

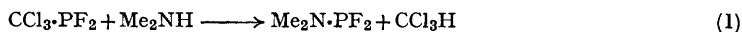
1155. Amine Substitution and Halogen Exchange Reactions of Dihalogenotrifluoromethylphosphines.

By J. F. NIXON and R. G. CAVELL.

Difluorotrifluoromethylphosphine reacts with dimethylamine to produce dimethylaminofluorotrifluoromethylphosphine, $\text{CF}_3\text{PFNMe}_2$, and bisdimethylaminotrifluoromethylphosphine, $\text{CF}_3\cdot\text{P}(\text{NMe}_2)_2$, which have been fully characterised. The latter compound has also been obtained by the direct action of excess of dimethylamine on dichlorotrifluoromethylphosphine, while dimethylaminofluorotrifluoromethylphosphine can also be obtained by the controlled aminolysis of dichlorotrifluoromethylphosphine to produce chlorodimethylaminotrifluoromethylphosphine, $\text{CF}_3\cdot\text{PClNMe}_2$, followed by fluorination with antimony trifluoride.

Hydrogen chloride reacts with $\text{CF}_3\cdot\text{P}[\text{N}(\text{Me}_2)]_2$ to regenerate $\text{CF}_3\cdot\text{PCl}_2$, while with $\text{CF}_3\cdot\text{PFN}(\text{Me})_2$ the products are $\text{CF}_3\cdot\text{PF}_2$ and $\text{CF}_3\cdot\text{PCl}_2$, resulting from disproportionation of the intermediate mixed chlorofluorophosphine, $\text{CF}_3\cdot\text{PFCl}$. N.m.r. studies show that the last-named is also formed by halogen exchange between $\text{CF}_3\cdot\text{PF}_2$ and $\text{CF}_3\cdot\text{PCl}_2$.

It has recently been shown that phosphorus trifluoride reacts readily with dimethylamine to form difluorodimethylaminophosphine.¹ This same product has also been obtained by the reaction of difluorotrichloromethylphosphine with dimethylamine,

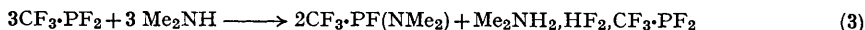


where the preferential cleavage of the phosphorus-carbon bond has been explained as arising from the stability of the intermediate trichloromethyl carbanion.² We have extended these studies, and now report that difluorotrifluoromethylphosphine, unlike its trichloromethyl analogue, is cleaved at the phosphorus-fluorine bond by dimethylamine, producing the new compounds dimethylaminofluorotrifluoromethylphosphine, $\text{CF}_3\cdot\text{PFNMe}_2$, and bisdimethylaminotrifluoromethylphosphine, $\text{CF}_3\cdot\text{P}(\text{NMe}_2)_2$.

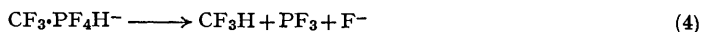
The reaction of dimethylamine with difluorotrifluoromethylphosphine does not follow the equation



as would be expected by analogy with the aminolysis of phosphorus trifluoride,¹ and excess of difluorotrifluoromethylphosphine over that required by equation (2) was not recovered. In fact difluorotrifluoromethylphosphine was recovered only if the ratio of difluorotrifluoromethylphosphine to dimethylamine was greater than 1 : 1, suggesting that the reaction follows the equation



and that the bifluoride salt complexes with difluorotrifluoromethylphosphine not consumed by reaction (2). It has been shown elsewhere that this complex is a dimethylammonium salt containing the hexaco-ordinate $\text{CF}_3\cdot\text{PF}_4\text{H}^-$ anion.³ Decomposition of such an anion could account for the very small amounts of fluoroform and phosphorus trifluoride which are also formed in the aminolysis of difluorotrifluoromethylphosphine:



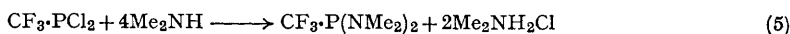
Dimethylaminofluorotrifluoromethylphosphine is a colourless liquid (b. p. 75° , extrapolated), the infrared spectrum and proton and fluorine n.m.r. spectra of which, described in the Experimental section, are entirely consistent with the formulation. It reacts further with dimethylamine to produce bisdimethylaminotrifluoromethylphosphine, $\text{CF}_3\cdot\text{P}(\text{NMe}_2)_2$, also

¹ Cavell, J., 1964, 1992.

