Chemistry of phosphorus fluorides. Part III. The reaction of thiophosphorylfluoride with dimethylamine and some properties of the dimethylaminothiophosphoryl fluorides[1]

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Dimethylamine reacts with thiophosphoryl fluoride with non-integral stoichiometry to yield the volatile compound dimethylaminothiophosphoryldifluoride and the solid products contained hexafluorophosphate and difluorodithiophosphate ions, and an unstable complex ion containing phosphorus and fluorine. The reaction of dimethylaminothiophosphoryldifluoride with dimethylamine to form bis-(dimethylamino)thiophosphorylfluoride has also been studied. The solid residues of this reaction contained hexafluorophosphate and difluorodithiophosphate ions and an unidentified phosphorus-fluoride salt. Dimethylaminothiophosphoryldifluoride did not complex with boron trifluoride but reacted with hydrogen halides to yield the halogenothiophosphoryldifluorides. Physical and spectroscopic data on the alkylaminothiophosphoryl fluorides are reported.

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Introduction

A variety of alkyl- and aryl-aminothiophosphoryl fluorides have been prepared from the appropriate amine and either thiophosphorylfluoride or monochlorothiophosphoryldifluoride (2, 3). In all cases the reactions were done in a solvent and were presumed to follow the equation

$$\text{[I]}\quad SPF_3 + 2R_2NH \rightarrow SPF_2{\cdot}NR_2 + R_2NH_2{}^+F^-,$$

analogous to the behavior of phosphorus chlorides (4). Our previous studies have shown that the aminolysis reactions of phosphorus fluorides are not simple analogues of the chloride reactions; for example dimethylamine reacts with phosphorus trifluoride to yield the *bifluoride* rather than the fluoride salt (5),

$$\text{[II]}\quad 2PF_3 + 3(CH_3)_2NH \rightarrow 2(CH_3)_2NPF_2 + (CH_3)_2\overset{+}{N}H_2{\cdot}H\overset{-}{F}_2,$$

and with phosphoryl fluoride (1) to yield the hexafluorophosphate and difluorophosphate salts according to the equation

$$\text{[III]}\quad 4POF_3 + 4(CH_3)_2NH \rightarrow 2(CH_3)_2NP(O)F_2 + (CH_3)_2\overset{+}{N}H_2{\cdot}P\overset{-}{F}_6 + (CH_3)_2\overset{+}{N}H_2{\cdot}PO_2\overset{-}{F}_2.$$

The reaction of thiophosphoryl fluoride with dimethylamine is also complex.

Results and Discussion

The Aminolysis of Thiophosphoryl Fluoride

In accord with the behavior of phosphoryl fluoride, gaseous thiophosphoryl fluoride reacted immediately and exothermally on contact with dimethylamine to form a white solid and volatile dimethylaminothiophosphoryldifluoride. Instead of the equimolar stoichiometry observed (1) in the case of phosphoryl fluoride however, 1.3 moles of dimethylamine reacted with each mole of thiophosphoryl fluoride. Although this stoichiometry is close to that expected for the formation of bifluoride ion according to eq. [IV],

$$\text{[IV]}\quad 2SPF_3 + 3(CH_3)_2NH \rightarrow 2SPF_2{\cdot}N(CH_3)_2 + (CH_3)_2\overset{+}{N}H_2{\cdot}H\overset{-}{F}_2,$$

the reaction is considerably more complicated. Small amounts of hydrogen sulfide were also recovered in the volatile products.

In the simplest case (illustrated in Fig. 1*b*) the residues were found to contain the difluorodithiophosphate (A) and hexafluorophosphate (C) ions, identified by comparison of the measured fluorine nuclear magnetic resonance (n.m.r.) parameters (Table I) with the literature (6, 7). Also present in the spectra were two broad singlets (E, G) which may be due to fluoride or bifluoride ions or both.

The principal reaction therefore appears to be the analogue of the aminolysis of phosphoryl fluoride (1).

$$\text{[V]}\quad 4(CH_3)_2NH + 4SPF_3 \rightarrow 2(CH_3)_2NP(S)F_2 + (CH_3)_2\overset{+}{N}H_2{\cdot}PF_6^- + (CH_3)_2\overset{+}{N}H_2{\cdot}PS_2F_2^-.$$

Secondary reactions and decompositions may account for the observed non-integral stoichiometry. For example, the observed hydrogen sulfide

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[1] Part II: ref. 1.

