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

Phosphorus Nitrogen Chemistry. V. New Synthetic Routes Leading to Oxidized Phosphorus Nitrogen Structures[1,2]

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

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The reaction of phosphoryl chloride with excess methylamine was studied. Evidence for the formation of phosphoric tri-N-methylamide, $PO(NHCH_3)_3$, is given. The latter substance undergoes pyrolytic condensation at 300°, splitting out amines and yielding diphosphoryl tri-N-methylimide, $P_2O_2(NCH_3)_3$. At lower temperatures compositions approaching $P_2O_2(NCH_3)_2NH$ are found with a corresponding increase in $(CH_3)_2NH$. $P_2O_2(NCH_3)_3$ also is formed by oxidation of phosphorus tri-N-methylimide, $P_4N_6(CH_3)_6$, at 170°. Heating $P_2O_2(NCH_3)_3$ toward 650° drives off condensable and non-condensable gases leaving a dark lustrous solid approaching PNO in composition. The structure of $P_2O_2(NCH_3)_3$ is discussed on the basis of available evidence.

Phosphorus tri-N-methylimide, $P_4(NCH_3)_6$, was described recently and a cage structure comparable to that found in P_4O_6 was proposed.[4,5] Structural arguments suggest that the oxidation of $P_4(NCH_3)_6$ might yield a compound whose geometry would bear close resemblance either to the known cage arrangement of molecular phosphorus pentoxide or to one of the known polymeric layer arrangements of phosphoric pentoxide.[6]

Preliminary investigation[4] showed that the oxidation of $P_4(NCH_3)_6$ proceeded smoothly at 170° yielding a white solid whose analysis was close to the expected composition, $P_2O_2(NCH_3)_3$; however, the product was contaminated by small amounts of a glassy material. Because of subsequent difficulties encountered in the purification process another synthetic route to the solid was sought.

Klement and Koch[7] isolated phosphoric triamide, $PO(NH_2)_3$, from the reaction between phosphoryl chloride and ammonia. One might expect that the corresponding reaction of phosphoryl chloride with methylamine would give $PO(NHCH_3)_3$. While the correct stoichiometry was realized, the expected product, $PO(NHCH_3)_3$, was not readily separated from the reaction mixture. If, however, the reaction mixture was heated to 300°, the desired condensation product diphosphoryl tri-N-methylimide, $P_2O_2(NCH_3)_3$, was obtained. By lowering the temperature to 230° a different product composition, $P_2O_2(NCH_3)_2NH$, was approached.

The present paper considers the synthetic route from $POCl_3$ to new diphosphoryl compounds, their resulting thermal behavior, and the structural principles suggested by the interrelations encountered.

Experimental and Results

Apparatus.—In general typical vacuum line procedures were used to study reaction products; the preparations were conducted outside the line in moisture-free systems.

N.m.r. measurements were made with a Varian Associates HR-60 spectrometer following the usual procedure using the side band technique.

Mass spectral analyses were obtained using a Consolidated Electrodynamics Corporation mass spectrometer, Type 21-103C; results are reported in mole percentages.

Infrared absorption spectra were recorded by a Perkin-Elmer Model 21 instrument.

Materials.—Phosphoryl chloride (Baker and Adamson, reagent) was distilled. A middle fraction (b.p. 105° at 731 mm.) was stored under nitrogen in sealed ampoules.

Tank methylamine (Matheson, anhydrous) was dried by slow passage through a tube packed with barium oxide. Mass spectral analysis indicated a purity of 98.28%. The contaminants were dimethylamine (1.55%) and trimethylamine (0.16%).

Phosphorus tri-N-methylimide, $P_4N_6(CH_3)_6$, was prepared and purified according to our previous method.[5]

Tank oxygen was used after passage through a 1.2 m. drying tube containing Drierite, potassium hydroxide, and phosphorus pentoxide.

Petroleum ether (30-60°, Hommel Company) was distilled and dried over sodium ribbon.