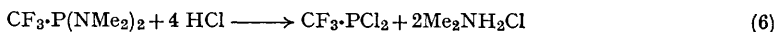
² Nixon, J., 1964, 2469.

³ Nixon and Cavell, *Proc. Chem. Soc.*, 1964, 229.

a colourless liquid (b. p. 135°, extrapolated). The latter can also be prepared in almost quantitative yield by the action of excess of dimethylamine on dichlorotrifluoromethylphosphine:



Its identity was confirmed by its infrared and proton and fluorine nuclear magnetic resonance spectra, and by the quantitative reaction with hydrogen chloride to regenerate dichlorotrifluoromethylphosphine:



When dichlorotrifluoromethylphosphine was treated with a deficiency of dimethylamine the main product (95%) was the monosubstituted compound chlorodimethylaminotrifluoromethylphosphine, $\text{CF}_3\cdot\text{PCl}(\text{NMe}_2)$, first reported by Burg and his co-workers.⁴ Fluorination of this compound with antimony trifluoride gave good yields of dimethylaminofluorotrifluoromethylphosphine, thus providing an alternative synthetic route to the direct aminolysis of difluorotrifluoromethylphosphine. No evidence for the formation of the pentavalent fluorophosphorane was observed, in accordance with the suggestion⁵ that the normal oxidative fluorination of chlorophosphines⁶ does not occur when strongly electronegative groups are attached to phosphorus.

In an attempt to prepare the chlorofluorophosphine $\text{CF}_3\cdot\text{PFCl}$, dimethylaminofluorotrifluoromethylphosphine was treated with anhydrous hydrogen chloride with immediate formation of the amine hydrochloride. In a preliminary reaction the volatiles were fractionated as soon as the reaction subsided and about 30% of each of the disproportionation products, difluorotrifluoromethylphosphine and dichlorotrifluoromethylphosphine, were recovered. In addition a fraction of intermediate volatility and molecular weight was obtained which exhibited a characteristic infrared absorption peak at 840 cm^{-1} , which was readily distinguished from the phosphorus-fluorine stretching frequency of difluorotrifluoromethylphosphine at 856 cm^{-1} . Such an absorption might be expected for the chlorofluorophosphine from a consideration of the phosphorus-fluorine infra-red stretching frequencies of related compounds listed in Table 1. A good linear relationship exists between the wavelength λ (in microns) at which the P-F absorption in PFXY compounds occurs and the sum of the electronegativities of the groups attached to phosphorus, as shown in the Figure. Values for individual atoms are taken from Pauling's tables⁷ of electronegativity while those for CF_3 (3.3) and CCl_3 (2.8) are taken from the literature.^{8,9} No previous estimate of the electronegativity of the perfluoropropyl group appears to have been made, but it is unlikely to be very different from the value for CF_3 , and a value of 3.2 leads to internal consistency for the two perfluoropropylphosphines studied.¹⁰ The value of 1.8 assigned to the electronegativity of the Me_2N groups is also self-consistent for the aminophosphines listed and obviously reflects the extent of π bonding between nitrogen and phosphorus which has previously been discussed for these systems,^{11,12} which reduces the electron density at the nitrogen atom.

The data fit the equation: $\lambda = 17.29 + 0.514[\text{sum of electronegativities of ligands}]$, thus the predicted value of λ for $\text{CF}_3\cdot\text{PClF}$, where the sum of the electronegativities of the groups attached to phosphorus is 10.3, is 12.00 μ (834 cm^{-1}), in fair agreement with the observed value of 11.90 μ (840 cm^{-1}).

The chlorofluorophosphine could not be isolated pure, for subsequent handglin in the vacuum fractionation train always led to further disproportionation into the less volatile

⁴ Burg *et al.*, W.A.D.C. Technical Report 57-126, part IV March, 1960.

⁵ Nixon, *Chem. and Ind.*, 1963, p. 1555.

⁶ Schmutzler, *Chem. and Ind.*, 1962, 1868; *Inorg. Chem.*, 1964, **3**, 410.

⁷ Pauling, "The Nature of the Chemical Bond," 3rd. edn. Cornell, Ithaca, 1960.

⁸ Lagowski, *Quart. Rev.*, 1959, **13**, 233.

⁹ Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377.

¹⁰ Nixon, *J.*, 1965, 777.

