Acknowledgment.—This work was supported in part by a grant from the U. S. Army Research Office. We wish to thank Mr. Ray Baughman, a sophomore student at Carnegie Institute of Technology, for his single crystal work on $P_4S_4N_6(CH_3)_6$ done at the University of Pittsburgh. Dr. R. McMullan acted as his advisor.

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Phosphorus Nitrogen Chemistry. VII. Reactions of Phosphorus Trichloride, Phosphoryl Chloride, and Thiophosphoryl Chloride with Primary Amines[1,2]

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Reaction of $PSCl_3$ with methylamine led to the formation of $PS(NHCH_3)_3$. By varying pyrolysis conditions $PS(NHCH_3)_3$ was made to yield $[(CH_3NH)_2PS]_2NCH_3$ and $PS(NCH_3)(NHCH_3)$. $PO(NHt\text{-}Bu)_3$ was formed from $POCl_3$ and *t*-butylamine while $P(Nt\text{-}Bu)(NHt\text{-}Bu)$ resulted from the corresponding reaction of PCl_3 and *t*-butylamine. By analogy with the oxygen system of compounds the condensation of amides is shown to correspond closely to the formal dehydration of orthophosphoric acid.

The reaction of ammonia with phosphorus trichloride has been shown to follow the sequence[4]

$$PCl_3 \xrightarrow{NH_3} \underset{\text{amide}}{P(NH_2)_3} \xrightarrow{-NH_3} \underset{\text{imide–amide}}{P(NH)(NH_2)} \xrightarrow{-NH_3} \underset{\text{imide}}{P_2(NH)_3}$$

Although the structures of $P(NH)(NH_2)$ and $P_2(NH)_3$ are unknown, the molecular formulations are thought to be some multiple of these representations.[4,5]

Michaelis[6,7] has shown that by heating triamides of the type $PX(NHR)_3$ ($X = O,S$), imide–amide compositions will result. Thus, $PO(NR)(NHR)$ ($R =$ *n*-propyl, isobutyl) and $PS(NR)(NHR)$ ($R =$ ethyl, *n*-propyl, isobutyl, isoamyl) have been prepared in this manner. However, thermal treatment of $PO(NHCH_3)_3$ was found to yield the imide composition, $P_2O_2(NCH_3)_3$,[8] while reaction of phosphorus trichloride and methylamine proceeded directly to the imide stage, giving $P_4N_6(CH_3)_6$ as the product.[9]

No imide–amide compounds are known as a result of reactions of primary aliphatic amines and phosphorus trichloride, although the aromatic derivatives, $P(NR)(NHR)$, where $R = C_6H_5$,[10] $o\text{-}CH_3OC_6H_4$,[11] and $p\text{-}CH_3C_6H_4$,[11] have been reported.

In an effort to obtain additional information on the condensation sequence, the reactions of *t*-butylamine with phosphorus trichloride and phosphorus oxychloride and the reaction of methylamine with thiophosphoryl chloride were studied.

Experimental and Results

Apparatus.—The apparatus for making physical measurements is the same as that reported earlier.[8] Proton n.m.r. measurements were made at 60 Mc. at room temperature. A Mechrolab vapor pressure osmometer (Model 301A) was used for some of the molecular weight measurements.

Materials.—Phosphorus trichloride (Baker and Adamson, reagent) was used directly. Phosphoryl chloride (Baker and Adamson, reagent) was distilled. A middle fraction (b.p., 105.0° at 731 mm.) was stored under nitrogen in sealed ampoules. Thiophosphoryl chloride (Victor Chemical Co.) was distilled (b.p., 125.0° at 740 mm.). *t*-Butylamine (Eastman) was distilled and stored over calcium hydride (b.p. 43.2–43.3° at 740.7 mm.). Ethylamine (Eastman, anhydrous) was used directly. Tank methylamine (Matheson, anhydrous) was dried by slow passage through a tube packed with barium oxide. The purification of petroleum ether, toluene, and other solvents was described previously.[8] Benzene (Fisher certified, thiophene-free) was dried over calcium hydride.

