deg.$^{-1}$ mole^{-1}; dimethylgermane, 3.0°, 5525 cal. mole^{-1}, and 20.0 cal. deg.$^{-1}$ mole^{-1}; trimethylgermane, 27.0°, 6097 cal. mole^{-1}, and 20.3 cal. deg.$^{-1}$ mole^{-1}. The melting points of methyl-, dimethyl-, and trimethylgermane were -154.5 ± 0.2, -144.3 ± 0.2, and $-123.1 \pm 0.2°$, respectively. Observed molecular weights were: CH_3GeH_3, 90.7, calcd. 90.6; $(CH_3)_2GeH_2$, 104.8, calcd. 104.6; $(CH_3)_3GeH$, 118.6, calcd. 118.6; CD_3GeH_3, 93.6, calcd. 93.6; $(CD_3)_2GeH_2$, 110.6, calcd. 110.6.

Germane.—Several experiments were conducted using the previously described procedure. Excess hydroborate solutions were added slowly to 20-ml. aliquots of GeO_2 (1.171 mmoles) dissolved in 1 *M* HBr and the product gas in the stream of evolved hydrogen was collected in *five* traps cooled to $-196°$. Pure germane was recovered in 96.0, 96.8, 96.2, 100.6, and 98.2% yields when the reaction temperatures were 0, 20, 40, 60, and 80°, respectively. Digermane was a minor product ($\leq 1\%$) at $t \leq 40°$. Experiments conducted at 40° using GeO_2 (1.245 mmoles) in 1 *N* HCl with *one*,[2] *two*,[1,3,4] and *five* traps at $-196°$ in the effluent gas stream gave yields of 56.4, 78.5, and 97.6%, respectively.

Discussion

The experimental results show that the reduction of an aqueous acid solution of a Ge(IV) compound with sodium hydroborate is the most efficient and general method of preparing monogermanium hydrides presently available. Germane and its alkyl derivatives $(CH_3)_nGeH_{4-n}$ (n = 1–3) were prepared in virtually quantitative yield and it is expected that the reaction could be further extended to include aryl and cycloalkyl derivatives. Furthermore, contrary to previous reports,[2] the yield of germane is temperature-independent in the range 0–80°, and earlier problems with yields appear to have arisen from the use of inefficient product collection techniques. This was demonstrated further by a parallel investigation[18] in which yields of 90 and only 70% were obtained in the preparation of trialkyl- and dialkylgermanes, respectively, using the hydroborate method.

A considerable body of evidence has now been collected[1-4,17] which suggests that an important species in the reaction may be represented by $\equiv GeBH_4$. Subsequent steps in the mechanism, however, are not known with certainty and, therefore, a definitive kinetic study of the process would be desirable.

[18] J. Satgé, *Ann. Chem.*, **6**, 519 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE INSTITUTE OF TECHNOLOGY, SCHENLEY PARK, PITTSBURGH, PENNSYLVANIA

Phosphorus Nitrogen Chemistry. VI. Preparation and Properties of Thiophosphorus Tri-N-methylimide, $P_4S_4N_6(CH_3)_6$[1,2]

BY ROBERT R. HOLMES[3] AND JAMES A. FORSTNER

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Thiophosphorus tri-N-methylimide, $P_4S_4N_6(CH_3)_6$, was prepared in high yield by the reaction of elemental sulfur and solid $P_4N_6(CH_3)_6$ at room temperature. Physical properties support a structure analogous to the cage structure for $P_4O_6S_4$. Additional properties of the related compounds, $P_4N_6(CH_3)_6$ and $As_4N_6(CH_3)_6$, are reported. Comparison of proton n.m.r. spectra and mass spectral cracking patterns substantiates a common structural basis for these molecules.

The properties of phosphorus tri-N-methylimide, $P_4N_6(CH_3)_6$, recently reported,[4,5] suggested a cage structure similar to the structure observed for phosphorus trioxide, P_4O_6. In later work[1] reaction of $P_4N_6(CH_3)_6$ with oxygen led to an apparent polymeric material having the empirical composition $P_2O_2N_3(CH_3)_3$. One might anticipate the formation of a molecular derivative as well. The latter expectation was realized on studying the properties of thiophosphorus tri-N-methylimide, $P_4S_4N_6(CH_3)_6$, the subject of the present paper.

Experimental and Results

Apparatus.—The apparatus used for making physical measurements is the same as that reported previously.[1] Proton n.m.r. measurements were made at 60 Mc. at room temperature. For the most part vacuum line procedures were used in conducting the various reactions.