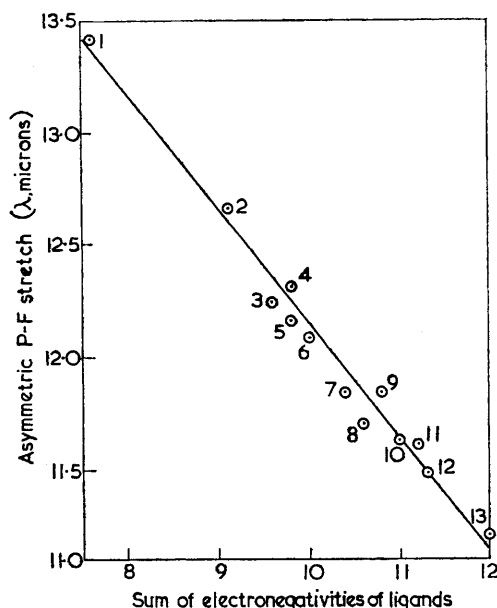
¹¹ Ewart, Payne, Porte, and Lane, *J.*, 1962, 3984.

¹² Schmutzler, *Inorg. Chem.*, 1964, **3**, 416.

TABLE I.

	Compound	Wavelength (microns)	Sum of electro- negativities of ligands	i.r. spectrum ref.
1.	(NMe ₂) ₂ PF	13.42	7.6	*
2.	CF ₃ ·PF(NMe ₂)	12.66	9.1	Present work
3.	PBr ₂ F	12.24	9.6	†
4.	(NMe ₂)PF ₂	12.31	9.8	1
5.	PBrClF	12.16	9.8	†
6.	PCl ₂ F	12.09	10.0	†
7.	(C ₃ F ₇) ₂ PF	11.84	10.4	10
8.	(CF ₃) ₂ PF	11.70	10.6	2
9.	CCl ₃ ·PF ₃	11.84	10.8	2
10.	PClF ₂	11.63	11.0	†
11.	C ₃ F ₇ ·PF ₂	11.61	11.2	10
12.	CF ₃ ·PF ₂	11.49	11.3	2
13.	PF ₃	11.21	12.0	‡

* Cf. ref. 13. † Data obtained from Raman spectrum; cf. ref. 14. ‡ Cf. ref. 15.



Comparison of asymmetric P-F stretching frequency (in microns) with the sum of the electronegativities of the ligands attached to phosphorus. The numbers refer to the compounds listed in Table I.

dichlorotrifluoromethylphosphine and more volatile difluorotrifluoromethylphosphine. Careful removal of these products appeared to induce further reorganisation of the mixed halide, and a separate experiment indicated that the rearrangement in the *absence* of the amine hydrochloride salt led to a 1:1 mixture of dichlorotrifluoromethylphosphine and difluorotrifluoromethylphosphine, but this process is still not quite complete even after two days at room temperature. Rearrangement of the mixed chlorofluorophosphine in the *presence* of the salt led to the isolation of 1.5 times the expected amount of dichlorotrifluoromethylphosphine and hardly any difluorotrifluoromethylphosphine, suggesting that the latter reacts further with the salt. This was confirmed by the reaction of difluorotrifluoromethylphosphine with dimethylammonium chloride in a sealed tube, to give a mixture of dichlorotrifluoromethylphosphine, difluorotrifluoromethylphosphine, and chlorofluorotrifluoromethylphosphine, all identified by i.r. and ¹⁹F n.m.r. spectroscopy. This is the first

¹³ Fleming, Ph.D. thesis, University of Michigan, 1962.

¹⁴ Delwaille and Francois, *J. Chim. phys.*, 1949, **46**, 87; Francois and Delwaille, *ibid.*, p. 80.

¹⁵ Gutowsky and Liehr, *J. Chem. Phys.*, 1952, **20**, 1652.

example of a reversal of the normal halogen displacement series¹⁶ and is unexpected in view of previous reports of the fluorination of phosphorus halides with ammonium fluoride.¹⁷

Fluorine n.m.r. studies on a 1:1 mixture of dichlorotrifluoromethylphosphine and difluorotrifluoromethylphosphine at room temperature showed initially no indication of the chlorofluorophosphine; however, after 18 hours at 60°, the spectrum clearly showed the presence of the chlorofluorophosphine, indicating that halogen exchange had occurred. Similar exchange reactions involving mixed trihalides of phosphorus are already well known.¹⁸

EXPERIMENTAL

Di-iodotrifluoromethylphosphine was prepared from trifluoromethyl iodide and red phosphorus¹⁹ and purified by vacuum fractionation. Difluorotrifluoromethylphosphine was prepared from the corresponding di-iodophosphine by reaction with antimony trifluoride in a sealed tube at 60° and characterised by its i.r. spectrum and molecular weight (Found: *M*, 139. Calc. for CF₅P: *M*, 138). Dichlorotrifluoromethylphosphine was conveniently prepared from the di-iodo-compound by reaction with mercuric chloride in a sealed tube at room temperature, a reaction which was complete in about 1 hr. in contrast with the slower silver chloride reaction,¹⁹ and was also characterised by its i.r. spectrum and molecular weight (Found: *M*, 173. Calc. for CCl₂F₃P: *M*, 171). Other reagents were purified before use by standard vacuum techniques.