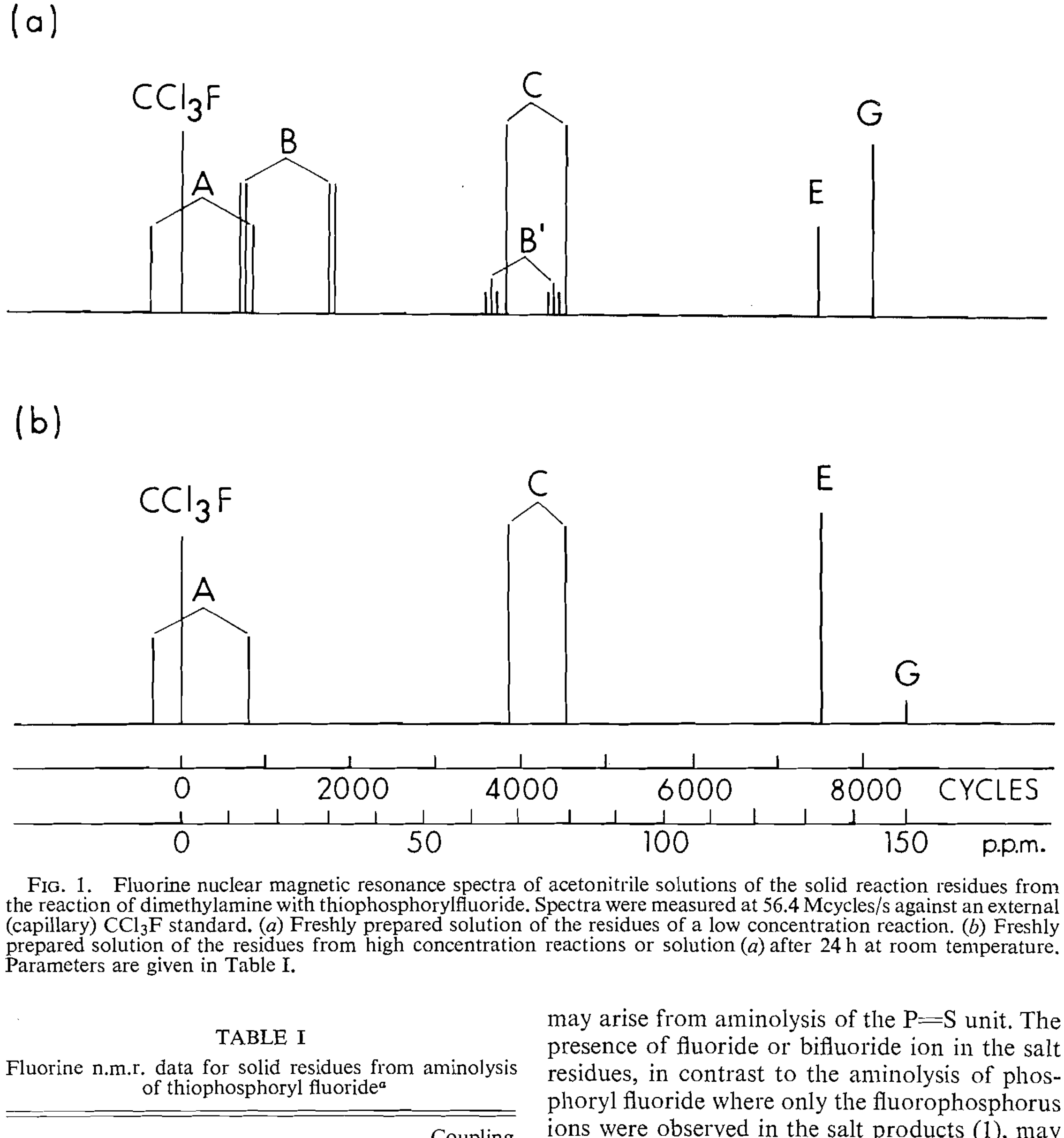


FIG. 1. Fluorine nuclear magnetic resonance spectra of acetonitrile solutions of the solid reaction residues from the reaction of dimethylamine with thiophosphorylfluoride. Spectra were measured at 56.4 Mcycles/s against an external (capillary) CCl_3F standard. (*a*) Freshly prepared solution of the residues of a low concentration reaction. (*b*) Freshly prepared solution of the residues from high concentration reactions or solution (*a*) after 24 h at room temperature. Parameters are given in Table I.

TABLE I

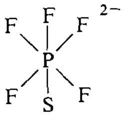
Fluorine n.m.r. data for solid residues from aminolysis of thiophosphoryl fluoride[a]

Line	Description	Chemical shift ϕ (p.p.m. vs. CCl_3F)	Coupling constants (cycles) J_{P-F}	J_{FF}
A	Doublet	+4.3	1146[c]	—
B	Pair of doublets	+22.0	909	48
B′	Pair of quintets[b]	+71.0	718	47
C	Doublet	+73.0	707[d]	—
E	Singlet	+132	—	—
G	Singlet	+148 (±5)	—	—

[a] Spectra illustrated in Fig. 1.
[b] Only three central lines of quintet (intensity 1:1.5:1) observed.
[c] $S_2PF_2^-$, see ref. 7.
[d] PF_6^-, see ref. 6.

may arise from aminolysis of the P=S unit. The presence of fluoride or bifluoride ion in the salt residues, in contrast to the aminolysis of phosphoryl fluoride where only the fluorophosphorus ions were observed in the salt products (1), may indicate incomplete formation of the phosphorus-fluoride complex ions or decomposition.