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[1] Previous paper in the series: R. R. Holmes and R. P. Wagner, *J. Am. Chem. Soc.*, in press. Presented before the Inorganic Division at the 140th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1961.

[2] 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] Research Assistant (1959-61), Office of Ordnance Research Contract.

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

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

[6] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 270-272.

[7] R. Klement and O. Koch, *Ber.*, **87**, 333 (1954).

Toluene (Hommel Company, certified pure) 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.

Reaction of Phosphoryl Chloride with Methylamine.—A preliminary study of the reaction of phosphoryl chloride and excess methylamine in the vacuum line suggested that the equation for the process is

$$POCl_3 + 6CH_3NH_2 \longrightarrow PO(NHCH_3)_3 + 3CH_3NH_3^+Cl^- \quad (1)$$

The product was a white pasty solid.

The reaction was studied further on a larger scale with the aid of the apparatus and attachments used earlier in the preparation of phosphorus tri-N-methylimide.[5]

Methylamine (64.6 ml., 1.6 moles) was condensed into a 2-l. resin kettle, the latter previously flushed with dry nitrogen and surrounded by a −78° bath. Phosphoryl chloride (18.3 ml., 0.2 mole), present in the dropping funnel, was added cautiously with stirring over an hour period. A white solid resulted. During the next four days the temperature of the bath rose slowly to 25°, while the reaction mixture, occasionally stirred, was maintained under a positive nitrogen pressure. Most of the excess methylamine volatilized leaving a white pasty solid. The remaining methylamine was removed by pumping on the reaction mixture while the temperature was maintained at 50°.

Portions of the pasty product were removed from the kettle and stirred with chloroform. The hydrochloride by-product was filtered off in an all-glass vacuum filtering apparatus and identified by its m.p., 226°, and infrared spectrum. The filtrate, warmed to 50°, was concentrated by vacuum distillation; however, the clear viscous liquid product still contained chloroform, as shown by a chlorine analysis (11.50%) and by the infrared spectrum. Intense peaks not assigned to chloroform were present at 3290(s), 2960(s), 1465(m), 1405(s), 1170(m), 1100(s), 985(m), and 875(s) cm.$^{-1}$. That the peak assignment is correct was substantiated by obtaining the infrared spectrum of the same sample with additional chloroform added and noting the drop in intensity of all of the above mentioned peaks.

Attempts to separate the hydrochloride from the desired amide, $PO(NHCH_3)_3$, by using solvents such as petroleum ether (both 20–40° and 30–60° fractions), toluene, diethyl ether, and benzene or by using a procedure similar to that developed by Klement and Koch[7] to separate $PO(NH_2)_3$ from NH_4Cl were unsuccessful.

A proton resonance spectrum of a chloroform solution of the viscous liquid product was obtained at 60 M.c.p.s. The results indicate that the product is $PO(NHCH_3)_3$. In addition to the chloroform peak at −2.5 p.p.m. the spectrum consisted of a broad peak at +1.8 p.p.m. and a sharp doublet at +2.5 p.p.m. (water is the reference liquid). The latter doublet in the region characteristic of a N–CH_3 grouping possessed a coupling constant of 12.7 c.p.s. ascribed to the methyl protons being split by spin–spin interaction with the phosphorus atom.[5] The doublet was approximately three times as intense as the broad peak (weighing peaks). Hence, the broad peak is assigned to the N–H protons. Poor resolution for N–H protons is observed frequently, as here, due to the quadrupolar effects of nitrogen.[8]

Preparation of Diphosphoryl Tri-N-methylimide, $P_2O_2(NCH_3)_3$. Procedure A.—Pyrolytic condensation of the unseparated phosphoric triamide–methylamine hydrochloride paste-like mixture resulting from the $POCl_3$–CH_3NH_2 reaction described above provided the best route to diphosphoryl tri-N-methylimide, $P_2O_2(NCH_3)_3$. The reaction represented by the equation

$$PO(NHCH_3)_3 \xrightarrow{300°} (PO)_2(NCH_3)_3 + \text{amines} \quad (2)$$

is summarized below.