Reaction of Difluorotrifluoromethylphosphine with a Deficiency of Dimethylamine.—The reaction was done in the gas phase in a reactor which consisted of a one-litre bulb with two cold fingers, A and B, one of which (B) was separated from the bulb by a tap. With difluorotrifluoromethylphosphine (0.812 g., 5.88 mmoles) in the bulb, dimethylamine (0.313 g., 6.95 mmoles) was slowly admitted from cold finger B by means of the tap. A white solid formed immediately on contact of the two vapours. After 2 hr. at room temperature the volatile materials were removed into the vacuum line and fractionated, leaving a yellow-white solid residue in the bulb. All the volatile materials passed a -45° bath and the main fraction was identified as *dimethylaminofluorotrifluoromethylphosphine* [Found: CF₃(as CF₃H), 42.55; (CH₃)₂N (as base), 26.0; P, 18.6%; *M*, 163.2. C₃H₆F₄NP requires CF₃, 42.25; (CH₃)₂N, 27.0; P, 19.0%; *M*, 163.0]. Analysis was carried out by heating a known amount of material with alkali (N; 5 ml.) at 80° for 2 days in a sealed tube. The volatile materials were fractionated in a vacuum, CF₃H was separated and the remainder of the volatile materials, a mixture of dimethylamine and water, was distilled into a known amount of standard hydrochloric acid and the excess of acid back-titrated against standard alkali.

The yield was 0.622 g. (4.11 mmoles) or 91% of the amount expected according to the equation (2). More volatile material (0.0430 g.) which was collected at -196° was shown by molecular weight and i.r. spectroscopy to be a mixture of 0.22 mmole of trifluoromethane and 0.32 mmole of phosphorus trifluoride. No unchanged difluorotrifluoromethylphosphine was recovered in spite of the excess of 1.24 mmoles over that required by equation (2). Hydrolysis of the off-white solid remaining in the bulb with normal alkali liberated 1.5 mmoles of trifluoromethane, identified by its molecular weight and i.r. spectrum, representing 97% of the deficiency of trifluoromethyl groups of 1.54 mmoles between the recovered volatile products containing trifluoromethyl groups and the initial amount of difluorotrifluoromethylphosphine taken. Analysis of the resulting solution showed that the solid residues also contained 1.57 mmoles of phosphorus.

In a second experiment, difluorotrifluoromethylphosphine (0.546 g., 3.95 mmoles) was treated in the same apparatus with a deficiency of dimethylamine (0.1345 g., 2.99 mmoles). As before, an off-white solid formed immediately on mixing the reagents and a yield of 1.90 mmoles (0.309 g.) of dimethylaminofluorotrifluoromethylphosphine was obtained. A more volatile fraction (0.154 g.) contained an inseparable mixture of phosphorus trifluoride, fluoroform, and unchanged difluorotrifluoromethylphosphine which was found to contain about 0.9 mmole (0.13 g.) of difluorotrifluoromethylphosphine by hydrolysis, suggesting that the reaction obeys the stoichiometry represented in equation (3).

The solid residues were hygroscopic but could be safely handled in the dry-box. Infrared spectra of the solid as a Nujol mull and in acetonitrile solution showed the characteristic dimethylammonium ion absorption frequencies at 3300 and 1025 cm.⁻¹, strong bands at 1210 and 1130 which can

¹⁶ Eaborn, "Organosilicon Compounds," Butterworths, London, 1960, p. 174.

¹⁷ Wilkins, *J.*, 1951, 2726.

¹⁸ Payne, *Quart. Rev.*, 1961, 15, 173.

¹⁹ Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565.

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be attributed to CF absorptions, and a strong band at 775 cm.^{-1} which may be due to P-F. The ^{19}F and ^1H n.m.r. spectra of the salt in acetonitrile solution have been described elsewhere.³ The acetonitrile solution appeared to be quite stable, and no volatile trifluoromethyl-containing species were evolved.