If the reaction was done under conditions of low reagent concentration, the residues contained, as illustrated in Fig. 1*a*, another species in addition to those already identified above. The multiplet patterns (B, B′) are assigned to a single species because of the similarity of the small splitting within the individual parts of the multiplet and because the whole multiplet disappears simultaneously when the solution is aged. The spectrum of the solution reverted to that illustrated in Fig. 1*b* upon aging and a black precipitate was formed. The species appears to be decomposing rather than reacting with the solvent because dry reaction residues, which initially gave the spectrum shown in Fig. 1*a*, decomposed slowly at room temperatures to form hydrogen sulfide and dimethylamine and the residues remaining after decomposition gave the simple spectrum shown in Fig. 1*b*. The observed n.m.r. parameters of the B–B′ multiplet are not consistent with any known phosphorus-fluorine species. They cannot be assigned to any species containing P—H or P—$N(CH_3)_2$ functions because the hydrogen n.m.r. spectra showed only the resonances of the dimethylammonium cation. All of the line spacings are regular so the spectrum is probably first order. The B′ component is best regarded as a doublet of quintets in view of the 1:1.5:1 intensity ratio of the three lines in each half, which is in better agreement with the expected 4:6:4 intensity ratio for the three central lines of a quintet than with the 1:2:1 intensity ratio expected for a triplet. We suggest that the spectrum arises from the hexacoordinate SPF_5^{2-} ion with the structure



in which the doublet of doublets (B) is due to the equatorial fluorine atoms (F_e) split into a doublet by the phosphorus ($J(P—F_e)$ = 909 cycles) further split by the single axial fluorine atom (F_a) ($J(F_a—F_e)$ = 48 cycles) and the pair of quintets (B′) is due to the resonance of the single axial fluorine atom split by phosphorus ($J(P—F_a)$ = 718 cycles) further split into a quintet by four equivalent equatorial fluorine atoms ($J(F_a—F_e)$ = 47 cycles). These values of axial–equatorial fluorine coupling and the two P—F coupling constants are similar to those reported (8) for the substituted fluorophosphates $CH_3PF_5^-$ and $C_6H_5PF_5^-$. Conclusive assignment of the spectrum is not possible in view of the approximate nature of our intensity data. The pentacoordinate SPF_4^- ion is a likely alternative although recent studies suggest that this would probably show only a simple doublet due to the 'pseudorotation' averaging process (9) rather than a resolved multiplet.

The unstable complex fluorophosphorus anion was obtained only under conditions of low reagent concentration probably because the exothermicity of the reaction can be dissipated effectively under these conditions. The complex ion may be a thermally unstable intermediate which eventually decomposes to hexafluorophosphate and difluorodithiophosphate ions.

[VI] $$2SPF_5^{2-} \rightarrow S_2PF_2^- + PF_6^- + 2F^-$$

It seems reasonable to suggest that the aminolysis reaction proceeds through the formation of dimethylammonium fluoride or bifluoride by means of an initial acid–base association of thiophosphoryl fluoride with dimethylamine followed by elimination of hydrogen fluoride from the complex. The complex fluorophosphate ions may be formed in a second step involving reaction between the fluorophosphorus compound and fluoride or bifluoride ion. In the former case the SPF_4^- ion would be a likely intermediate analogous to our previous suggestion (1) of the POF_4^- ion as the intermediate ion in the aminolysis of phosphoryl fluoride. The latter case could lead to an ion such as SPF_5^{2-}, e.g.

[VII] $$SPF_3{\cdot}(CH_3)_2NH + (CH_3)_2\overset{+}{N}H_2{\cdot}HF_2^- \rightarrow [(CH_3)_2NH_2]_2{\cdot}SPF_5^{2-}.$$

Fluoride salts have been reported to react with thiophosphoryl fluoride (see footnote in ref. 10) to yield the difluorodithiophosphate and hexafluorophosphate ions but the intermediates are unknown. In the present case the intermediate *may* have been identified by the n.m.r. spectrum but further studies must be undertaken before a definite conclusion can be reached.

The aminolysis of dimethylaminothiophosphoryldifluoride proceeds slowly, with *equimolar* stoichiometry, in contrast to the rapid spontaneous reaction of thiophosphoryl fluoride. Similar behavior has been observed in the aminolysis of dimethylamino-phosphoryldifluoride (1) and -difluorophosphine (5) and can be attributed to the increased basicity of the dimethylamino derivatives which inhibits the reaction by retarding the formation of the primary acid–base adduct of the phosphorus fluoride with the amine.