Materials.—Phosphorus tri-N-methylimide was prepared and purified according to our previous method.[5] Sulfur (Baker and Adamson, flowers) and arsenic trichloride (Baker and Adamson, reagent) were used directly. Tank hydrogen chloride (Matheson) was fractionated in the vacuum line. The vapor pressure at $-111.7°$ was 125 mm. Tank methylamine (Matheson, anhydrous) was dried with barium oxide before use. Benzene (Fisher certified reagent, anhydrous) was dried over calcium hydride. Petroleum ether (Hommel Company, 30–60°) was distilled and dried over sodium ribbon. Toluene (Hommel Company, C.P.) was distilled (b.p. 107.5–107.8° at 748 mm.) and dried over calcium hydride. Other solvents were dried with an appropriate agent and used directly.

Preparation of Thiophosphorus Tri-N-methylimide.—Freshly sublimed phosphorus tri-N-methylimide, $P_4N_6(CH_3)_6$, was pressed into pellets in a 6-mm. glass tube using a concentric glass rod. The operation was performed in a nitrogen-filled drybox. After the pellets had been placed in a weighing bottle and the total weight determined, the pellets were dropped into a reaction ampoule which consisted of a tube 25 mm. in diameter and 50 mm. in length connected to an 8 mm. tube ending in a male 12/30 ground-glass joint. The bottle was reweighed. A known amount of sulfur then was introduced in a similar fashion. One

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[1] Previous paper in the series: R. R. Holmes and J. A. Forstner *Inorg. Chem.*, **1**, 89 (1962).

[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] R. R. Holmes and J. A. Forstner, *J. Am. Chem. Soc.*, **82**, 5509 (1960).

[5] R. R. Holmes, *ibid.*, **83**, 1334 (1961).

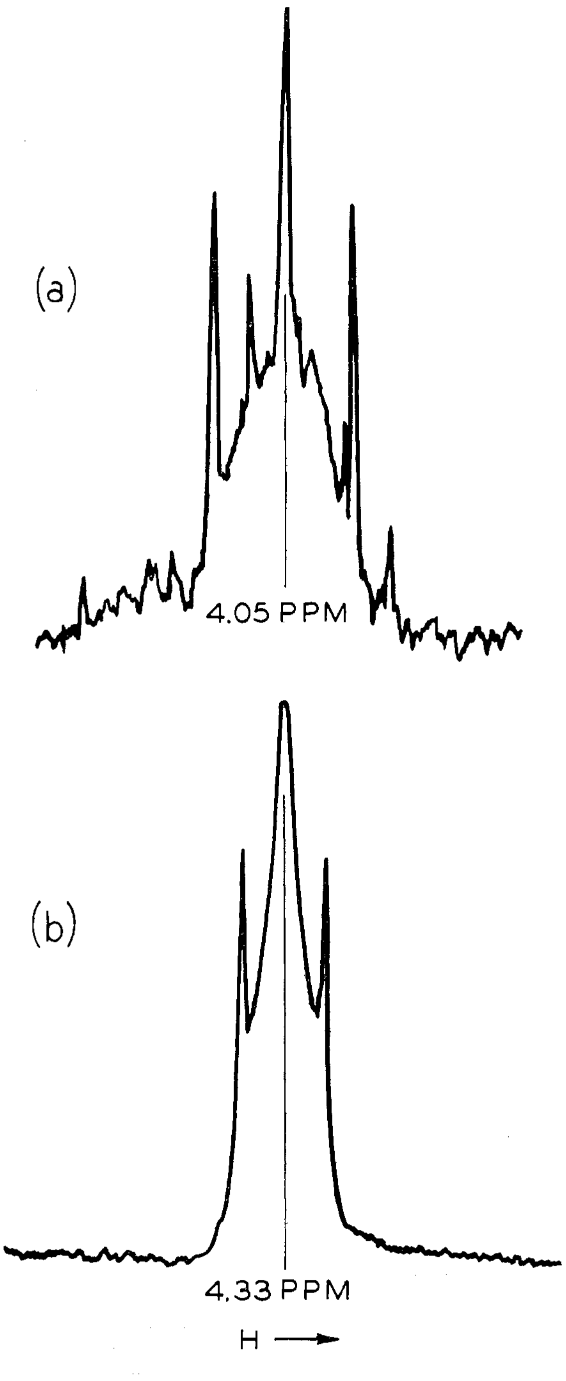

Fig. 1.—Proton n.m.r. spectra of benzene solutions of (a) $P_4S_4N_6(CH_3)_6$ and (b) $P_4N_6(CH_3)_6$. The chemical shift is relative to benzene.

reaction utilized 0.6105 g. (2.05 mmoles) of phosphorus tri-N-methylimide and 0.2630 g. (8.20 mmoles) of sulfur; *i.e.*, stoichiometric amounts.

