

SYNTHESIS AND SOME REACTIONS OF SOME
DIAMINO- AND TRIAMINOPHOSPHONIUM
CHLORIDES

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CHAPTER I

INTRODUCTION

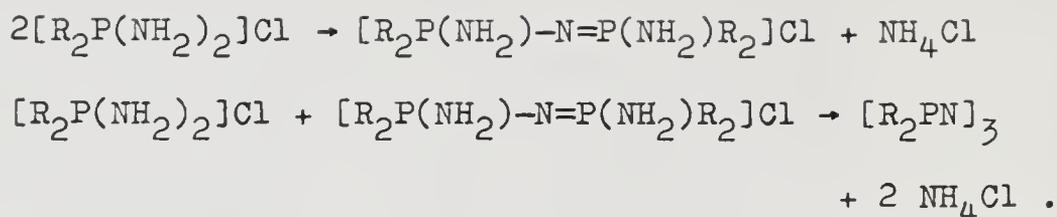
In recent years an area of study dealing with the synthesis of phosphonitrilic derivatives and precursors has been under investigation in our laboratories. Our interest in this study was heightened by the discovery⁽¹⁾ that diphenylchlorophosphine undergoes ammonolysis and chloramination producing diphenylphosphonitrilic trimer and a phosphonitrilic precursor,^(2,3,4) $[(C_6H_5)_2P(NH_2)-N=P(NH_2)(C_6H_5)_2]Cl$. On the basis of this discovery a general reaction sequence was postulated in which it was proposed that the chlorophosphine is ammonolyzed with excess ammonia,



the aminophosphine reacts with chloramine to yield the diaminophosphonium chloride,



and the diaminophosphonium salt undergoes condensation giving the observed products,



Further evidence for this reaction sequence was found in the study of the ammonolysis and chloramination of dialkylchlorophosphines.⁽⁵⁾ With dialkylchlorophosphines the chloramine-ammonia reaction produced dialkyldiaminophosphonium salts in which the alkyl group was methyl, ethyl or n-butyl. In addition, the salt, $[(\text{C}_2\text{H}_5)_2\text{P}(\text{NH}_2)-\text{N}=\text{P}(\text{NH}_2)(\text{C}_2\text{H}_5)_2]\text{Cl}$, and the trimer, $[(\text{n-C}_4\text{H}_9)_2\text{PN}]_3$ ⁽⁶⁾ were produced. It was postulated that these phosphonium salts should undergo self-condensation reactions eliminating ammonium chloride and forming phosphonitrilic derivatives. In addition, it was predicted that interesting phosphonitrilic derivatives should result from the reactions of these salts with PCl_5 , RPCl_4 , or R_2PCl_3 where R can be either an alkyl or an aryl group. It was hoped that a study of these processes would not only reveal a method by which cyclic derivatives could be synthesized, but would also lead to high-molecular-weight phosphonitrilic polymers.

Although it had been shown that diamminophosphonium salts can be synthesized by chloramination and ammonolysis of dialkylchlorophosphines, it was thought that these salts

might also result from the chloramination of substituted diphosphines. An extension of this method to polyphosphines, $(RP)_n$, might also result in the synthesis of triaminophosphonium chlorides.

Therefore, the purpose of this study was (1) to investigate the chloramination-ammonolysis of substituted diphosphines and tetraphenylcyclotetraphosphine; (2) to investigate the self-condensation reactions of diamino- and triamino-phosphonium salts and $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$; and (3) to investigate the condensation reactions of some diaminophosphonium salts with PCl_5 , CH_3PCl_4 , and $(CH_3)_2PCl_3$.

CHAPTER II

HISTORICAL BACKGROUND

Phosphonitrilic Derivatives

The first phosphonitrilic derivatives to be synthesized were the phosphonitrilic chlorides, $[\text{Cl}_2\text{PN}]_n$, formed by the reaction of PCl_5 and ammonia. This reaction was noted by Liebig in 1834.⁽⁷⁾ Although Liebig did not correctly deduce the empirical formula of the product of this reaction, it was not long before other workers⁽⁸⁾ confirmed the formula $[\text{Cl}_2\text{PN}]_n$. The most significant early study in this field was carried out by Stokes who published a series of papers⁽⁹⁾ dealing with the reaction of PCl_5 with NH_4Cl . He confirmed the formation of $\text{P}_3\text{N}_3\text{Cl}_6$ and $\text{P}_4\text{N}_4\text{Cl}_8$, obtained the first reliable physical data on these compounds, and studied their ammonolytic and hydrolytic reactions. Stokes perfected the method of forming these derivatives and discovered higher members of the homologous series, $[\text{Cl}_2\text{PN}]_n$, from $n=3$ to $n=7$. It was Stokes who originated the name "phosphonitrilic" polymer and who first postulated, for the lower members, cyclic structures with alternating phosphorus and nitrogen atoms. He also isolated a highly polymeric phosphonitrilic "rubber," a discovery

which has contributed to the renewed interest in phosphonitrilic derivatives in recent years.