The stoichiometry of the aminolysis is equimolar as in the case of the phosphoryl analogue (1) and the principal residual ions, identified by comparison of the fluorine n.m.r. parameters

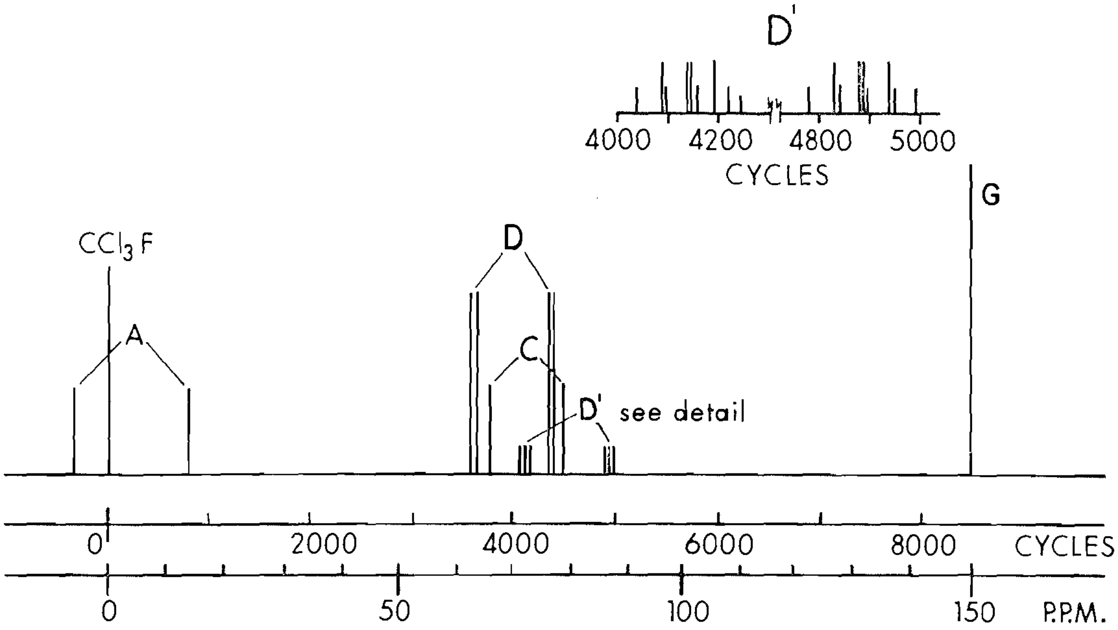


FIG. 2. Fluorine nuclear magnetic resonance spectrum, measured at 56.4 Mcycles/s, of an acetonitrile solution of the solid residues resulting from the reaction of dimethylamine with dimethylaminothiophosphoryldifluoride. Parameters are given in Table III.

obtained on the residues (Fig. 2 and Table II) with the literature (6, 7), are the analogous difluorodithiophosphate (A), hexafluorophosphate (C), and either fluoride or bifluoride (G) ions. In addition, however, a complex multiplet (D, D') was observed which did not decompose over an extended period of time. As before the hydrogen n.m.r. spectra show only the resonances due to the dimethylammonium cation so species containing P—N$(CH_3)_2$ and P—H functions can be excluded as well as all known fluorophosphorus anions. Since the spectrum appears to be second order we cannot assign a structure to the multiplet without additional information although the line spacing is reminiscent of the hexacoordinate RPF_5^- ions (8).

TABLE II

Fluorine n.m.r. data for solid residues from aminolysis of dimethylaminophosphoryl fluoride[a]

Line	Description	Chemical shift ϕ (p.p.m. vs. CCl_3F)	Coupling constants (cycles) J_{P-F}	J_{FF}
A	Doublet	+4.0	1150[b]	—
C	Doublet	+73.0	708[c]	—
D	Pair of doublets	+70.9	796	52
D'	Complex multiplet[d]	+79.0	740?[e]	?[d]
G	Broad, single line	+150	—	—

[a] Spectrum illustrated in Fig. 2.
[b] $S_2PF_2^-$, see ref. 7.
[c] PF_6^-, see ref. 6.
[d] Apparently second order since the spacing between adjacent lines is irregular.
[e] A constant separation of 740 cycles is observed between each corresponding line in the two halves of the D' doublet.

It is somewhat surprising that unusual complex ions have been observed only in the aminolysis of the thiophosphoryl compounds and not the phosphoryl compounds, suggesting that species formed in the thiophosphoryl system are more stable. Conclusive identification of the species which give rise to the B–B' and D–D' multiplets is necessary before complete understanding of this system can be achieved.

Properties of the Alkylaminothiophosphorylfluorides

Dimethylaminothiophosphoryldifluoride is a clear liquid with a foul odor. Its vapor pressure obeys the equation

$$\log_{10} P\ (\text{mm}) = 8.213 - \frac{2082}{T},$$

giving an extrapolated boiling point of 117°, heat of evaporation of 9530 cal/mole and a Trouton constant of 24.4.

Dimethylaminothiophosphoryldifluoride has also been prepared by fluorination of dimethylaminothiophosphoryldichloride with antimony trifluoride at 70–80°. Fluorination of the P=S group was not observed in contrast to the facile conversion of alkylphosphine sulfides to the fluorophosphoranes by antimony trifluoride under similar conditions (10). The difference in fluorination reactions can be attributed to the substitution of electron-withdrawing substituents such as chlorine or fluorine for alkyl groups on the phosphorus (11). Various other fluorinating agents were also tried: potassium fluorosulfinate produced a mixture of the phosphoryl and thiophosphoryl fluoride compounds and zinc fluoride gave a very low yield of impure dimethylaminothiophosphoryldifluoride and no other volatile products.