Reaction of Thiophosphoryl Chloride and Methylamine.—Thiophosphoryl chloride was treated with methylamine in a 2-l. deep-well resin kettle. The apparatus, attachments, and general procedure followed were similar to that described[9] in connection with the preparation of $P_4N_6(CH_3)_6$. The equation for the process is

$$PSCl_3 + 6CH_3NH_2 \longrightarrow PS(NHCH_3)_3 + 3CH_3NH_3{}^+Cl^-$$

Methylamine (64.6 ml., 1.60 moles) was passed through an 18-in. tube filled with barium oxide and then condensed into the resin kettle. The latter was flushed previously with dry nitrogen and surrounded by a −78° bath. Thiophosphoryl chloride (15 ml., 0.145 mole) present in the dropping funnel was added cautiously with stirring over a 1-hr. period. A white solid formed. The temperature of the bath was maintained at −78° for 2 days, allowed to warm to 0° over the next 2-day period, held at 0° for 1.5 days, allowed to warm to room temperature overnight, and finally brought to 45° for 3 hr. The solid white product remaining was crushed in dry benzene. The insoluble hydrochloride by-product was filtered off in an all-glass vacuum filtering apparatus and identified by its m.p., 226°, and infrared spectrum. The product obtained by pumping off the benzene

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[1] Previous paper in the series: R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, **2**, 377 (1963).

[2] Presented in part before the Inorganic Division at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962. This paper represents part of the work submitted by James A. Forstner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

[3] Bell Telephone Laboratories, Inc., Murray Hill, N. J.

[4] H. Moureau and G. Wetroff, *Bull. soc. chim. France*, **4**, 918 (1937).

[5] M. Becke-Goehring and J. Schulze, *Ber.*, **91**, 1188 (1958).

[6] A. Michaelis, *Ann.*, **326**, 129 (1903).

[7] A. Michaelis, *ibid.*, **407**, 290 (1915).

[8] R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, **1**, 89 (1962).

[9] R. R. Holmes, *J. Am. Chem. Soc.*, **83**, 1334 (1961).

[10] A. Michaelis and G. Schroeter, *Ber.*, **27**, 490 (1894).

[11] H. W. Grimmel, A. Guenther, and J. F. Morgan, *J. Am. Chem. Soc.*, **68**, 539 (1946).

was an amorphous white solid. Elemental analysis gave the formula $PS(NHCH_3)_3$.

Anal. Calcd. for $C_3H_{12}N_3PS$: C, 23.53; H, 7.84; N, 27.45; P, 20.23; S, 20.94; Cl, 0.00. Found: C, 23.59; H, 7.64; N, 27.18; P, 20.27; S, 20.70; Cl, 0.00.

The reaction time sequence reported above was found to be necessary. Using a shorter time sequence leads to incomplete displacement of the chlorine from $PSCl_3$. For example, using a similar excess of methylamine to that reported above, the reaction with $PSCl_3$ was conducted according to the following time–temperature program: the bath temperature was held at −78° for 1 day, allowed to rise to 0° over the next day, warmed to 20° the third day, and held at 50° for 1 hr. Elemental analysis of the product separated as before showed the presence of chlorine.

Anal. Found: C, 23.11; H, 7.42; N, 25.82; P, 20.95; S, 19.77; Cl, 3.28.

Properties of Thiophosphoryl Tri-N-methylamide.—The product, $PS(NHCH_3)_3$, begins to melt with decomposition at 65° under vacuum. It is very soluble in water, acetone, glacial acetic acid, and chloroform; soluble in toluene, benzene, nitrobenzene, cyclohexane, and pyridine; and slightly soluble in carbon tetrachloride. Infrared data are reported in Table I.

The molecular weight was determined cryoscopically in glacial acetic acid. A sample of $PS(NHCH_3)_3$, dissolved in glacial acetic acid, was allowed to stand for 1 day to ascertain whether an irreversible reaction was occurring. On recovery by pumping off the solvent under vacuum, an elemental analysis showed that the sample was unchanged.

Anal. Calcd. for $C_3H_{12}N_3PS$: C, 23.53; H, 7.84; N, 27.45. Found: C, 23.58; H, 7.89; N, 27.15. Molecular weight determinations on samples from two preparations gave 154.4 (0.07136 *m*) and 154.2 (0.1046 *m*); calcd. for $PS(NHCH_3)_3$, 153.1.

The proton n.m.r. spectrum consists of an unsymmetrical doublet, +4.86 p.p.m. relative to the chloroform peak (internal reference), the lower field peak being more intense. For $PS(NHCH_3)_3$, one would expect a symmetrical doublet arising from $-CH_3$ protons being split by spin–spin coupling with phosphorus and a broad peak of reduced intensity due to –NH protons. The spectrum of $PO(NHCH_3)_3$ discussed previously[8] is of this type. It is suggested that in $PS(NHCH_3)_3$ the resonance for –NH protons is superimposed on the lower field half of the methyl doublet.

