84**, 1767.

⁹ Booth and Bozarth, *J. Amer. Chem. Soc.*, 1939, **61**, 2927.

with a Perkin-Elmer 137 UV instrument. Nuclear magnetic resonance spectra were recorded with a Varian Associates 4300 A spectrometer equipped with a 12 in. magnet with flux stabilization and a Varian 4356 field homogeneity control unit. Proton and fluorine resonance measurements were made at 40 mc./sec. with trichlorofluoromethane and cyclohexane as internal standards. Phosphorus resonance was measured at 16.2 mc./sec. with 85% phosphoric acid as the external standard.

Reaction of Dimethylamine with Phosphorus Trifluoride.—The 1 l. reaction vessel was connected by a tap to the vacuum line; it had two cold fingers A and B, A being separated from the bulb by a tap. In a typical experiment three molecular proportions of dimethylamine were condensed in A and two molecular proportions of phosphorus trifluoride were introduced into the bulb by using the cold finger B. The contents of A were then slowly admitted to the bulb. A white precipitate formed immediately. After 2 hr. the volatile products were separated by fractional condensation at -78 and -120° . No residual phosphorus trifluoride was isolated. The condensate at -120° was dimethylaminodifluorophosphine with a small amount of dimethylamine which was removed by addition of small amounts of phosphorus trifluoride and by separation (Found: P, 27.4%; *M*, 113.0. Calc. for $C_2F_2H_6NP$: P, 27.4%; *M*, 113.0).

Vapour pressures measured over the range -10 to 40° with a mercury isoteniscope obey the equation: $\log_{10}P(\text{mm.}) = 7.609 - 1530/T$ which yields an extrapolated boiling point of 50.3° , a heat of vaporization of 7000 cal./mole, and a Trouton's constant of 21.6. The data are as follows:

<i>t</i> ($^\circ\text{C}$) ...	0.2	0.2*	5.1	11.0	15.7	20.5	20.5*	25.0	29.75	30.6*	34.85	39.9
<i>p</i> (mm.)	93.10	95.11	119.14	159.35	196.73	238.17	242.99	294.0	355.32	368.39	433.24	524.19

* Descending temperature.

The i.r. spectrum show the following peaks: 2900m, 2805sh, 1475w,br, 1308m, 1198m, 1075w, 990s, and 812vs, partially resolved *PQR*, 772vs and 700s cm.^{-1} .

Reaction of Dimethylamine with Difluorochlorophosphine.—Chlorodifluorophosphine (0.53 g., 5 mmoles) and dimethylamine (0.45 g., 10 mmoles) react immediately on contact at room temperature to give, on separation of the products, dimethylaminodifluorophosphine (*M*, 112), further characterized by its i.r. spectrum. The solid product was identified as dimethylammonia chloride by comparison of its *X*-ray powder photograph with that of an authentic sample.

Reaction of Dimethylaminodifluorophosphine with Dimethylamine.—Dimethylaminodifluorophosphine (0.640 g., 5.7 mmoles) and dimethylamine (0.487 g., 10.8 mmoles) did not react in a sealed ampoule at 20° but did react slowly at 50° . The products resulting from 1 hour's heating at 50° could not be adequately separated from the reagents by vacuum fractionation, therefore the fluorine and proton nuclear magnetic resonance spectra were used to identify bisdimethylaminofluorophosphine in the crude product.

Reaction of Dimethylaminodifluorophosphine with Boron Trifluoride.—Dimethylaminodifluorophosphine (0.150 g., 13.2 mmoles) and boron trifluoride (0.259 g., 3.81 mmoles) reacted in a sealed tube at room temperature to give a volatile solid. Fractionation of the volatile products by fractional condensation at -78 and -196° gave at -196° a mixture of phosphorus trifluoride (0.017 g., 0.19 mmole) and boron trifluoride (0.159 g., 2.36 mmoles). The latter was separated by formation of the complex with pyridine. From the measurement of the excess of reactant, the molar composition ratio of the boron trifluoride and dimethylaminodifluorophosphine complex is 1:1:1. The condensate at -78° (0.155 g.) was a volatile white solid, the vapour of which has *M*, 90.2, corresponding with an equimolar mixture of dimethylaminodifluorophosphine and boron trifluoride (*M*, 90.5). I.r. spectra also indicate that the vapour is a mixture of the two components. Small amounts of an involatile, unidentified material remain in the reaction tube indicate slight decomposition of the 1:1 complex. The dissociation pressure of the complex was measured ($4-50^\circ$) with a mercury isoteniscope; the results which are given below obeyed the equation: $\log_{10}P(\text{mm.}) = 10.80 - 2580/T$:

<i>t</i> ($^\circ\text{C}$)	3.6	9.3	15.25	22.0	27.1*	28.0	35.4*	44.2	50.5
<i>p</i> (mm.)	19.65	26.02	39.84	63.06	92.95	99.45	160.55	270.58	393.04

The normal sublimation temperature was estimated as 61° ; the heat of dissociation is 23,620 cal./mole.