A portion of the paste-like mixture was heated in an evacuated 25-mm. diameter tube surrounded by a horizontal tube furnace. A ground glass joint connected the tube to a U-trap cooled with liquid nitrogen to collect the amines coming off; the trap in turn was connected to a pump. The temperature was brought to 300° in a 2-hr. period.[9] At 150° gaseous products first were being condensed in the U-trap while hydrochloride sublimate appeared on the walls of the tube just outside the furnace area. At 215° the paste had completely liquefied and the hydrochloride sublimate increased in amount. At 240° tannish solid began to appear in the liquid, the conversion to solid being completed by the time the temperature had reached 300°. The temperature then was maintained at 240° for 3 hr. to insure completion of the reaction. The cooled tube was broken between the hydrochloride sublimate and the amorphous tan product. Analysis of the latter showed it to be diphosphoryl tri-N-methylimide, $P_2O_2(NCH_3)_3$, uncontaminated by any hydrochloride as shown by the chlorine analysis.

Anal. Calcd. for $P_2O_2N_3C_3H_9$: C, 19.90; H, 5.01; N, 23.21; P, 34.21. Found: C, 19.60; H, 5.26; N, 23.52; P, 34.26; Cl, 0.00. In one preparation the total gases evolved were subjected to mass spectral analysis. Found: CH_3NH_2, 86.37%; $(CH_3)_2NH$, 11.27%; $(CH_3)_3N$, 2.35%.

$P_2O_2(NCH_3)_3$ also may be prepared in a fashion similar to that described above but first the methylamine hydrochloride is separated from the paste-like mixture using chloroform, followed by thermal treatment of the resulting viscous oil; however, analysis of the product does not provide as good agreement with the formula, $P_2O_2(NCH_3)_3$, as in the first preparation described.

Anal. Found: C, 19.15; H, 5.17; N, 23.98; P, 35.89. Mass spectral analysis of the total gases evolved in the thermal treatment was similar. In addition the first fraction of gas coming off in this preparation was analyzed, *i.e.*, in the temperature range 140 to 220° (140° being the temperature where evolution first is noticed). Found: CH_3NH_2, 83.01%; $(CH_3)_2NH$, 0.72%; $(CH_3)_3N$, 0.18%; $CHCl_3$, 16.17%.

If the paste-like product of the $POCl_3$–CH_3NH_2 reaction is heated at 230° instead of 300° in an evacuated tube furnace, the hydrochloride sublimes out much more slowly, taking three days to reduce the chlorine content to 0.32% as shown by elemental analysis on samples periodically taken. The material remaining at the end of the heating period was a non-sublimable, insoluble white solid having a composition approaching $P_2O_2N_3C_2H_7$.

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(8) 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. 102.

(9) Above 300° non-condensable gases are given off as discussed under the thermal behavior of diphosphoryl tri-N-methylimide.

Anal. Calcd. for $P_2O_2N_3C_2H_7$: C, 14.38; H, 4.22; N, 25.16; P, 37.08. Found: C, 13.16; H, 4.22; N, 23.59; P, 36.30. The gases evolved consisted of an amine mixture shown by mass spectral analysis to have the composition: CH_3NH_2, 69.6; $(CH_3)_2NH$, 27.1; $(CH_3)_3N$, 3.4. The infrared spectrum of a Nujol mull of the white solid was similar to that of $P_2O_2(NCH_3)_3$ (Table I), except for the introduction of a moderate band at 3175 cm.$^{-1}$ in the region assigned to N–H imide stretching.[10] Heating the solid to 300° caused the evolution of a small amount of gas; however, the infrared spectrum remained unchanged.