Pyrolysis of Thiophosphoryl Tri-N-methylamide.—The reaction temperature was varied in an attempt to form $P_4S_4N_6(CH_3)_6$ by condensation of $PS(NHCH_3)_3$. A 2-g. sample of $PS(NHCH_3)_3$ was heated in an evacuated, 25 mm. diameter glass tube attached to the vacuum line. The heating was accomplished by means of a small tube furnace. The temperature was brought to 200° in 0.5 hr. and held there for 22 hr. Gaseous evolution ceased as noted by no further pressure increase on a mercury manometer. Orange-yellow solid sublimed out of the hot zone. Part of the sublimate was needle-like and part amorphous. An orange liquid remained in the hot zone. On cooling it became glassy. Elemental analysis of the products indicated that partial rupture of the P–S bond was occurring; the sulfur to phosphorus ratio was observed to be less than one in each case. Found for needle-like sublimate: P, 21.28, S, 13.69 (mole ratio 0.62). Found for the glass: P, 25.57; S, 19.57 (mole ratio 0.74). Mass spectral analysis of the evolved gases gave the results (mole percentages): CH_3NH_2, 76.8; $(CH_3)_2NH$, 21.1; $(CH_3)_3N$, 2.1. In addition very low intensity mass peaks were present at 79 and 94. With P–S rupture indicated it seems reasonable to suspect that a small amount of $(CH_3)_2S_2$ was produced. It is a liquid[12] (b.p. 116°) with a parent mass at 94. Loss of one methyl group during ionization agrees with the appearance of a 79 peak.

In a second pyrolysis experiment conducted at 100° analysis of the products from a sample of $PS(NHCH_3)_3$ (0.2698 g., 1.761 mmoles) heated in an evacuated 500-ml. sealed bulb for 1 day showed that little reaction occurred. The heating was accomplished by placing the bulb in a constant temperature oven. Only 0.0814 mmole of gaseous products was obtained; mass spectral analysis: CH_3NH_2, 85.4; $(CH_3)_2NH$, 14.4; $(CH_3)_3N$, 0.13. Two very minor peaks again appeared at 79 and 94. At 100° an opaque liquid and crystalline white solid were present. On cooling, the opaque liquid became a wet solid. Analysis of the latter indicated the formula $[(CH_3NH)_2PS]_2NCH_3$.

Anal. Calcd. for $C_5H_{19}N_5P_2S_2$: C, 21.80; H, 6.95; N, 25.42. Found: C, 22.24; H, 7.20; N, 24.92.

The white crystalline material proved to be the original starting material as shown by elemental analysis.

Anal. Found: C, 23.47; H, 8.02; N, 27.43; P, 20.15; S, 20.84.

In a third pyrolysis experiment a sample of $PS(NHCH_3)_3$ (0.3637 g.) in a 500-ml. evacuated sealed bulb was placed on its side in the oven and heated as follows: 145° for 2 days, 160° for 1 day, and 175° for 1 day. During this period the sample remained liquid. Maintaining the temperature at 190° for 1 day resulted in the formation of crystals on the upper surface of the bulb. Visual examination indicated about one-third conversion. Upon cooling, the remaining liquid became a wet solid. Mass spectral analysis of the evolved gases gave these mole percentages: CH_3NH_2, 97.0; $(CH_3)_2NH$, 2.77; $(CH_3)_3N$, 0.24 (two very low intensity peaks were observed at 79 and 94). The crystalline product was scraped out of the bulb and sublimed at 160° under vacuum. Analysis indicated the formation of thiophosphoryl N-methylimide-N-methylamide, $PS(NCH_3)(NHCH_3)$.

Anal. Calcd. for $C_2H_7N_2PS$: C, 19.67; H, 5.78; N, 22.94; P, 25.36; S, 26.25. Found: C, 19.84; H, 5.67; N, 22.15; P, 25.45; S, 26.16.

Repetition of the above experiment with a new sample of $PS(NHCH_3)_3$ gave reproducible results. Infrared data are shown in Table I.