Measurement of the vapour pressure of dimethylaminofluorotrifluoromethylphosphine in the range $0\text{--}55^\circ$ resulted in the following values:

Temp. ($^\circ\text{C}$)	0.1	6.6	12.3	17.4	22.3	27.3	32.9	37.9	43.8	47.6	54.5	25.0
P mm.	28.14	40.73	55.29	71.00	90.42	113.88	146.70	181.67	232.26	271.57	352.15	104.54

The data are well represented by the equation:

$$\log_{10}P\text{ (mm.)} = 8.024 - 1794/T$$

which leads to a calculated boiling point of 75.5° , $\Delta H_{\text{vap}} = 8210\text{ cal./mole}$, and a Trouton's constant of 23.6.

Reaction of Dimethylaminofluorotrifluoromethylphosphine with Dimethylamine.—Dimethylaminofluorotrifluoromethylphosphine (1.631 mmoles) and dimethylamine (2.266 mmoles) were sealed and warmed slowly to room temperature. Solid was deposited when the mixture was set aside. After 2 hr. at room temperature the volatile products were fractionated *in vacuo* producing 1.182 mmoles bisdimethylaminotrifluoromethylphosphine, $\text{CF}_3\text{-P}(\text{NMe}_2)_2$, which was trapped out at -45° . The more volatile material which passed -78° was shown to be unchanged dimethylamine (0.0146 g., 0.32 mmole) and trifluoromethane (0.0102 g., 0.14 mmole), the latter identified by its i.r. spectrum. No dimethylaminofluorotrifluoromethylphosphine was recovered, although a small excess was taken; the excess may have been adsorbed on the bifluoride salt.

Reaction of Dichlorotrifluoromethylphosphine with Excess of Dimethylamine.—Dichlorotrifluoromethylphosphine (2.578 mmoles) and dimethylamine (10.240 mmoles) were mixed and warmed to room temperature in a sealed tube; a white solid was produced. After two days the volatiles were fractionated *in vacuo*, producing 2.436 mmoles of bisdimethylaminotrifluoromethylphosphine (melting point -39.9° to -39.4°) collected at -45° , the vapour pressure and i.r. spectrum of which were identical with those of the sample prepared from the aminolysis of dimethylaminofluorotrifluoromethylphosphine. Analysis was carried out by heating bisdimethylaminotrifluoromethylphosphine with alkali (N; 5 ml.) at 80° for 8 days. The volatile material was subjected to high-vacuum fractionation, trifluoromethane was separated, and amine determined as before [Found: CF_3 (as CF_3H), 35.6; Me_2N (as base), 44.9; P, 16.4. $\text{C}_5\text{F}_3\text{H}_{12}\text{N}_2\text{P}$ requires CF_3 , 36.7; Me_2N , 46.8; P, 16.5%].

The vapour pressure was measured over the range $0\text{--}78^\circ$. The data, which are shown below, were fitted to the Nernst equation

$$\log_{10}P\text{ (mm.)} = 6.766 + 1.75 \log T - 0.005 T - 2618/T$$

to give an extrapolated boiling point of 135° , $\Delta H_{\text{vap}} = 9430\text{ cal./mole}$, and Trouton constant of 23.1.

Temp. ($^\circ\text{C}$)	0.0	22.3	36.0	44.8	54.0	63.0	77.6
P mm. (measured)	1.45	5.65	13.0	21.1	34.5	52.9	100.7
P mm. (calc.)	1.22	5.65	13.0	21.0	34.0	52.8	101.0

Reaction of Bisdimethylaminotrifluoromethylphosphine with Hydrogen Chloride.—Bisdimethylaminotrifluoromethylphosphine (0.2109 g., 1.122 mmoles) was sealed with excess of hydrogen chloride (0.2310 g., 6.336 mmoles), and the mixture slowly warmed to room temperature. Reaction occurred readily, a white solid being formed. Vacuum fractionation of the volatile products led to the recovery of hydrogen chloride (1.770 mmoles) identified by its volatility and molecular weight (Found: 37.3. Calc. for HCl : 36.5) and dichlorotrifluoromethylphosphine (1.123 mmoles) identified by its molecular weight (Found: 170.3. Calc. for $\text{CCl}_2\text{F}_3\text{P}$: 170.9) and its i.r. spectrum. The combining ratio, calculated from the above data, of bisdimethylamino-compound with hydrogen chloride of 1:4.07 and the yield of dichlorotrifluoromethylphosphine of 100% are in excellent accord with the requirements of equation (6), thus providing further confirmation of the identity of the bisdimethylamino-compound.