A further check on the identity of the complex was made by mixing dimethylaminodifluorophosphine (0.171 g.) with excess of boron trifluoride (0.285 g.) and removing all the material volatile at -78° . It was boron trifluoride (Found: M , 67.0. Calc. for BF_3 : M , 67.9). From the total recovered (0.190 g.) the composition of the complex was deduced as $\text{Me}_2\text{N}\cdot\text{PF}_2\cdot 0.93\text{BF}_3$. Phosphorus analysis confirmed this composition (Found: P, 17.7. Calc. for $\text{C}_2\text{F}_{4.8}\text{H}_6\text{B}_{0.93}\text{NP}$: P, 17.6%).

Reaction of Dimethylaminodifluorophosphine with Hydrogen Chloride.—Dry hydrogen chloride (0.48 g., 13.3 mmoles) and dimethylaminodifluorophosphine (0.79 g., 7.0 mmoles) were allowed to react as before; a white precipitate formed immediately. Fractionation of the products gave a small amount of dimethylaminodifluorophosphine (condensed at -100°) and a small amount of phosphorus trifluoride (condensed at -196°) together with chlorodifluorophosphine (0.5 g.) (Found: M , 103.5. Calc. for PF_2Cl : M , 105.5), which was condensed at -160° . The i.r. spectrum shows characteristic peaks at 855 vs and 540 vs cm^{-1} . The P-X i.r. absorption frequencies in PX_3 are 892 for PF_3 and 507 for PCl_3 .¹⁰ The solid residue was dimethylammonium chloride (Found: Cl, 43.4. Calc. for $\text{C}_2\text{H}_5\text{NCl}$: Cl, 43.5%). The identity was confirmed by its X-ray powder photograph. Further experiments show that the reaction is not strictly stoichiometric in a sealed tube.

Reaction of Dimethylaminodifluorophosphine with Hydrogen Iodide.—Dry hydrogen iodide (8.6 mmoles) and dimethylaminodifluorophosphine (4.3 mmoles) react immediately at room temperature to give a pale yellow solid. This contained 4.8 mmoles of iodine (estimated by Andrew's method¹¹) compared with 4.3 mmoles expected for the dimethylammonium iodide formed in the reaction: $\text{Me}_2\text{NPF}_2 + 2\text{HI} \longrightarrow \text{Me}_2\text{NH}_2\text{I} + \text{PF}_2\text{I}$. An unstable volatile product, condensed in vacuum at -120° , was also obtained. It decomposed at room temperature to form phosphorus trifluoride and a red-yellow solid. The i.r. spectra showed no feature attributable to the dimethylamino-group. The u.v. absorption spectrum shows a band of medium intensity at 245 $\text{m}\mu$ as a shoulder to a strong band with a maximum below 200 $\text{m}\mu$.

This material was too unstable for the molecular weight of the vapour to be determined. A further sample was prepared from hydrogen iodide (5.1 mmoles) and dimethylaminodifluorophosphine (2.49 mmoles). The solid residue contained 2.43 mmoles of iodine (theoretical 2.49 mmoles). The -120° fraction was allowed to decompose at 20° and gave phosphorus trifluoride (1.59 mmoles) and a red solid. The latter was soluble in water and the resulting solution titrated with standard potassium iodate (Andrew's method¹¹) which oxidizes P(III) to P(V) as well as iodide. The total of 2.9 mequivs. of oxidizable material therefore corresponds to 0.74 mmole of phosphorus tri-iodide, the oxidation of phosphorus being assumed to be complete. The PF_3 : PI_3 ratio is therefore 2.2:1, in fair agreement with the ratio of 2:1 expected for decomposition of PF_2I according to the equation: $3\text{PF}_2\text{I} \longrightarrow 2\text{PF}_3 + \text{PI}_3$.

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¹⁰ Nakomoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1963.

¹¹ Vogel, "Textbook of Quantitative Inorganic Analysis," 3rd Edn., Longmans, London, 1961.