$PS(NCH_3)(NHCH_3)$ melts under vacuum at 221–223°. Redetermination of the melting point on the same sample gave 203–223°, indicating decomposition. Limited solubility of $PS(NCH_3)(NHCH_3)$ in CS_2 and CCl_4 was shown by lack of signals from proton n.m.r. measurements of samples in contact with these solvents. With benzene only the solvent signal was observed.

An attempt was made to obtain the molecular weight by mass spectroscopy. Using a heated inlet system the mass spectrum was obtained on a sample heated to 250°. The ionizing voltage was 70 and the ionizing current, 37.5 ma. Most peak intensities recorded were extremely low (apparently due to the low volatility of the sample); however, peaks at 180 and 244 had considerably greater intensity than those in the nearby mass region. These peaks would correspond to the unipositive ions, $[P(NCH_3)(NHCH_3)]_2^+$ and $[PS(NCH_3)(NHCH_3)]_2^+$, respectively, and might lead one to suspect a dimer formulation; however, a small number of very low intensity peaks were present at mass numbers extending as high as 400.

Reaction of Phosphorus Trichloride and *t*-Butylamine.—The reaction of phosphorus trichloride and *t*-butylamine was conducted with the kettle apparatus and attachments previously described.[9] In the presence of a nitrogen atmosphere, *t*-butylamine (170 ml., 1.60 moles) in 150 ml. of petroleum ether (30–60° fraction) was added to the kettle. The kettle and contents were surrounded by a 0° bath. Phosphorus trichloride (17.5 ml., 0.191 mole) in 100 ml. of petroleum ether, present in the dropping funnel, was added slowly over a 1-hr. period. A white solid formed. After maintaining the bath temperature at 0° for 3 days (the product was occasionally stirred), the temperature was allowed to rise to room temperature over a 1-day period. The reaction product then was heated at 45° for 2 hr. Separation of the product from the accompanying hydrochloride using petroleum ether was shown to be incomplete by elemental analysis.

Separation was effected by crushing the product in distilled water to dissolve the hydrochloride. The insoluble portion was

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[12] N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, Amen House, London, 1950, p. 887.

TABLE I

INFRARED DATA IN CM.$^{-1a}$

$PO(NHCH_3)_3$	$PO(NHt\text{-}C_4H_9)_3$	$PS(NHCH_3)_3$		$PS(NCH_3)\text{-}(NHCH_3)^b$	$P(Nt\text{-}C_4H_9)\text{-}(NHt\text{-}C_4H_9)$
$CHCl_3$	$CHCl_3$	CS_2	Nujol	CS_2	Nujol
480 w	4240 w	3850 w	4270 w	3490 w	3320 w
3290 s	4050 w	3720 w	3270 m	2960 w	2915 s
2940 s	3585 w	3410 w	2910 s	2310 w	1465 s
2520 sh	3370 m	3270 w	1455 s	2155 w	1360 s
2145 w	3175 sh	2915 w	1375 s	1450 s,br	1220 s
1645 m	2925 s	2820 w	1095 s	1375 w	1045 m
1465 s	2450 w	2290 m	973 w	1185 m	1030 m
1405 s	1855 w	2145 s	855 w	1095 m	997 s
1170 s	1727 w	1560–1430 s	775 w	870 s	919 w
1100 s	1632 w	1375 s	719 w	827 w	875 s
992 m	1468 m	1095 s			823 m
936 sh	1372 s	970 w			794 m
985–850 s	1237 s	865 s			739 m
752 w	1192 s	795 m			
	1168 sh	717 w			
	1035 s				
	1006 s				
	913 w				
	855 s				

[a] w, weak; m, medium; s, strong; sh, shoulder; br, broad. [b] Poor spectrum due to low solubility.

filtered and then dried with a nitrogen stream. The water-insoluble solid then was dissolved in benzene, a small amount of residue filtered off, and the benzene transferred to a Dry Ice trap by vacuum distillation. A tannish white product resulted which was further purified by sublimation at 90–100°. Most of the product sublimed, resulting in a white sublimate. Elemental analysis showed the formation of phosphorus N-(*t*-butylimide)-N-(*t*-butylamide), $P(NC_4H_9)(NHC_4H_9)$, m.p. 138–142°. Infrared data are in Table I. It is soluble in toluene, pentane, acetone, glacial acetic acid, chloroform, benzene, and carbon tetrachloride. It appeared insoluble in water. When exposed to air for 6 weeks no increase in weight was observed with a 0.0581-g. sample.