Hydrogen chloride and hydrogen bromide react slowly at room temperatures with dimethylaminothiophosphoryldifluoride (in contrast to the rapid reaction with dimethylaminodifluorophosphine (5)) to yield the halogenothiophosphoryl difluorides in high yield according to the equation

$$\text{[VIII]}\quad (CH_3)_2NP(S)F_2 + 2HX \rightarrow XP(S)F_2 + (CH_3)_2\overset{+}{N}H_2\overset{-}{X}.$$

Previous reports of low yields from the analogous reaction with the diethylamino derivatives may be due to the higher reaction temperatures used (3).

Thiophosphoryl fluoride does not complex with boron trifluoride (12). We suggested above that the increase in basicity of the molecule upon substitution of a dimethylamino group for a fluoride results in much slower reaction of the substituted molecule with basic reagents. It was of interest therefore to see if the increased basicity of dimethylaminothiophosphoryldifluoride was sufficient to permit formation of a complex with boron trifluoride as has been demonstrated for dimethylaminodifluorophosphine (5, 13). Boron trifluoride did not complex with dimethylaminothiophosphoryldifluoride, even at −78 °C, so neither the sulfur nor the nitrogen atom appears to be an effective donor. The lack of basicity associated with the nitrogen atom, which appears to be the effective donor in dimethylaminodifluorophosphine (13), suggests that the lone pair is delocalized onto the phosphorus, although we cannot exclude the possibility that stable complex formation is prevented by steric considerations.

TABLE III

Nuclear magnetic resonance parameters for methylaminothiophosphoryl fluorides

	$(CH_3)_2NP(S)F_2$	$[(CH_3)_2N]_2PSF$
Chemical shift		
τ ^1H vs. TMS (τ = 10.0)	6.67	7.42
ϕ ^{19}F p.p.m. vs. CCl_3F	+51.6	+62.3
Coupling constant (cycles)		
$J(P—F)$	1079	1016
$J(P—H)$	12.2	12.6
$J(F—H)$	2.1	1.70

Partial mass spectra of the mono- and disubstituted alkylaminothiophosphoryl fluorides are given in Table IV and the n.m.r. parameters are given in Table III. The hydrogen and fluorine n.m.r. spectra of dimethylaminothiophosphoryldifluoride show a pair of triplets and a doublet of septets respectively as expected for first order spin coupling interaction of six equivalent hydrogens and two equivalent fluorine atoms with phosphorus. The hydrogen spectrum of bis(dimethylamino)thiophosphorylfluoride showed the expected pair of doublets but the fluorine spectrum showed only a pair of fairly broad lines with unresolved fluorine–hydrogen coupling.

The infrared spectra of the two compounds, given in Table V, are similar to each other and to the phosphoryl analogues. The assignments are based on the analysis of the vibrational spectrum of dimethylaminodifluorophosphine (14) and the available data on alkylaminophosphorylhalides (1, 15) and alkylaminothiophosphorylhalides (15, 16).

Dimethylaminothiophosphoryldifluoride does not have the absorption band at 1365 cm^{-1} which was assigned to the P=O stretch of the phosphoryl compound (1) and instead of two bands in the 950–700 cm^{-1} region there are three. There are four vibrational modes to be assigned; the symmetric and antisymmetric PF stretch, the P=S, and the P—N stretch. Since these vibrations may be mixed, particularly the last named which has been reported as a weak, easily mixed band (14), we can only make a tentative assignment at present. The 910 cm^{-1} band is

TABLE IV

Mass spectra of methylaminothiophosphoryl fluorides[a]

$(CH_3)_2NP(S)F_2$			$[(CH_3)_2N]_2P(S)F$		
m/e	Rel. int.	Assignment	*m/e*	Rel. int.	Assignment
146	3.5	M + 1 isotope of parent	171	3	M + 1 isotope of parent
145	74	$C_2H_6NPSF_2$	170	52	$C_4H_{12}N_2PSF$
144	13	$C_2H_5NPSF_2$			
143	tr[b]	$C_2H_4NPSF_2$	137	8	$C_4H_{11}N_2PSF$
142	tr	$C_2H_3NPSF_2$	128	1	M + 2 isotope of 126
130	1	CH_3NSPF_2	127	2	C_2H_7NPSF or M + 1 isotope of 126
129	tr	CH_2NSPF_2			
128	1	$CHNSPF_2$	126	18	C_2H_6NSPF
126	2.8	C_2H_6NPSF, $CNPSF_2$			
116	1	?	95	3	M + 1 isotope of 94
115	tr	$NSPF_2$	94	100	C_2H_6NPF
113	4	$C_2H_6NPF_2$	93	1	C_2H_5NPF
112	100	$C_2H_5NPF_2$	83	2	SPFH
110	1.5	$C_2H_3NPF_2$			
103	1	M + 2 isotope of 101	78	3	CH_2NPF, N_2PF
102	2	SPF_2H			
101	11	SPF_2	65	2	NHPF
98	1.5	CH_3NPF_2, C_2NPF			
96	1.5	NPSF	63	1.3	SP
94	1.5	C_2H_6NPF			
93	tr	C_2H_5NPF	60	1.3	CH_3NP
83	1	NPF_2, SPFH			
82	1	SPF	51	1	PFH
78	1	H_2CNPF	50	0.5	PF
75	1	C_2H_6NP	45	4	C_2H_7N, NP
69	14	PF_2	44	91	C_2H_6N
63	tr	PS	43	5	C_2H_5N
61	1.4		42	16	C_2H_4N
60	1.4	CH_3NP	41	1	C_2H_3N
51	1				
50	1.5	PF			
45	1.5	C_2H_7N, NP			
44	3	C_2H_6N			
43	18	C_2H_5N			
42	53	C_2H_4N			
41	3	C_2H_3N			
40	1.5	C_2H_2N			
32	1.5	S			