Since the discovery of the phosphonitrilic chlorides, a large number of derivatives have been synthesized in which the substituents on the phosphorus atoms vary widely. These substituents can be halogens, pseudo-halogens, alkyl-, perfluoroalkyl-, aryl-, aryloxy-, and alkoxy-groups, N-substituted primary and secondary amines, OH and several others.

The phosphonitrilic structure, first suggested by Stokes, has been investigated and confirmed by infrared and ultraviolet spectroscopy, nuclear magnetic and quadrupole resonance studies, and electron and X-ray diffraction. References to these works are listed in the various reviews available on this subject.^(10,11,12) The phosphonitrilic derivatives are now known to contain a backbone of alternate phosphorus and nitrogen atoms in which all of the P-N bonds are of equal length. The trimer, the first member of the homologous series, has a planar, six-membered cyclic structure



The tetramer and higher members of the $(R_2PN)_n$ series ($R=Cl, F$) through $n=17$ are also cyclic.⁽¹³⁾ They are not planar but have puckered configurations which give improved overlap of d-orbitals on phosphorus with the lone-pair orbitals on nitrogen providing increased delocalization of the lone-pairs and hence, greater stability. In a number of derivatives for which measurements have been made, the average length of the P-N bond is 1.56 Å. This bond length depends on the group attached to phosphorus and on the size of the ring since it is affected by delocalization of the unshared pair on nitrogen. The N-P-N bond angles are all about 120°, however, the P-N-P angle varies from 120° to 150° depending on the ring size and the substituents on phosphorus. The P^{31} magnetic resonance spectra of the cyclic derivatives in which the phosphorus atoms have the same substituents have a single peak indicating that the equivalence of the phosphorus atoms is independent of ring conformation.

The bonding in phosphonitrilic derivatives is quite interesting and a number of structural features can be rationalized in terms of the bonding theories which have been proposed. X-ray studies have shown that the phosphorus atom is in an almost tetrahedral environment in the derivatives studied. Thus its single bonds may be considered to be formed using principally sp^3 hybrid orbitals. In the

trimer the P-N-P angle is nearly 120° and the nitrogen atom is in a trigonal environment. The sigma-bonding electron pairs and the lone-pair occupy approximate sp^2 hybrid orbitals. The fourth nitrogen electron pair occupies a p -orbital and can contribute to pi-bonding with phosphorus. The pi-bonding in phosphonitrilics has excited a lively controversy in the recent literature.^(14,15) The structures shown above imply a resonance of the double bonds and a bonding picture which is similar to that employed for benzene. However, this analogy is complicated by the necessity of using phosphorus d-orbitals in forming pi-bonds. The d-orbitals are arranged in space in such a way that considerable overlap with the nitrogen p -orbital, the sp^2 -hybridized lone-pair orbital and with ligand orbitals occurs. Several theoretical descriptions have been proposed for this type of system.

Craig⁽¹⁶⁾ has stated that because of the low local symmetry of the phosphorus atom in phosphonitrilics, the d-orbitals are completely non-degenerate. Four d-orbitals, d_{xy} , d_{xz} , d_{yz} , $d_{x^2-y^2}$, contribute to the overall pi-bonding (the d_z^2 -orbital can be involved in exocyclic pi-bonding but this is not considered to be of importance), and the contributions need not be equal.

For pi-bonding, Craig considers the overlap of phosphorus d_{xz} -orbitals with nitrogen p_z -orbitals, shown in

Figure 1. The results of his molecular orbital calculations show that, unlike benzene, the highest energy bonding orbital is non-degenerate, as shown in Figure 2. This leads to an aromatic system of delocalized electrons which is distinctly different from that encountered in carbon compounds which utilize only p -orbital overlap. Any even number of pi-electrons gives a closed shell. Huckel's $4n + 2$ rule does not hold. This theory predicts that the delocalization energy per electron increases steadily to a limiting value as the number of pi electrons increases with increasing ring size. Thus the trend in average P-N bond energy (Table 1) is cited as a confirmation of this theory.