Anal. Calcd. for $C_8H_{19}N_2P$: C, 55.15; H, 10.99; N, 16.08; P, 17.78. Found: C, 55.13; H, 11.01; N, 16.34; P, 17.89.

The molecular weight was determined cryoscopically in benzene solution, 417 (0.04818 *m*) and 402 (0.07691 *m*). The molality is based on the formula $P(NC_4H_9)(NHC_4H_9)$ (mol. wt. calcd., 174.2). Mass spectral results at operating conditions identical with those used for $PS(NCH_3)(NHCH_3)$ showed a prominent peak at the mass number, 348, corresponding to the dimer fragment $[P(NC_4H_9)(NHC_4H_9)]_2$, but small peaks appeared at higher mass numbers extending to over 400, similar to the observation in the mass spectrum of $PS(NCH_3)(NHCH_3)$.

The proton n.m.r. spectrum of a sample dissolved in benzene showed two peaks (+5.73 p.p.m. and +5.94 p.p.m.) of approximately equal intensity shifted upfield from the benzene reference line. The lack of fine structure for *t*-butyl groups in $PO(NHC_4H_9)_3$ reported below suggests that the two peaks observed here are due to two types of *t*-butyl groups expected for the imide–amide compound. Two much smaller peaks of about equal intensity were present at +5.69 p.p.m. and 5.88 p.p.m. and may indicate the presence of a small amount of the imide–amide in a different structural environment.

The reaction of phosphorus trichloride and ethylamine was conducted analogously to the thiophosphoryl chloride–methylamine reaction described above. An orange oil was obtained which could not be crystallized despite attempts using a variety of solvents; however, ethylamine hydrochloride was identified as one of the products. Elemental analysis of the oil gave the empirical formula $C_{4.15}H_{11.53}N_{2.08}P_{1.00}Cl_{0.25}$, close to that expected for $P(NC_2H_5)(NHC_2H_5)$ but containing some chlorine.

Reaction of Phosphoryl Chloride with *t*-Butylamine.—The reaction of phosphoryl chloride (18.5 ml., 0.202 mole) in 75 ml. of petroleum ether (30–60° fraction) with *t*-butylamine (150 ml., 1.43 moles) in 300 ml. of petroleum ether was carried out at 0° using the same equipment and procedure described for the reaction of phosphorus trichloride and *t*-butylamine except that a motor-driven stirrer replaced the manually operated one. The greater quantity of petroleum ether used in this preparation aided the ease of stirring. At the end of the reaction period (4 days) a white solid and colorless liquid layer remained. The latter was partially distilled off at 45°; the remainder was removed by vacuum transfer.

The product was obtained as a fluffy white solid by washing the hydrochloride by-product away with distilled water and drying the solid with a nitrogen stream. Elemental analysis on the product showed it to be $PO(NHC_4H_9)_3$. The m.p. on a sample sublimed at 120° was 246–247°. The compound was soluble in chloroform, toluene, acetic acid, and pyridine; partly soluble in benzene and nitrobenzene; and appeared to be insoluble in *n*-hexane and cyclohexane. Infrared data are listed in Table I.

Anal. Calcd. for $C_{12}H_{30}N_3PO$: C, 54.73; H, 11.48; N, 15.96; P, 11.76. Found: C, 54.68; H, 11.62; N, 16.00; P, 12.05.