[a] Only ^{32}S mass assignments indicated.
[b] tr = trace.

therefore assigned to the antisymmetric and the 858 cm^{-1} band to the symmetric P—F stretching motions leaving the 790 cm^{-1} band to be assigned to a vibration which is principally P=S stretching, noting, however, that the last two are probably mixed with the P—N stretch.

The spectrum of the monofluorothiophosphoryl compound is similar to that of the difluoro analogue except for doubling of the 1000 cm^{-1} absorption band into two strong absorption bands at 975 and 995 cm^{-1} respectively. The band observed at 910 cm^{-1} in the difluoro compound is not observed in the monofluoro derivative. Instead absorption bands are found at 820 cm^{-1}, 765 cm^{-1}, and 745 cm^{-1}. The first is probably the PF stretching vibration and the second the N_2P valence vibration characteristic of N_2P compounds. Comparison of the spectra of bis(dimethylamino)thiophosphorylfluoride with the phosphoryl analogue (1) indicates that the medium intensity band at 745 cm^{-1} is unique to the thiophosphoryl compound and hence is reasonably assigned to the P=S stretch. Considerable mixing of vibrations may occur, however, which may require modification of these assignments (14).

Experimental

Standard vacuum techniques were used throughout. Infrared spectra were measured with Perkin-Elmer 421 or

TABLE V

Infrared spectra of alkylaminothiophosphoryl fluorides*

$(CH_3)_2NPSF_2$ (gas)	$[(CH_3)_2N]_2PSF$ (film)	Assignment
3000 (w)	3000 (w)	
2940 (s)	2940 (s)	CH_3 antisymmetric stretch
2910 (sh)	2890 (m)	
2865 (m)	2850 (m)	CH_3 symmetric stretch
2820 (m)	2810 (m)	
	1473 (sh)	
1460 (m,br)	1458 (s)	CH_3 deformation
	1410 (w)	
1313 (s)	1302 (s)	CH_3 symmetric deformation
	1278 (sh)	
1182 (s)	1180 (s)	Antisymmetric C—N stretch
	1160 (s)	
1070 (w)	1060 (m)	CH_3 rocking
1005 (s)	1000 (vs)	Symmetric C_2NP stretch
	978 (vs)	
910 (vs)	825 (vs)	P—F stretch
858 (s)	—	See text
790 (sh)	—	
782 (s)		
—	765 (vs)	PN_2 skeletal vibration
—	745 (m)	P=S stretch
620 (w)	—	
425 (m)	—	Symmetric PF_2 deformation

*All values given in cm^{-1}. br = broad, w = weak, m = medium, s = strong, sh = shoulder, v = very.

337 spectrophotometers covering the ranges 5000–600 and 4000–400 cm^{-1} respectively. Hydrogen nuclear magnetic resonance spectra were measured with Varian HA100 or A60 instruments and compared with the tetramethylsilane ($\tau = 10.0$) reference. All fluorine n.m.r. were measured at 56.4 Mc/s with a Varian HA60 instrument. Mass spectra were measured with A.E.I. MS-9 double focussing spectrometer. Thiophosphoryl fluoride was prepared from zinc fluoride and thiophosphoryl chloride (10*a*, 17).