Procedure B.—Compositions approaching $P_2O_2(NCH_3)_3$ also may be realized by oxidation of the recently reported[4,5] phosphorus tri-N-methylimide, $P_4N_6(CH_3)_6$. In a typical preparation $P_4N_6(CH_3)_6$ (1.091 mmoles) was measured out in a small glass weighing tube and placed inside an ampoule using dry-box techniques. The ampoule had a main stem connected to a ground glass joint surrounded by a mercury well. A side arm led to a break tip and then returned at a higher point on the main stem. A seal-off area on the main stem was provided between the side arm extension and return. The ampoule was evacuated after attachment to a special "reaction" section of the vacuum line, previously described.[11] After sublimation of the imide out of the weighing tube onto the walls of the ampoule, dry oxygen was admitted (4.21 mmoles) and the pressure recorded. The ampoule was sealed at the seal-off area and heated at 175° in an oven for 8 hr. Within the first 20 min. of heating, white solid started to form from the liquid imide. At the end of the heating period mostly whitish-tan solid was present; in addition, a small amount of glassy material was noted. The reaction stoichiometry was determined by re-attaching the ampoule to the "reaction" section, opening the ampoule via the break tip (after having determined the volume above the break tip, 44.5 ml.) and recording the pressure, 390.5 mm. The volatile contents were non-condensable with liquid nitrogen as noted by slow passage through a trap so cooled. The entire "reaction" section volume, 249.3 ml., was determined with dry oxygen and by assuming the volatile component of the reaction product to be unreacted oxygen it was found that 2.43 mmoles of oxygen had reacted, or 2.2 moles of oxygen per mole of imide. Prolonging the heating period to five days did not significantly change the stoichiometry nor the appearance of the products. Elemental analyses varied, a typical preparation showing these results.

Anal. Calcd. for $P_2O_2N_3C_3H_9$: C, 19.90; H, 5.01; N, 23.21; P, 34.21. Found: C, 19.81; H, 5.19; N, 21.26; P, 31.35.

Properties of Diphosphoryl Tri-N-methylimide.—Products of both procedures described above were tannish in appearance, did not melt, dissolved slowly in water with the release of bubbles, but did not visually appear to react with atmospheric moisture during the course of one week; however, after prolonged exposure they liquefied. The products were found to be insoluble in benzene, carbon tetrachloride, chloroform, petroleum ether, diethyl ether, nitrobenzene, absolute alcohol, acetone, pyridine, toluene, phosphorus trichloride, and phosphoryl chloride.

Infrared spectra of samples in Nujol mulls are compared in Table I and seen to be the same except for a peak at 1720 cm.$^{-1}$ in the sample obtained from $P_4N_6(CH_3)_6$.

TABLE I

INFRARED DATA FOR DIPHOSPHORYL COMPOUNDS

$P_2O_2(NCH_3)_3$ from $POCl_3$ Procedure A cm.$^{-1}$	$P_2O_2(NCH_3)_3$ from $P_4N_6(CH_3)_6$ Procedure B cm.$^{-1}$	$P_2O_2(NCH_3)_2NH$[a] cm.$^{-1}$
		3175 m
2940 s	2960 s	2910 s
2875 s	2875 s	2830 s
	1720 m	
1650 m	1650 m	1655 w
1460 s	1460 s	1465 s
1380 s	1380 s	1375 s
1090 m	1090 m	1080 m

[a] Formulation indicated.

Thermal Behavior of Diphosphoryl Tri-N-methylimide.—Thermal treatment of products from both procedures A and B was accomplished by means of a small tube furnace surrounding an ampoule attached vertically to the vacuum line. The gases evolved from the samples in the ampoules were collected in the line. The behavior was similar in each case. Evolution of gases (mostly non-condensable) initiated at 320° and continued up to 550° where heating was discontinued. The samples were held at 550° until gas evolution seemed to cease. Mass spectral analysis of the gaseous mixture from the thermal treatment of the product of procedure B gave the following mole percentages: H_2, 34.6; NH_3, 31.6; CH_4, 22.9; $(CH_3)_3N$, 5.4; $(CH_3)_2NH$, 2.4; CH_3NH_2, 1.9; N_2, 1.0. The solids remaining in both cases were lustrous in appearance, grayish-black, and had compositions intermediate between the starting composition and PNO. Thus in one treatment of $P_2O_2(NCH_3)_3$ prepared by procedure A, the solid remaining at 550° had the composition $P_{1.00}N_{0.98}C_{0.72}H_{1.28}O_{1.00}$, as shown by elemental analysis (oxygen by difference). Further heating to 650° lowered the CH content and gave the formula $P_{1.00}N_{1.00}C_{0.48}H_{0.56}O_{0.87}$.