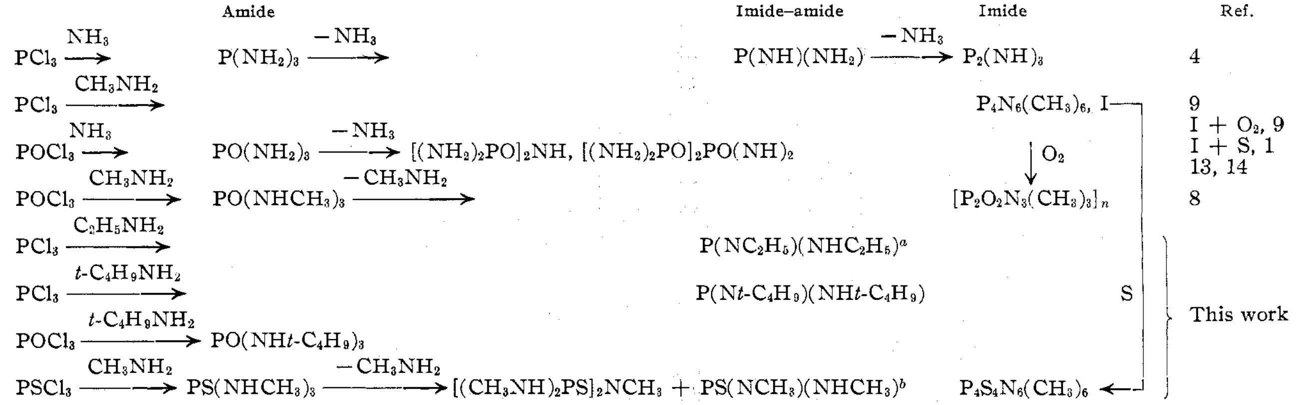
The molecular weight determined by vapor pressure osmometry was 250 at a molality of 0.0112 and 253 at a molality of 0.0321 (calcd. for $PO(NHC_4H_9)_3$, 263). The proton n.m.r. spectrum of a sample in chloroform solution showed, in addition to the reference chloroform peak, a peak at +4.67 p.p.m. assigned to the NH protons and a sharp peak at +6.02 p.p.m. having an intensity of approximately nine times the lower field peak. The latter is assigned to the protons of the C_4H_9 groups. The spectrum is similar to that for $PO(NHCH_3)_3$[8] except that the doublet character of the high field peak is not present.

Discussion

From the summary in Table II it is apparent that the general sequence of products obtained by reaction of primary aliphatic amines with phosphorus trihalides is analogous to that reported in the PCl_3–NH_3 sequence.[4] For one reason or another some of the expected products are not observed. Thus, despite attempts to cause thermal condensation of $PO(NHt\text{-}C_4H_9)_3$ no characterizable product resulted, while condensation of the related compound, $PO(NHCH_3)_3$, proceeded readily to the imide stage. In the reaction

TABLE II

REACTIONS OF PRIMARY ALIPHATIC AMINES WITH PHOSPHORUS TRICHLORIDES



	Amide		Imide–amide	Imide	Ref.
$PCl_3 \xrightarrow{NH_3}$	$P(NH_2)_3 \xrightarrow{-NH_3}$		$P(NH)(NH_2) \xrightarrow{-NH_3}$	$P_2(NH)_3$	4
$PCl_3 \xrightarrow{CH_3NH_2}$				$P_4N_6(CH_3)_6$, I	9 I + O_2, 9 I + S, 1
$POCl_3 \xrightarrow{NH_3}$	$PO(NH_2)_3 \xrightarrow{-NH_3}$	$[(NH_2)_2PO]_2NH$, $[(NH_2)_2PO]_2PO(NH)_2$		$\downarrow O_2$	13, 14
$POCl_3 \xrightarrow{CH_3NH_2}$	$PO(NHCH_3)_3 \xrightarrow{-CH_3NH_2}$			$[P_2O_2N_3(CH_3)_3]_n$	8
$PCl_3 \xrightarrow{C_2H_5NH_2}$			$P(NC_2H_5)(NHC_2H_5)$[a]		This work
$PCl_3 \xrightarrow{t\text{-}C_4H_9NH_2}$			$P(Nt\text{-}C_4H_9)(NHt\text{-}C_4H_9)$	S	
$POCl_3 \xrightarrow{t\text{-}C_4H_9NH_2}$	$PO(NHt\text{-}C_4H_9)_3$				
$PSCl_3 \xrightarrow{CH_3NH_2}$	$PS(NHCH_3)_3 \xrightarrow{-CH_3NH_2}$	$[(CH_3NH)_2PS]_2NCH_3$ +	$PS(NCH_3)(NHCH_3)$[b]	$P_4S_4N_6(CH_3)_6 \leftarrow$	

[a] Formulation indicated. [b] Attempted formation of $P_4S_4N_6(CH_3)_6$ from $PS(NCH_3)(NHCH_3)$ was unsuccessful.

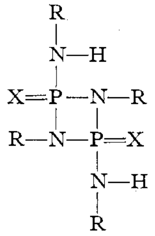
of PCl_3 with t-butylamine, no amide was isolated; instead the imide, $P(Nt\text{-}C_4H_9)(NHt\text{-}C_4H_9)$, formed directly. In the $PSCl_3$–CH_3NH_2 sequence, on the other hand, products corresponding to each stage of the condensation process have been isolated; although formation of the imide, $P_4S_4N_6(CH_3)_6$, from $PS(NCH_3)(NHCH_3)$ proved unsuccessful.