TABLE 1⁽¹⁶⁾AVERAGE P-N BOND ENERGY IN $(\text{PNCl}_2)_n$

n in $(\text{PNCl}_2)_n$	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
$E(\text{P-N})_n - E(\text{P-N})_3$ (Kcal)	0	0.39	0.54	0.60	0.62

Dewar,⁽¹⁵⁾ on the other hand, takes advantage of the favorable symmetry properties of the d_{yz} orbital on phosphorus as well as the favorable overlap properties of the d_{xz} orbital. Thus he has hybridized these orbitals to form two new pi-orbitals: $d_{\pi a} = \frac{1}{2}(d_{xz} + d_{yz})$ and $d_{\pi b} = \frac{1}{2}(d_{xz} - d_{yz})$.

Figure 3 shows a N-P-N segment of the phosphonitrile structure and illustrates the approximate geometry of the

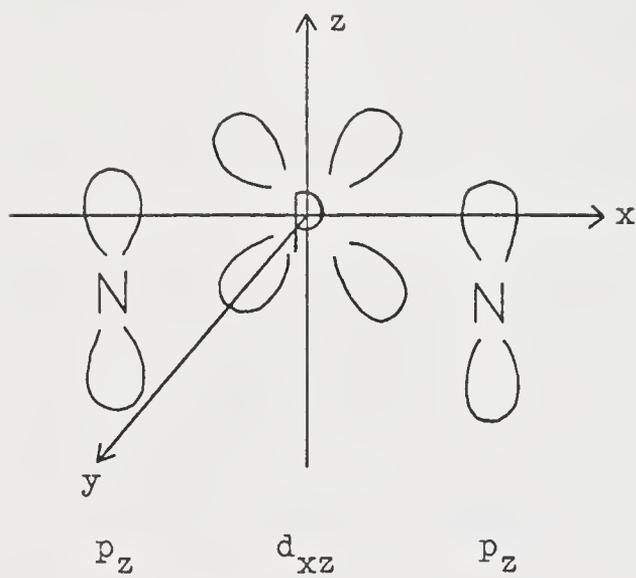


Fig. 1.-Overlap of N_{p_z} Orbitals with $P_{d_{xz}}$ Orbital.

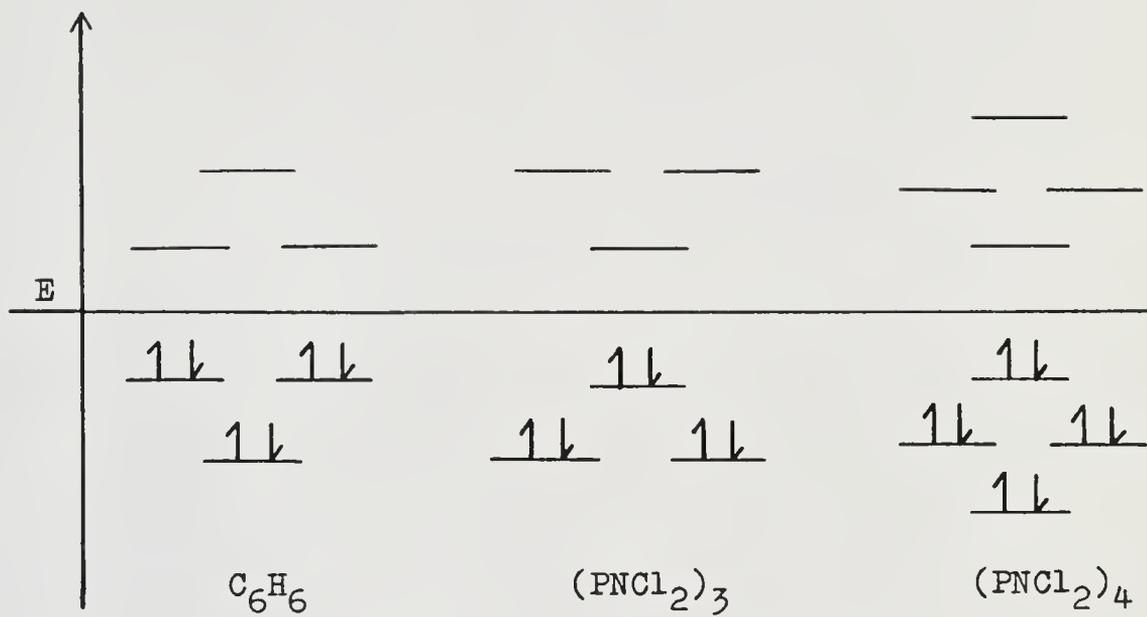


Fig. 2.-Pi-Electron Energy Levels of C_6H_6 , $(PNC1_2)_3$ and $(PNC1_2)_4$. (16,17)