The ampoule and contents were attached to the vacuum line and evacuated. Shortly thereafter a vigorous exothermic reaction took place; the solids were converted to a liquid. On cooling, the liquid became a white solid. No pressure was present at the end of the process. To ensure complete reaction, the tube was sealed off under vacuum and placed in an oven which was brought slowly to a temperature of 185°. The latter temperature was maintained for 5 hr. Then it was lowered to 160°. After one day the ampoule was removed from the oven and the product was scraped out, transferred to another tube, and sublimed at 180° under vacuum. Little residue remained on sublimation, indicating the formation of thiophosphorus tri-N-methylimide in near quantitative yield. The product is a white crystalline solid which melts with decomposition at 240°.

Anal. Calcd. for $P_2S_2N_3C_3H_9$: C, 16.90; H, 4.22; N, 19.72; P, 29.07; S, 30.09. Found: C, 16.57; H, 4.06; N, 19.34; P, 29.29; S, 30.00.

In one preparation sulfur and $P_4N_6(CH_3)_6$ were mixed in an ampoule in near stoichiometric quantities in a dry helium atmosphere. The purpose of the experiment was to see if the lack of reaction of the two solids in the presence of a nitrogen atmosphere was due to surface adsorption of the gas. Helium presumably would be adsorbed to a lesser degree on the solid surface; however, on addition of sulfur to $P_4N_6(CH_3)_6$ in the presence of helium no reaction occurred. The sulfur was present in an angular glass appendage which could be rotated by means of a glass joint to allow the sulfur to drop on the imide. After 1 hr., during which no reaction was visible, the ampoule was evacuated. As before, vigorous reaction took place.

Properties of Thiophosphorus Tri-N-methylimide. General.—$P_4S_4N_6(CH_3)_6$ is soluble in benzene, chloroform, carbon disulfide, pyridine, and carbon tetrachloride. Slight solubility was noted on contact with water, increasing slowly over a period of weeks. Upon exposure to air for 4 months, a 0.1228-g. sample was not visibly changed but a 29% increase in weight was noted. No observable reaction took place when hydrogen chloride was condensed on a benzene solution of $P_4S_4N_6(CH_3)_6$ at −78° and allowed to warm to room temperature.

The infrared spectrum of $P_4S_4N_6(CH_3)_6$ dissolved in CS_2 showed these bands: 2970 (w), 2310 (w), 2155 (m), 1560–1450 (s), 1255 (w), 1175 (m), 1045 (s), 905 (s), 775 (w), and 730 (w). The CS_2 showed bands at 2275 (w), 2125 (s), 1740 (w), 1560–1430 (s), and 850 (w).

Vapor Pressure.—The vapor pressure was determined in a tensimeter similar to that used previously.[5] After the highest reading was recorded, the sample was cooled to room temperature. A residual pressure of 0.2 mm. remained, indicating little decomposition. The residual pressure was removed and the vapor pressures were redetermined (run 2). The results are shown in Table I.

TABLE I

VAPOR PRESSURES OF THIOPHOSPHORUS TRI-N-METHYLIMIDE

	Temp., °C.				
	175	180	190	200	210
Run 1, *p*, mm.	0.1	0.5	1.8	2.7	6.0
Run 2, *p*, mm.	0.2	0.7	1.3	3.0	6.0

Molecular Weight.—A freshly sublimed sample of $P_4S_4N_6(CH_3)_6$ was dissolved in benzene solution for ebullioscopic measurements, using a Menzies-Wright apparatus. Molecular weights in good agreement with the formula $P_4S_4N_6(CH_3)_6$ resulted (theory, 426). Values of 418 using 0.1341 g. of solute in 32.4 ml. of benzene and 420 using 0.2287 g. of solute in 32.0 ml. of benzene were obtained.

N.m.r. Measurements.—The proton n.m.r. spectrum was determined at 60 Mc.p.s. on two samples of thiophosphorus tri-N-methylimide which had been synthesized independently by starting with phosphorus trichloride and methylamine forming phosphorus tri-N-methylimide,[4] followed by reaction of the latter with sulfur. The n.m.r. results were identical.