Synthesis of Chlorodimethylaminotrifluoromethylphosphine.—Dichlorotrifluoromethylphosphine (3.938 mmoles) and a deliberate deficiency of the required ratio of 1:2 of dimethylamine (7.041 mmoles) were sealed together *in vacuo* and warmed to room temperature; immediate formation of a white solid was observed. Fractionation of the volatile products led to the recovery

of 0.434 mmole unchanged dichlorotrifluoromethylphosphine and a colourless liquid, which passed a trap at -36° but stopped at -45° , and which was identified as chlorodimethylaminotrifluoromethylphosphine (3.373 mmoles, 95.7% yield) by its vapour pressure (18.0 mm. at 20° , 5.5 mm. at 0°), which was identical with previously reported values,⁴ and molecular weight (Found: 182.5. Calc. for $C_3ClF_3H_6NP$: 179.5). There was no formation of bisdimethylaminotrifluoromethylphosphine. The identity of the chlorophosphine was confirmed by analysis [Found: CF_3 (as CF_3H), 38.0; P, 17.6; Cl, 19.65. Calc. for $C_3ClF_3H_6NP$: CF_3 , 38.4; P, 17.3; Cl, 19.75%].

Fluorination of Chlorodimethylaminotrifluoromethylphosphine.—In a sealed tube 2.16 mmoles of $CF_3 \cdot PCl(NMe_2)$ were heated at 60° with an excess of antimony trifluoride for 3 hr. The antimony trifluoride turned black. Fractionation of the volatiles led to the recovery of 1.815 mmoles of dimethylaminofluorotrifluoromethylphosphine (84% yield) which was identified by its i.r. spectrum, molecular weight (Found: 164. Calc. for $C_3F_4H_6NP$: 163), and vapour pressure (28.0 mm. at 0°) which was identical with the vapour pressure of the analysed specimen prepared earlier. No unchanged chlorophosphine was recovered, and about 0.1 mmole of very volatile material which may have been $CF_3 \cdot PF_2$ was recovered.

Reaction of Dimethylaminofluorotrifluoromethylphosphine with Hydrogen Chloride.—Hydrogen chloride gas (0.160 g., 4.40 mmoles) was admitted slowly from cold finger B to 0.329 g. (2.02 mmoles) of dimethylaminofluorotrifluoromethylphosphine in the gas-phase reactor described above. A white solid was formed immediately on contact. After $\frac{1}{2}$ hr. at room temperature the volatiles were taken into the vacuum line and fractionated, leaving a white solid residue, which contained 2.01 mmoles of chloride, in the bulb. All the volatile materials passed a trap at -78° (showing that all the aminophosphine had been consumed) and 0.233 g. of material (M , 158.5) was collected at -126° (Calc. for $CClF_4P$, 154.5; for CCl_2F_3P , 171). Immediate distillation of this material from -96° yielded 0.32 mmole of dichlorotrifluoromethylphosphine remaining at -96° (Found: M , 175. Calc. for CCl_2F_3P : 171) and 1.16 mmoles of material which volatilised from -96° . The molecular weight suggested that the volatile material was a mixture of chlorofluorotrifluoromethylphosphine and difluorotrifluoromethylphosphine (Found: M , 148. Calc. for CF_5P : 138; for $CClF_4P$: 154.5) and the i.r. spectrum showed a new peak at 840 cm.^{-1} —which was distinct from the PF vibration in $CF_3 \cdot PF_2$. At -131° difluorotrifluoromethylphosphine (0.0607 g., 0.44 mmole) was collected (Found: M , 138. Calc. for CF_5P : 138) and at -196° a mixture of approximately 0.12 mmole of difluorotrifluoromethylphosphine and 0.23 mmole of hydrogen chloride with traces of PF_3 and SiF_4 was collected. The total volatile material recovered amounted to 0.3145 g. or 97% of that expected for 2.02 mmoles chlorofluorotrifluoromethylphosphine (0.3120 g.) and 0.36 mmole excess of hydrogen chloride (0.0132 g.). Repeated fractionation of the material volatilised from -96° did not yield pure $CF_3 \cdot PFCl$ because removal of the dichlorotrifluoromethylphosphine and difluorotrifluoromethylphosphine appeared to induce further reorganisation of the mixed halide. The remaining volatile material was allowed to rearrange at room temperature for 24 hr. and refractionated. Only $CF_3 \cdot PF_2$ and $CF_3 \cdot PCl_2$ were obtained although there still appeared to be trace amounts of $CF_3 \cdot PFCl$. Only 80% of the volatile material was recovered on refractionation—probably because of the handling losses in the repeated fractionations.