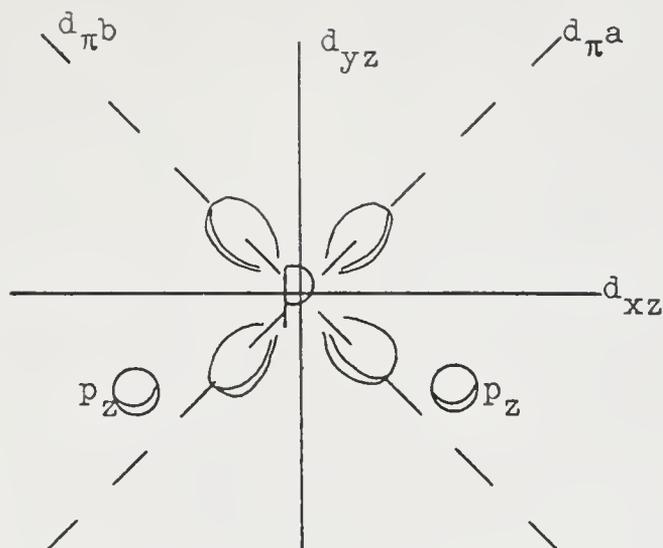


Fig. 3.-Overlap of $P_{d_{\pi}}$ -Orbitals with N_{p_z} -Orbitals.

new pi-orbitals. These hybridized pi-orbitals overlap nitrogen p_z orbitals on both sides of the phosphorus atom to form the pi-bonding system. Instead of an extensive aromatic system, however, this method describes P-N-P units connected by localized three-center bonds (Fig. 4). The



Fig. 4.-Localized, Three-Center P-N-P Bonds in a Phosphonitrile Segment.

relatively simple molecular orbital calculations indicate that the delocalization energy is on the order of $0.82 n\beta$ where β is the resonance integral and n is the number of P-N units. This is considered a high value and therefore the theory predicts high stability for the phosphonitrilic structure. Unlike Craig's theory, this approach indicates that the properties which depend on the pi-system alone should not change with increasing ring size. Certain spectral measurements are cited in support of this approach. (18)

Superimposed on the sigma- and pi-bonding in phosphonitriles is a third bonding system referred to as the pi'-system. This system arises from the overlap of the $d_{x^2-y^2}$ and d_{xy} -orbitals of phosphorus with nitrogen lone-pair orbitals. As mentioned above, the unshared pair of electrons on nitrogen occupies an s-p hybridized orbital. In the trimeric molecules where the P-N-P bond angle is about 120° this orbital is an sp^2 hybrid. However, in the tetramer and larger derivatives the bond angle becomes greater, the lone-pair orbital obtains more p-character, and greater overlap with phosphorus d-orbitals can occur. Electron density can therefore increase on phosphorus at the expense of nitrogen in this second delocalized system.

In rationalizing the chemical and physical properties of phosphonitrile derivatives it is difficult to separate

the several effects arising from interactions of the three bonding systems and the inductive effects of the substituents on phosphorus. An example of this is presented by Feakins et al.,⁽¹⁹⁾ in a thorough study of the basicity of phosphonitrilic derivatives. The observed trend in base strength as the ligands on phosphorus were changed, or as trimers and tetramers were compared, could not be explained by either pi-bonding theory alone. The data could be rationalized, however, by considering the various effects mentioned above, and the conclusion was reached that the base strengths depend in a complex way on a number of parameters.

It has been established that the base strength of⁽²⁰⁾ phosphonitrilic derivatives is dependent upon the availability of nitrogen lone-pair electrons in the ring and that protonation occurs on the ring. Thus, delocalization of the nitrogen lone-pair into the region of the P-N bond has the effect of decreasing the base strength and increasing the P-N bond strength. Both of these effects are sensitive to small changes in the ability of the substituent on phosphorus to accept electrons and can therefore be roughly correlated with the electronegativity of the substituent. Table 2 shows the increase in base strength of certain derivatives with a decrease in the electronegativity of the ligand.