Discussion

The reactions may be summarized by the equations

$$POCl_3 + 6CH_3NH_2 \longrightarrow PO(NHCH_3)_3 + 3CH_3NH_3^+Cl^- \quad (1)$$

$$2PO(NHCH_3)_3 \xrightarrow{300°} P_2O_2(NCH_3)_3 + \text{amines} \quad (2)$$

$$2PO(NHCH_3)_3 \xrightarrow{230°} P_2O_2(NCH_3)_2NH + \text{amines} \quad (3)$$

$$P_4(NCH_3)_6 + 2O_2 \xrightarrow{170°} P_2O_2(NCH_3)_3 \quad (4)$$

$$(PO)_2(NCH_3)_3 \xrightarrow{650°} PNOC_xH_y + \text{gases} \quad (5)$$

The stoichiometry established for the first reaction, identification of the hydrochloride formed, and n.m.r. spectrum of the chloroform solution of the product establish reasonably well

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(10) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 265.

(11) H. C. Brown, L. P. Eddy, and R. Wong, *J. Am. Chem. Soc.*, **75**, 6275 (1953).

the amide formulation, $PO(NHCH_3)_3$. The strong peak in the infrared at 3290 cm.$^{-1}$ is in the region assigned by Steger[12] to N–H stretching in the related $PO(NH_2)_3$ and serves as additional support, particularly since it is noted to be absent in $P_2O_2(NCH_3)_3$.

The pyrolytic condensation of the amide at 300° (reaction 2) led to the characterizable substance, $P_2O_2(NCH_3)_3$. One would expect only CH_3NH_2 to be evolved in the condensation. This is what was observed in the initial stages (99.00% CH_3NH_2) but as the reaction continued some $(CH_3)_2NH$ and $(CH_3)_3N$ were formed indicating the presence of small amounts of additional products, not isolated.

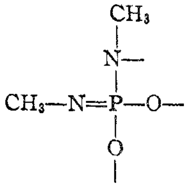
Taking note of the work of Goehring and Niedenzu[13] who prepared $(NH_2)_2P(O){-}N(H){-}P(O){-}(NH_2)_2$ from $PO(NH_2)_3$ suggests analogous substances may be involved as intermediates in the formation of $P_2O_2(NCH_3)_3$ from $PO(NHCH_3)_3$, for example, $(NHCH_3)_2P(O){-}N(CH_3){-}P(O)(NHCH_3)_2$; however, an attempt to isolate such substances by lowering the temperature of the thermal treatment to 230° yielded white solids having somewhat varying compositions near $P_2O_2(NCH_3)_2NH$ (reaction 3). The mass spectral analyses of the amines given off increased in $(CH_3)_2NH$ composition at the lower temperature in agreement with the latter formulation, as is the appearance of a peak at 3175 cm.$^{-1}$ in the region of the N–H stretching frequency in the infrared.[10] The lower temperature then apparently is more favorable to the breakage of N–C bonds.

The formation of $P_2O_2(NCH_3)_3$ most likely results as an end product of the condensation process. Initial condensation of $PO(NHCH_3)_3$ to give an intermediate of the type mentioned above followed by further condensations is readily seen to result in the formulation $P_2O_2(NCH_3)_3$, wherein tetrahedral phosphorus would exist in the basic unit, $PO(NCH_3)_3$, provided the CH_3 groups remain attached to nitrogen and do not rearrange to phosphorus during the polymerization. Some evidence supporting the retention of the $N{-}CH_3$ grouping is provided by the fact that during the thermal treatment of $P_2O_2(NCH_3)_3$ no methylphosphines were produced, only methylamines and non-condensable gases.