Members having larger alkyl groups and a greater degree of coördination around phosphorus appear more resistant to hydrolysis than the others. For example, the butyl derivative, $PO(NHt\text{-}C_4H_9)_3$, may be separated from the hydrochloride by-product with water and on standing in air for several weeks no change in weight or appearance is detected.

Concerning the structure of the various compounds in the condensation sequence, it is clear that the initial members, $PX(NHR)_3$, have a simple amide structure. Molecular weight data and proton n.m.r. measurements for amide compounds prepared in this work support the formulation in each case.

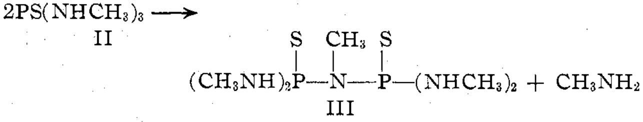
The structure of the imide–amide compounds, the next most important step in the sequence, is less clear. Previous molecular weight results on compounds such as $PS(NR)(NHR)$ ($R = C_2H_5$, $n\text{-}C_3H_7$, $i\text{-}C_4H_9$) show monomer formulas[7] in ethanol (ebullioscopic). In benzene $PS(NC_2H_5)(NHC_2H_5)$ exhibited a dimer formula[7] (cryoscopic). The compounds $PO(Nn\text{-}C_3H_7)(NHn\text{-}C_3H_7)$ and $PO(Ni\text{-}C_4H_9)(NHi\text{-}C_4H_9)$ are monomeric[7] in glacial acetic acid, while aromatic derivatives are in general dimeric[7] even in glacial acetic acid (all determined cryoscopically).

Both the molecular weight (cryoscopically determined in benzene) and mass spectroscopic data we obtained for $P(t\text{-}C_4H_9)(NHt\text{-}C_4H_9)$ and $PS(NCH_3)(NHCH_3)$ are best interpreted in terms of a dimer representation, although there is some indication of the presence of higher molecular weight species. The infrared spectrum of each (Table I) showed absorptions in the region expected for N–H stretching frequencies (3300–3500 cm.$^{-1}$).[15] Hence the presence of the structural type

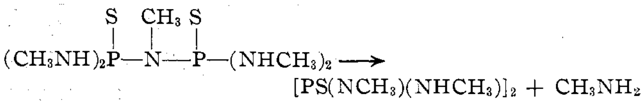


in solution is supported. In solvents such as ethanol or glacial acetic acid, protonation may aid in stabilizing monomer species referred to above. The fact that the aromatic derivatives are dimeric, even in glacial acetic acid, suggests that the phenyl groups reduce the basicity at the nitrogen centers and lessen the tendency for protonation by the solvent, assuming protonation is acting as a competing process.

If one views the formation of the various products in the condensation sequence up to and including the imide–amide in terms of simple molecular coupling, then the reactions for the stepwise condensation of $PS(NHCH_3)_3$, for example, could very likely follow the routes



$$\underset{\text{II}}{2PS(NHCH_3)_3} \longrightarrow \underset{\text{III}}{(CH_3NH)_2\overset{S}{\overset{|}{P}}-\overset{CH_3}{\overset{|}{N}}-\overset{S}{\overset{|}{P}}-(NHCH_3)_2} + CH_3NH_2$$



$$(CH_3NH)_2\overset{S}{\overset{|}{P}}-\overset{CH_3}{\overset{|}{N}}-\overset{S}{\overset{|}{P}}-(NHCH_3)_2 \longrightarrow [PS(NCH_3)(NHCH_3)]_2 + CH_3NH_2$$

Such reasoning would lead one to suspect the ready formation of trimer and tetramer structures for the imide–amide. Coupling between II and III could give the trimer, while dimerization of III could give the tetramer; however, evidence for such processes is lacking at present.

Previous evidence[1,8,9,16] shows that the structures of the imides are similar to the structures of the phosphorus tri- and pentoxides. Both $P_4N_6(CH_3)_6$[1,9,16]

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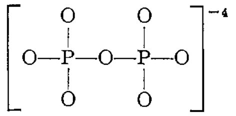
and $P_4S_4N_6(CH_3)_6$[1] are molecular, while data at present suggest that $P_2O_2N_3(CH_3)_3$[8,16] is polymeric. The possible routes leading to such imides from previous members of the condensation process are numerous and a beginning discussion must await clarification of the structure of the imide–amide class.