A typical spectrum is shown in Fig. 1 and compared with the spectrum of $P_4N_6(CH_3)_6$.[6] It is seen that the fine structure is enhanced in the sulfur derivative. The chemical shift of the central peak of the multiplet in the spectrum of $P_4S_4N_6(CH_3)_6$ relative to benzene (internal reference), +4.05 p.p.m., is in the range found for protons of N–CH_3 groups.[7] The spectrum may

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[6] Previously[4,5] the proton n.m.r. spectrum of $P_4N_6(CH_3)_6$ was reported relative to water. More properly relative to the internal reference, benzene, it is +4.33 p.p.m.

[7] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 272.

be interpreted as a triplet showing a one–two–one intensity pattern with spacing of 14 c.p.s. and additional structure of reduced intensity. Such a spectrum is consistent with one type of proton, the multiplet structure arising from spin–spin coupling with two near phosphorus atoms and additional coupling effects due to two phosphorus atoms further removed.

X-Ray Data.—Single crystals of $P_4S_4N_6(CH_3)_6$ were readily grown by heating a sample of the material in an evacuated tube at 150°. Oscillation and zero and first order Weissenberg photographs were obtained on the crystals sealed in 0.3-mm. diam. borosilicate capillaries. The camera diameter was 57.3 mm. Ni filtered CuKα radiation was used. Interpretation showed the crystal to have at least orthorhombic symmetry with unit cell dimensions: $a = 9.52 \pm 0.02$ Å., $b = 9.92 \pm 0.02$ Å., and $c = 9.50 \pm 0.02$ Å. The resulting volume was 897.16 Å.^{3}. Density determinations gave a value of 1.59 g./cc. (single crystal suspended in a tetrachloroethane–trichloroethylene mixture). Using the latter information 2.01 molecules per unit cell are calculated. The X-ray density is 1.579 g./cc.

Preparation and Properties of Arsenic Tri-N-methylimide.—The reaction of methylamine (64.6 ml., 1.60 moles) and arsenic trichloride (7.43 ml., 0.145 mole) was performed in the absence of solvent using the identical apparatus and procedure described for the preparation of $P_4N_6(CH_3)_6$.[5] The product obtained after petroleum ether extraction was a sublimable white solid melting with decomposition in the range 126–132° (previously reported,[8] 122–125°). It was moderately soluble in water, chloroform, and benzene and slightly soluble in toluene, cyclohexane, acetone, and ethanol. It dissolved in phosphorus trichloride with bubbling. Infrared data were in good agreement with previous data.[8]

The proton magnetic resonance spectrum using benzene as an internal reference showed a single sharp peak at +4.21 p.p.m.

Further Properties of Phosphorus Tri-N-methylimide.—When placed in contact with distilled water most of a 1-g. sample of $P_4N_6(CH_3)_6$ had not dissolved at the end of 2 weeks.[9] Heating the sample at 65° for 30 hr. in contact with 2 N aqueous ammonia failed to cause solution; however, continued hydrolysis effected solution after 3 days. On standing in air, a 0.5-g. sample experienced a 23% weight increase after 1 week. After 3 weeks, the crystalline sample had changed to a clear viscous liquid.

A study of the action of hydrogen chloride (16.93 moles) on $P_4N_6(CH_3)_6$ (0.4728 mole) at −78° showed that after 6 days the reaction

$$P_4N_6(CH_3)_6 + 18HCl \longrightarrow 4PCl_3 + 6CH_3NH_3{}^+Cl^-$$

had proceeded to 98.3% completion based on the amount of HCl consumed. The white solid remaining was identified as $CH_3NH_3{}^+Cl^-$ by its m.p., 226°. PCl_3 was identified by its v.p., 35.3 mm. at 0°.

Mass Spectral Data.—Using a heated inlet system attached to the mass spectrometer, the molecular weights of $P_4N_6(CH_3)_6$, $P_4S_4N_6(CH_3)_6$, and $As_4N_6(CH_3)_6$ were substantiated from observations of the highest mass peak[10] in the spectrum of each obtained at 250° (operating voltage, 70; ionizing current, 37.5 ma.). Proceeding from the parent peak to lower mass numbers in the mass spectrum of $P_4N_6(CH_3)_6$ and $As_4N_6(CH_3)_6$ peaks corresponding to fragments having CH_3 groups successively removed were observed. Phosphorus–sulfur bond breakage acted as a competing process in the fragmentation of $P_4S_4N_6(CH_3)_6$. In the case of $P_4N_6(CH_3)_6$ the vapor pressure at 250° was high enough to observe the parent peak at a lower ionizing voltage, 11.5. The latter peak was the most intense and the only additional peak observed were 283, 268, 253, 238, and 60, corresponding to the unipositive fragments $P_4N_6(CH_3)_5$, $P_4N_6(CH_3)_4$, $P_4N_6(CH_3)_3$, $P_4N_6(CH_3)_2$, and $PNCH_3$, respectively.