The Reaction of Thiophosphoryl Fluoride with Dimethylamine

(*a*) Dimethylamine (0.518 g, 11.7 mmoles) was added slowly to an equimolar quantity of gaseous thiophosphoryl fluoride (1.404 g, 11.7 mmoles) at room temperature in a 1 l reaction vessel similar to that described previously (5). A white solid precipitated immediately on mixing the gaseous reactants and a volatile liquid was also formed in the reaction. The reagents were allowed to mix thoroughly for approximately 1 h and then the volatile materials were withdrawn from the reaction vessel and fractionated to yield, in the most volatile fraction, an inseparable mixture of unreacted thiophosphoryl fluoride (0.337 g, 2.8 mmoles), identified by its infrared spectrum, and hydrogen sulfide (0.3 mmole), identified by its n.m.r. chemical shift (6). The consumption of thiophosphoryl fluoride by 11.7 mmoles dimethylamine was thus 8.9 mmoles for a reacting ratio of amine/SPF_3 of 1.3/1. The least volatile fraction, collected at −78°, contained dimethylaminothiophosphoryldifluoride, identified by molecular weight (M) (Found: M, 145. Calcd. for $C_2H_6F_2NPS$: M, 145), analysis (Found: P, 21.10; S, 22.15; F, 26.41; N, 9.63. Calcd. for $C_2H_6F_2NPS$: P, 21.34; S, 22.05; F, 26.2; N, 9.65%), and by measurement of the accurate mass of the molecular ion at 145 atomic mass units with the MS-9 spectrometer (Found: *m*/*e*, 144.9934. Calcd. for $C_2H_6F_2NP^{32}S$: *m*/*e*, 144.9926).

(*b*) In a second experiment, about 30 mmoles of thiophosphoryl fluoride was combined with a 1.30 molar ratio of dimethylamine in the same reaction vessel. No unreacted thiophosphoryl fluoride was recovered; the most volatile reaction product was identified as impure hydrogen sulfide (0.028 g, about 0.6 mmoles). The only other volatile product obtained was dimethylaminothiophosphoryldifluoride, identified by comparison with an authentic sample prepared earlier.

The residual solid remaining in the reaction bulb after removal of the volatile reaction products was kept at room temperature for 4 weeks in the evacuated bulb. After this period of time it was found that the reaction bulb contained impure hydrogen sulfide, identified by molecular weight (Found: M, 38. Calcd. for H_2S: M, 34.0) and accurate mass measurement by mass spectrometry (Found: *m*/*e*, 34.9875. Calcd. for $H_2{}^{32}S$: *m*/*e*, 34.9877). Dimethylamine was also identified as a minor constituent of the volatile products by its mass spectrum.

(*c*) Several small scale experiments were done to provide samples of the solid reaction products for nuclear magnetic resonance studies. Gaseous dimethylamine and thiophosphoryl fluoride were combined in an equimolar ratio in a 100 cc reaction vessel. In each case unreacted thiophosphoryl fluoride was recovered (contaminated with hydrogen sulfide) in sufficient quantity to yield a reacting ratio of amine/SPF_3 of 1.3/1. A 0.57/1 molar ratio of dimethylaminothiophosphoryldifluoride relative to the amount of amine taken was recovered in each case. Reactions done on a 1 mmole scale in the 100 cc vessel and those done in the 1 l vessel described above (section *a*) yielded solid residues with the fluorine n.m.r. spectrum illustrated in Fig. 1*a*. Reactions done on a 5 mmoles scale in the 100 cc vessel gave solid residues with the n.m.r. spectrum shown in Fig. 1*b*.

The solid residues were dissolved in carefully dried acetonitrile or deuterated acetonitrile in vacuum by distilling 0.5 ml of the solvent into the reaction vessel after removal of the volatile products. The residues appeared to dissolve quickly and completely in acetonitrile. The reaction vessel was then opened to a nitrogen atmosphere and the solution pipetted quickly into a n.m.r. tube containing a reference CCl_3F capillary, degassed, and sealed. The initial n.m.r. spectra were run within 2 h of the sample preparation. The results are given in Fig. 1 and Table I. Rigorous exclusion of moisture from the solvent and apparatus was necessary during preparation of the residue solutions for n.m.r. studies otherwise additional doublet resonances due to the $PO(S)F_2^-$ (18) and $PO_2F_2^-$ (6*a*) ions were observed in the spectrum.

The Vapor Pressure of Dimethylaminothiophosphoryldifluoride

The vapor pressure was measured with a glass spiral microtensimeter over the range 0 to 68 °C. The data are given in the following table (*descending temperature).

t (°C)	0.1	0.1*	7.2	10.7*	13.0
P (mm)	4.2	4.1	6.1	7.1	7.9
t (°C)	20.5	26.8*	29.5	43.1	50.95
P (mm)	13.0	18.3	22.3	43.5	62.2
t (°C)	51.4*	58.3	67.9		
P (mm)	62.9	85.3	123.6		

The Reaction of Dimethylamine with Dimethylaminothiophosphoryldifluoride

(*a*) A mixture of dimethylaminothiophosphoryldifluoride (0.76 g, 5.23 mmoles) and 0.32 g (7.06 mmoles) dimethylamine was heated to 80° for 6 h. Fractionation of the volatile products yielded, in the most volatile fraction, unreacted dimethylamine (0.074 g, 1.65 mmole) thus indicating a ratio of amine consumed to dimethylaminothiophosphoryldifluoride taken of nearly 1:1. The least volatile fraction was bis(dimethylamino)thiophosphoryl-fluoride, identified by analysis (Found: P, 17.74; S, 18.30; F, 10.56; N, 16.29. Calcd. for $C_4H_{12}FN_2PS$: P, 18.2; S, 18.6; F, 11.2; N, 16.48) and mass measurement of the molecular ion with the MS-9 mass spectrometer (Found: *m*/*e*, 170.0438. Calcd. for $C_4H_{12}FN_2P^{32}S$: *m*/*e*, 170.0442). Bis(dimethylamino)thiophosphoryl fluoride was not very volatile and appeared to react with mercury, thus the vapor pressure could not be determined accurately. The compound has a vapor pressure of approximately 1.4 mm at 27 °C.