The polymeric structure[14] described for $P_2O_2(NCH_3)_3$ is consistent with the properties obtained, for example, insolubility, no detectable vapor pressure at 300°, and lack of melting on heating to 650° (the latter heating corresponding to a conversion toward a PNO composition, reaction 5).

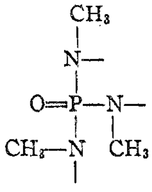
The preparation of $P_2O_2(NCH_3)_3$ by the direct oxidation of $P_4(NCH_3)_6$ (reaction 4) logically would lead one to suppose that a structure analogous to phosphorus pentoxide would result for $P_2O_2(NCH_3)_3$, since data[4,5] support a structure analogous to phosphorus trioxide for $P_4(NCH_3)_6$. On the basis of the previous argument this may very well be the case. When one links up $PO(NCH_3)_3$ tetrahedra through the N atoms leaving the O atom singly coördinated a layer arrangement results. The latter arrangement could correspond closely to the known layer arrangements in the isoelectronic P_4O_{10} structures.[6]

It is necessary to leave one of the atoms singly coördinated in order to have agreement with the empirical formula, $P_2O_2(NCH_3)_3$; however, it does not have to be an oxygen atom. It could equally well be a $N{-}CH_3$ group, especially since the latter is isoelectronic with oxygen. The basic unit then would be



$$\mathrm{CH_3{-}N{=}\underset{\underset{|}{\overset{|}{O}}}{\overset{\overset{\overset{CH_3}{|}}{N-}}{\overset{|}{P}}}{-}O{-}}$$

rather than



$$\mathrm{O{=}\underset{\underset{|}{\overset{|}{CH_3{-}N}}}{\overset{\overset{\overset{CH_3}{|}}{N-}}{\overset{|}{P}}}{-}\underset{\overset{|}{CH_3}}{N}{-}}$$

$PO_2(NCH_3)_2$
(I)

$PO(NCH_3)_3$
(II)

Information is lacking to decide among the structural possibilities. Infrared data were found to be of little use (Table I). For one, the phosphoryl stretching frequency usually occurs in the region[15] 1170–1310 cm.$^{-1}$. The corresponding frequency for P=N— is in a similar region,[16] 1170–1380 cm.$^{-1}$. The nearest peaks observed for $P_2O_2(NCH_3)_3$ are 1090 and 1380 cm.$^{-1}$, the former being outside the "normal" region and the latter just at the upper end of the P=N— region. Structure (II) might seem to be ruled out on this basis; however, phosphorus pentoxide itself has no band in the region cited for the P=O vibration,[15] the nearest peaks[17] being moderate to weak

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[12] E. Steger, *Z. Elektrochem.*, **61**, 1004 (1957).

[13] M. Goehring and K. Niedenzu, *Ber.*, **89**, 1771 (1956).

[14] Condensations of $PO(NHCH_3)_3$ could equally well be expected to give a molecular structure in agreement with the observed formula, $P_2O_2(NCH_3)_3$; however, properties indicate that this is not what is occurring.

[15] L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).

[16] N. L. Paddock and H. T. Searle, "Advances in Inorganic Chemistry and Radiochemistry," ed., H. J. Emeleus and A. G. Sharpe, Vol. I, Academic Press, Inc., New York, N. Y., 1959, p. 372.

[17] T. Sidorov and N. Sobolev, *Optika i Spectroskopiya*, **2**, 717 (1957).

at 1150 and 1140 cm.$^{-1}$ with a strong peak at 1390 cm.$^{-1}$. Accordingly, it is not unusual then to note a similar absence for a substance presumed to be related structurally. Regarding the presence of a P═N group, again caution must be exercised since assignments on analogous compounds are lacking.