In a second experiment hydrogen chloride (0.157 g., 4.3 mmoles) and dimethylaminofluorotrifluoromethylphosphine (0.274 g., 1.68 mmoles) were combined in a sealed tube and maintained at room temperature for 3 days allowing the chlorofluorophosphine formed by cleavage by hydrogen chloride to rearrange in the presence of the solid dimethylammonium chloride residue. Fractionation yielded $CF_3 \cdot PCl_2$ (0.210 g. 1.23 mmoles) identified by its molecular weight (Found: M , 169. Calc. for CCl_2F_3P : 171) containing a trace of $CF_3 \cdot PFCl$ identified by its i.r. spectrum. A small amount of very volatile material (0.03 g.) was collected at -196° and identified as principally hydrogen chloride with difluorotrifluoromethylphosphine and silicon tetrafluoride impurities (M , 46. Calc. for HCl : 36.5) as indicated by the i.r. spectrum. The residue of dimethylammonium chloride remaining in the tube was hydrolysed with water and yielded trifluoromethane (0.342 mmole) or 75% of the CF_3 deficiency. The residues also contained phosphorus (0.43 mmole) or 95.5% of the deficiency of phosphorus in the volatile material from the expected amount. The difference in trifluoromethyl and phosphorus recovery may be due to incomplete hydrolysis of the residues in water, as strong alkali is frequently necessary for complete hydrolysis.⁸

In a third experiment 1.541 mmoles of dimethylaminofluorotrifluoromethylphosphine were treated with 3.017 mmoles of hydrogen chloride in a sealed tube at room temperature with immediate formation of a white solid as before. After $\frac{1}{2}$ hr., the volatiles were removed to a second tube and left for 2 days. The volatile products were found to be dichlorotrifluoromethylphosphine

(0.636 mmole), identified by its molecular weight (Found: M , 171.6. Calc. for CF_3PCl_2 : M , 171) and its i.r. spectrum, and difluorotrifluoromethylphosphine (0.657 mmole) similarly identified (Found: M , 137.5. Calc. for CF_3PF_2 : 138.0). In addition there was 25.8 mg. of a liquid, which exhibited a strong i.r. absorption at 840 cm.^{-1} , and which on standing gave further amounts of difluorotrifluoromethylphosphine and may have been the mixed chlorofluorophosphine.

Reaction of Difluorotrifluoromethylphosphine with Dimethylammonium Chloride.—Dimethylammonium chloride was prepared from hydrogen chloride (0.145 g., 3.975 mmoles) and dimethylamine (0.1074 g., 2.386 mmoles) in a sealed tube at room temperature. The excess of hydrogen chloride was removed and difluorotrifluoromethylphosphine (0.2239 g., 1.622 mmoles) was added to the salt and the tube resealed. After 24 days at room temperature fractionation of the products yielded difluorotrifluoromethylphosphine (0.0634 g.), identified by its i.r. spectrum, and 0.0545 g. of a mixture of chlorofluorotrifluoromethylphosphine and dichlorotrifluoromethylphosphine, the former exhibiting the characteristic P–F stretching frequency at 840 cm.^{-1} . Absolute confirmation of the identity of $\text{CF}_3\text{-PF}_2$ and $\text{CF}_3\text{-PCl}_2$ was ^{19}F n.m.r. of the volatile material, the chemical shifts and coupling constants being identical with those of authentic samples.¹⁰ The spectrum also showed absorptions which are consistent with the presence of chlorofluorotrifluoromethylphosphine (see n.m.r. data).

Halogen Exchange Reaction of Difluorotrifluoromethylphosphine and Dichlorotrifluoromethylphosphine.—An equimolar mixture, measured by gas volume, of dichlorotrifluoromethylphosphine and difluorotrifluoromethylphosphine was combined in an n.m.r. tube. Measurement of the ^{19}F n.m.r. spectrum at room temperature immediately after mixing showed only the two parent compounds but subsequent heating to 60° for 18 hours produced weak extra peaks in positions identical with those attributed to chlorofluorotrifluoromethylphosphine.