The white solid residue which remained in the reaction vessel was dissolved in acetonitrile in vacuum and transferred, in an atmosphere of nitrogen, to a nuclear magnetic resonance tube which was then degassed and sealed in vacuum. The spectrum was obtained within a few hours of preparing the sample and again after several weeks at room temperatures. The results are given in Fig. 2 and Table II.

Fluorination of Dimethylaminothiophosphoryldichloride

Dimethylaminothiophosphoryldichloride was prepared as described in the literature (4) and characterized by n.m.r. spectroscopy (19).

(*a*) *With Potassium Fluorosulfinate*

Dimethylaminothiophosphoryldichloride (25 g) was heated with 60 g KSO_2F. Reaction began at 60°. The products were collected and identified by infrared and n.m.r. spectroscopy as sulfur dioxide, thiophosphoryl fluoride, dimethylaminothiophosphoryldifluoride, and dimethylaminophosphoryldifluoride, as well as traces of dimethylaminothiophosphorylchlorofluoride.

(*b*) *With Zinc Fluoride*

Dimethylaminothiophosphoryldichloride (20 g) was heated to 80° for 3 h with zinc fluoride (50 g) in a sealed evacuated vessel. Fractionation of the volatile products yielded silicon tetrafluoride, thiophosphoryl fluoride, and a material of low volatility which could not be identified, but was not the desired dimethylaminothiophosphoryldifluoride. The products were identified by n.m.r. and infrared spectroscopy.

(*c*) *With Antimony Trifluoride*

Antimony trifluoride (10 g) was slowly added to 5 g of dimethylaminothiophosphoryldichloride in an evacuated flask with stirring. No reaction was observed until the vessel was warmed to 70–80°, whereupon the reaction proceeded smoothly. Fractionation of the products in the vacuum system yielded mainly dimethylaminothiophosphoryldifluoride plus a small amount of thiophosphoryl fluoride impurity, both identified by infrared and n.m.r. spectroscopy.

The Reaction of Dimethylaminothiophosphoryldifluoride with Hydrogen Chloride

Dimethylaminothiophosphoryldifluoride (0.200 g, 1.37 mmoles) was combined with hydrogen chloride (0.101 g; 2.78 mmoles) in a large bulb. No visible signs of reaction were observed at room temperature even after several hours, so the contents of the reaction vessel were transferred to a smaller sealed tube whereupon visible signs of reaction appeared within 1/2 h at room temperature (probably because of the greater hydrogen halide pressure). Separation of the volatile products from the white crystalline solid yielded a trace of hydrogen chloride and 0.173 g of chlorothiophosphoryldifluoride, identified by molecular weight (Found: M, 139. Calcd. for ClF_2PS: M, 136.5) and mass spectrometric measurement of the accurate mass of the parent ion (Found: *m*/*e*, 135.9110. Calcd. for $^{35}ClF_2P^{32}S$: *m*/*e*, 135.9116). The yield was 1.27 mmoles or 93% of theoretical (eq. [VIII]).

The Reaction of Dimethylaminothiophosphoryldifluoride with Hydrogen Bromide

Dimethylaminothiophosphoryldifluoride (0.391 g, 2.7 mmoles) was combined with excess hydrogen bromide (0.484 g, 6.0 mmoles) in a sealed glass ampoule. Long white needle-like crystals formed within 15 min of warming the vessel to room temperature and the reaction was complete after 1 h. Separation of the volatile products yielded unreacted hydrogen bromide (0.042 g, 0.55 mmole) corresponding to a consumption of 2.1 moles of hydrogen bromide by each mole of dimethylaminothiophosphoryldifluoride. The least volatile fraction was identified as monbromothiophosphoryldifluoride by molecular weight

(Found: M, 178. Calcd. for BrF_2PS: M, 181) and mass spectrometry (Found: *m/e*, 179.8609. Calcd. for $^{79}BrF_2P^{32}S$: *m/e*, 179.8611).

The Reaction of Dimethylaminothiophosphoryldifluoride with Boron Trifluoride

Dimethylaminothiophosphoryldifluoride (0.134 g, 0.94 mmole) was combined with boron trifluoride (0.134 g, 1.98 mmole) in a sealed glass ampoule and allowed to react at room temperature for 2 days. Fractionation of the volatile materials through a −78 trap led to nearly quantitative (98%) recovery of each of the starting materials. The purity of the recovered reactants was verified by molecular weight and infrared measurements.

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