By analogy between the nitrogen and oxygen system of compounds, the condensation of amides, such as $PS(NHCH_3)_3$, corresponds to a formal dehydration of orthophosphoric acid according to the sequence

$$\underset{\text{orthophosphoric acid}}{H_3PO_4} \longrightarrow \underset{\text{pyrophosphoric acid}}{H_4P_2O_7} \longrightarrow \underset{\text{metaphosphoric acids}}{[HPO_2]_x} \longrightarrow \underset{\text{phosphorus pentoxide}}{P_4O_{10}}$$

Structures of salts of the oxygen acids are known[17] and follow closely the structural assignments in the amide series. Thus the phosphate ion has an analogous structure to the amide, $PS(NHCH_3)_3$; the pyrophosphate ion



$$\left[\begin{array}{c} \text{O} \quad \text{O} \\ | \quad\ \ | \\ \text{O—P—O—P—O} \\ | \quad\ \ | \\ \text{O} \quad \text{O} \end{array}\right]^{-4}$$

has a structure similar to that suggested for $[(CH_3NH)_2PS]_2NCH_3$. The tri- and tetrametaphosphates have ring structures and suggest that analogous structures should be searched for in the imide–amide class. The close structural correspondence between the imides and phosphorus pentoxide already has been referred to.

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The Systems Phosphorus Trifluoride–Trimethylamine, Phosphorus Trifluoride–Triethylamine, and Methyldichlorophosphine–Trimethylamine[1,2]

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The binary systems PF_3–$(CH_3)_3N$, CH_3PCl_2–$(CH_3)_3N$, and PF_3–$(C_2H_5)_3N$ were studied and the solid complexes $F_3P{\cdot}N(CH_3)_3$ and $CH_3Cl_2P{\cdot}N(CH_3)_3$ characterized. Dissociation pressures were measured for each complex. Both complexes lose their existence in the vapor state. Interpretation of pressure composition data established a dissociation equilibrium for $CH_3Cl_2P{\cdot}N(CH_3)_3$ in the liquid state. An energy of complexing of 2.9 kcal./mole resulted. Large negative deviations were observed in the $PF_3{\cdot}(C_2H_5)_3N$ system, supporting association tendencies. The acceptor properties of PF_3 are discussed.

Previous work in this Laboratory established the complexes $Cl_3P{\cdot}N(CH_3)_3$[4] and $Br_3P{\cdot}N(CH_3)_3$[5] and supported the presence of a phosphorus–nitrogen linkage in each wherein phosphorus is acting as an acceptor atom. Griffiths and Burg[6] mention that PF_3 and $(CH_3)_3N$ form an unstable adduct at −78° and Parry and Bissot[7] have shown that PF_3 and $(CH_3)_3N$ react in an approximately 1:1 ratio. To define the PF_3–$(CH_3)_3N$ system precisely a more complete study was undertaken. Also to gain further information on the tendency for complex formation in this series the systems PF_3–$(C_2H_5)_3N$ and CH_3PCl_2–$(CH_3)_3N$ were investigated.

Experimental

Materials.—Trimethylamine generated from the hydrochloride (Matheson, reagent grade) was dried by passing the vapor through a barium oxide tube and then condensed at −78° on sodium chips. After being in contact overnight the amine was fractionated in the line. A tensiometrically homogeneous middle fraction was used, v.p. 681 mm. at 0.0°. A refractionated sample of triethylamine previously purified was used.[8]

Phosphorus trifluoride was prepared by the two step procedure described in *Inorganic Syntheses*,[9] the preparation of arsenic trifluoride from arsenic III oxide followed by fluorination of phosphorus trichloride. The phosphorus trifluoride was trapped at −78° as it formed and then slowly fractionated in the line using traps cooled to −78, −119, −160, and −196°. Most of the product was present in the −160° trap. This fraction was found to show a vapor pressure variation from 372 to 376 mm. at −111.7° when divided into fractions. A mass spectral analysis showed mass peaks attributed to small amounts of PF_2Cl and POF_3. The latter contaminants were readily removed by condensing a 10 mole % quantity of $(CH_3)_3N$ on the PF_3 sample at −196°, warming to −111.7° and cooling to −196°

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(2) This paper represents part of the work submitted by Raymond P. Wagner in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Carnegie Institute of Technology.

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