Nuclear Magnetic Resonance Spectra.—The ^{19}F and ^1H n.m.r. spectra were recorded at 40 Mc./sec. using a Varian V-4300 n.m.r. spectrometer and 12 in. electromagnet, with flux stabilization and a field homogeneity control unit. Measurements were made on the pure liquids sealed under vacuum into Pyrex tubes (5 mm. o.d.) together with fluorotrichloromethane and cyclohexane as internal standards. The samples were spun in the magnetic field, and the spectra calibrated by the normal sideband technique. The values quoted in Table 2 are the average of several determinations.

TABLE 2.

	$\text{CF}_3\text{-PF}(\text{NMe}_2)$	$\text{CF}_3\text{-P}(\text{NMe}_2)_2$	$\text{CF}_3\text{-PClF}$
Chemical shifts (in p.p.m.)			
^1H (τ)	7.13	7.24	—
ϕCF_3 (vs. CCl_3F)	+70.6	+62.0	+76.1
ϕF (vs. CCl_3F)	+134.3	—	+144.0
Coupling constants (c./sec.)			
J_{PH}^a	9.01	9.27	—
J_{FH}^a	5.6	—	—
$J_{\text{CF}_3\text{-H}}^a$	0.71	0.70	—
$J_{\text{CF}_3\text{-F}}^b$	0.69	0.7	—
$J_{\text{P-F}}^b$	1010	—	1178
$J_{\text{P-CF}_3}^b$	86.7	87.4	84.6
$J_{\text{CF}_3\text{-F}}^b$	~2–3	—	Not obs.

^a Derived from ^1H spectra. ^b Derived from ^{19}F spectra.

(a) *Proton spectra.* (i) *Dimethylamino fluorotrifluoromethylphosphine.* The spectrum consisted of two doublets of quartets, the doublets arising from spin-spin coupling of the protons with phosphorus and the fluorine attached to phosphorus. Each line of the doublets was split into the quartet structure by coupling of the protons with the three equivalent fluorine atoms of the trifluoromethyl group.

(ii) *Bisdimehylaminotrifluoromethylphosphine.* The spectrum consisted of a doublet arising from spin coupling with the phosphorus nucleus, with each line of the doublet split further into a quartet by the three fluorine atoms of the trifluoromethyl group.

(b) *Fluorine n.m.r. spectra.* (i) *Dimethylamino fluorotrifluoromethylphosphine.* The ^{19}F spectrum shows two types of fluorine in approximate intensity ratio 3:1. The CF_3 resonance was a doublet which exhibited multiplet fine structure presumably arising from two overlapping septets. The observed $J_{\text{F-H}}$ coupling constant of 0.69 c./sec. was close to that obtained from the proton

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spectrum and the J_{F-F} coupling constant was estimated from the width of the absorption band to be about 2—3 c./sec.

The resonance of the fluorine atom attached directly to phosphorus occurred at higher field as a doublet. Further coupling was apparent but was not resolved.

(i) *Bisdimethylaminotrifluoromethylphosphine*. The ^{19}F n.m.r. spectrum showed the expected doublet arising from the interaction of the fluorine nuclei with phosphorus. Each peak of the doublet showed further multiplet structure with spacing of 0.7 c./sec. arising from interaction of the fluorine with twelve equivalent protons of the methyl groups. The coupling constant is in good agreement with that obtained from p.m.r.

(iii) *Chlorofluorotrifluoromethylphosphine*. The ^{19}F n.m.r. spectrum showed the presence of two types of fluorine in approximate ratio 3:1. The CF_3 resonance was a doublet which lay between the CF_2 resonances of dichlorotrifluoromethylphosphine and difluorotrifluoromethylphosphine. The fluorine-fluorine coupling was not resolved. The resonance of the fluorine directly attached to phosphorus occurred at higher field than that of difluorotrifluoromethylphosphine, also as a doublet with indications of further splitting. The data are given in Table 2.

Infrared Spectra.—The spectra of the gaseous compounds were recorded on a Perkin-Elmer Infracord spectrometer, and the data are given in Table 3.

TABLE 3.

$CF_3 \cdot P(NMe_2)_2$		$CF_3 \cdot PF(NMe_2)$
2890 (m) } 2795 (sh) }	C-H str	{ 2940 (m) 2830 (sh)
1458 (w) } 1280 (m) }	C-H bend	{ 1490 (sh) 1460 (w) 1305 (s)
1176 (s) } 1124 (s) } 1105 (s) }	C-F str	{ 1200 (vs) 1130 (vs)
980 (s)	N-(CH ₃) rock wag.	{ 1070 (w) 1005 (vs)
	P-F str	790 (vs)
694 (m)	{ C-F bend } { P-C str? }	702 (ms)

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