In phosphoric triamide, $PO(NH_2)_3$, Steger[12] assigned an observed 1200 cm.$^{-1}$ peak to the P═O group, which is close to the 1170 cm.$^{-1}$ peak observed (Table I) for the related phosphoric tri-N-methylamide, $PO(NHCH_3)_3$ (chloroform solution).

The above discussion is given as an insight into the structural features that may be encountered and it is hoped that it will prove useful as a guide to future research.

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CONTRIBUTION FROM THE WHITTIER RESEARCH LABORATORY,
AMERICAN POTASH & CHEMICAL CORPORATION, WHITTIER, CALIFORNIA

Preparation of Some Unsymmetrically Substituted Borazines[1,2]

BY ROSS I. WAGNER AND JAMES L. BRADFORD

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N-Lithio-substituted borazine compounds, N-lithio-B-trimethylborazine, N-dilithio-B-trimethylborazine, N-lithiopentamethylborazine, and N-dilithiotetramethylborazine, have been prepared as a new class of derivatives which enable a ready preparation of unsymmetrically substituted N-alkylborazines by reaction with alkyl halides. Reaction of partially B-alkylated borazines with a stoichiometric quantity of hydrogen halide yields the corresponding B-alkyl-B-haloborazine derivatives in high purity and yield. Physical constants for a number of new borazine derivatives are given together with newly determined physical constants for several known borazine derivatives.

Since the discovery of borazine by Stock[3] a considerable volume of literature on the chemistry of borazine and its derivatives has been published and reviewed extensively.[4] Synthetic approaches to borazine derivatives fall into two principal classifications: (1) those in which the substituents are attached either to the nitrogen or boron precursors or both, and (2) those in which one substituent is replaced by another on a borazine nucleus. Both of these synthetic approaches lead generally to derivatives in which substitution is symmetrical with respect to the nitrogen and boron atoms.

Only a few borazine derivatives which are unsymmetrically substituted with respect to one or both of the skeletal atoms have been reported. Schlesinger, Burg, and co-workers report the only use of a mixture of precursors to prepare B-methyl- and B-dimethylborazines[5] and also N-methyl- and N-dimethylborazines.[6] A greater but limited number of examples of replacement reactions are to be found wherein unsymmetrically substituted borazines have been prepared. In each of these references replacement has been limited to boron substituents only. Trimethylborine,[6] elemental chlorine and bromine,[7] trichloro- and tribromo-

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(2) Throughout this paper the use of N defines a mono-substitution product on nitrogen. Di- and tri-substitution products on nitrogen (or similarly on boron) are indicated by the symbol of the element and the appropriate Greek numerical prefix eliminating the superfluous N′, and N″ symbols of the often used N,N′,N″ nomenclature, *e.g.*, N-methylborazine, N-dilithio-B-trimethylborazine, N-trimethyl-B-methylborazine, etc. For the sake of brevity simple names which connote a unique structure are used rather than the more generally definitive nomenclature just described, *i.e.*, pentamethyl-B-chloroborazine rather than N-trimethyl-B-dimethyl-B-chloroborazine or 1,3,4,5,6-pentamethyl-2-chloroborazine, N-dilithiotetramethylborazine rather than N-methyl-N-dilithio-B-trimethylborazine or 1,3-dilithio-2,4,5,6-tetramethylborazine, etc.

(3) A. Stock and E. Pohland, *Ber.*, **59**, 2215 (1926).

(4) (a) F. G. A. Stone, *Quart. Revs.* (London), **9**, 174 (1955); (b) E. M. Smolin and L. Rapoport, "*s*-Triazine and Derivatives," Interscience Publishers, New York, N. Y., 1959, Chapter XI; (c) J. C. Sheldon and B. C. Smith, *Quart. Revs.* (London), **14**, 200 (1960).

(5) H. I. Schlesinger, L. Horvitz, and A. B. Burg, *J. Am. Chem. Soc.*, **58**, 409 (1936).

(6) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *ibid.*, **60**, 1296 (1938).

(7) E. Wiberg and A. Bolz, *Ber.*, **73**, 209 (1940).