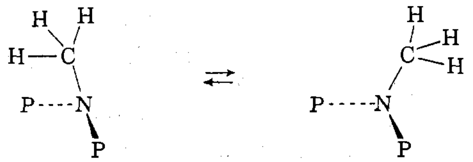
Discussion

From the results presented here it is apparent that $P_4S_4N_6(CH_3)_6$ and $As_4N_6(CH_3)_6$ have the same structural basis as that cited[4,5] for $P_4N_6(CH_3)_6$, a phosphorus oxide molecular cage structure.

For example, the most intense peaks observed in the mass spectrum of $P_4N_6(CH_3)_6$, obtained at either an ionizing voltage of 11.5 or 70, agree well with fragmentation expected from such a structure. Accordingly, there are no prominent peaks alone assignable to unipositive fragments of the type P_3N, P_2N_6, $PN(CH_3)_2$, etc. Examination of the mass spectra of $P_4S_4N_6(CH_3)_6$ and $As_4N_6(CH_3)_6$ leads one to a similar conclusion.

The proton n.m.r. spectra of $P_4N_6(CH_3)_6$ and $P_4S_4N_6(CH_3)_6$ compared in Fig. 1 also offer good support for the structures suggested.[11] The shift from +4.33 p.p.m. in $P_4N_6(CH_3)_6$ to 4.05 p.p.m. in $P_4S_4N_6(CH_3)_6$ is consistent with an electron drift toward sulfur, $S \leftarrow P{-}N{-}C{-}H$. The fact that a simple sharp peak is observed in the proton n.m.r. spectrum of $As_4N_6(CH_3)_6$ in $CHCl_3$ solution is in accord with a P_4O_6 cage structure as well.[12,13] Quadrupolar effects of As^{75} most likely render spin–spin splitting inoperative in this case and hence fine structure is not seen.

As a consequence of the interpretation of a cage structure for these compounds and the presence of but one type of proton, the methyl groups must on the average be in the planes of the P–N–P linkages. As in the ammonia molecule,[14] the bonding most likely involves a pyramidal distribution with rapid inversion occurring.[15]



The possibility of a non-planar arrangement around nitrogen in $As_4N_6(CH_3)_6$ involving rapid inter- or intramolecular exchange could exist and if so would result in a sharp singlet. Such a possibility would be ruled out in $P_4N_6(CH_3)_6$ and $P_4S_4N_6(CH_3)_6$ since definite spin–spin splitting patterns are observed.

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(8) Recently H. Nöth and H. J. Vetter, *Naturwiss.*, **48**, 553 (1961), reported the preparation of $As_4N_6(CH_3)_6$ and established the formula by elemental analysis and molecular weight measurements.

(9) Previously[5] a much smaller sample was used and it appeared to dissolve over a period of several days.

(10) The mass spectrum of $P_4N_6(CH_3)_6$ had a very low intensity peak at 314 (intensity 1.5 relative to 100 for the parent peak). The appearance of this peak is thought to arise from a small amount of impurity giving $OP_4N_6(CH_3)_6{}^+$. The latter peak was absent in the mass spectrum obtained at lower ionizing voltage.

(11) The structure suggested for $P_4S_4N_6(CH_3)_6$ is similar to the known structures P_4O_{10} and $P_4O_6S_4$.

(12) The proton n.m.r. spectrum of hexamethylenetetramine, $N_4(CH_2)_6$, which has the type of structure discussed here, shows one intense signal at +2.59 p.p.m. relative to $CHCl_3$ (internal reference). For structural details, see L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, Burlington House, London, 1958, p. M205.

(13) Nöth and Vetter[8] proposed a P_4O_6 structure for $As_4N_6(CH_3)_6$ but did not include any supporting evidence other than noting our structural assignment[4] for $P_4N_6(CH_3)_6$.

(14) R. E. Weston, Jr., *J. Am. Chem. Soc.*, **76**, 2645 (1954).

(15) A planar arrangement around nitrogen (sp^2 hybridization) involving restricted movement of the methyl groups also is an attractive possibility; however, at present there is nc direct evidence supporting P–N double bonding (π_{d-p}) in these compounds.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARNEGIE INSTITUTE OF TECHNOLOGY, SCHENLEY PARK, PITTSBURGH, PENNSYLVANIA

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

BY ROBERT R. HOLMES[3] AND JAMES A. FORSTNER

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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*-$CH_3OC_6H_4$,[11] and *p*-$CH_3C_6H_4$,[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.

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

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

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