TABLE 2⁽¹⁹⁾

BASE STRENGTH OF PHOSPHONITRILIC DERIVATIVES TOWARD
PROTONS IN NITROBENZENE AND WATER

<u>R</u>	<u>Cl</u>	<u>OC₂H₅</u>	<u>C₆H₅</u>	<u>C₂H₅</u>	<u>NHC₂H₅</u>	<u>N(C₂H₅)₂</u>
pK _a (NPR ₂) ₃	<-6.0	-0.2	1.5	6.4	8.2	8.5
pK _a (NPR ₂) ₄	<-6.0	0.6	2.2	7.6	8.1	8.3
				5.9 (water)	8.7 (water)	
				6.5 (water)	8.7 (water)	

In the infrared spectra of phosphonitrilic derivatives there occurs a strong band in the region of 1100-1400 cm⁻¹ (see Table 3) which is attributed to P-N ring stretching. The position of this peak is quite variable and the variation can be correlated with the electronegativity of the group attached to phosphorus. If the group has a high electronegativity the nitrogen lone-pair electrons can be delocalized into the region of the P-N bond, strengthening that bond and increasing the frequency at which the infrared peak occurs. Conversely, if the group has a low electronegativity or is an electron releasing group such as an amine, the nitrogen lone-pair is localized on the nitrogen atom and the P-N stretching frequency occurs at lower energy. This effect is illustrated in Table 3.

TABLE 3

VARIATION OF P-N STRETCHING FREQUENCY WITH ELECTRONEGATIVITY OF EXOCYCLIC GROUPS

Group	Electro- negativity ^(a)	P-N Stretching Frequency, Cm ⁻¹		Ref.
		Trimer, <u>(R₂PN)₃</u>	Tetramer, <u>(R₂PN)₄</u>	
F	4.0	1305	1435	23
Cl	3.0	1218	1315	24
C ₆ H ₅	1.74	1190	1213	25
CH ₃	1.57	1180	1220	26
NH ₂	--	1175	1240	27
C ₂ H ₅	1.2	1157	1280	25
n-C ₄ H ₉	0.9	1155	--	6

^(a)Electronegativities of F and Cl are Pauling's⁽²¹⁾ values; others are calculated from the formula,⁽²²⁾ $X_R = X_H \pm 0.183 \{D(R-H) - [D(R-R) - D(H-H)]^{1/2}\}^{1/2}$.

Obviously the foregoing discussion is a simplification. Such properties as the base strength and P-N stretching frequency also depend on a number of factors not mentioned in connection with the bonding theory. In any thorough analysis one must consider the steric requirements of the ligands, hydrogen-bonding of the ligands, and ring conformation. These factors affect the overlap of ligand orbitals and ring-nitrogen orbitals with phosphorus d-orbitals and thus may change the expected order of base

strengths or the expected P-N stretching frequency. In addition, the electron releasing or accepting abilities of the groups on phosphorus will not affect the pi'-electrons alone but will also affect the sigma- and pi-electrons to some extent.

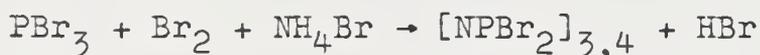
This brief discussion indicates the advancements which have been made since Stokes' pioneering work in understanding the structure and bonding in phosphonitrilic derivatives. Clearly, more experimental data are necessary for a complete evaluation of the bonding theories.

Since the work of Stokes, a wide variety of phosphonitrile derivatives have been synthesized. A large number of derivatives may be synthesized because of the wide variety possible in the nature of the groups attached to the phosphorus atom. In addition, the groups on phosphorus in a given molecule can be different from each other. In the cyclic trimer, for example, the groups on neighboring phosphorus atoms can differ. The methods of synthesis of phosphonitrilic derivatives can be considered in two general classes: synthesis from non-phosphonitrilic starting materials, and substitution of the desired group on a previously synthesized P-N backbone. An example of the first method is the synthesis of the phosphonitrilic bromides from PBr_5 and NH_4Br . This method is analogous to Stokes' synthesis of the phosphonitrilic chlorides and gives the trimer and

tetramer in about 50 per cent yield.^(28,29) If one uses mixtures of PCl_5 and NH_4Br or



or



PBr_5 and NH_4Cl the products are mixed chlorobromides such as $\text{P}_3\text{N}_3\text{Cl}_5\text{Br}$, $\text{P}_3\text{N}_3\text{Cl}_4\text{Br}_2$ and $\text{P}_3\text{N}_3\text{Cl}_2\text{Br}_4$.⁽³⁰⁾

Most syntheses of new phosphonitrilic derivatives have involved the substitution of different groups on previously synthesized phosphonitrilic backbones. The usual starting material for such a synthesis is the phosphonitrilic chloride trimer or tetramer. Thus, the fluorides can be synthesized by reaction of the chlorine derivatives with fluorinating agents. A number of examples of substitution reactions of this type are presented in Table 4. This method is suitable for the synthesis of a large number of phosphonitrilic derivatives⁽⁴⁸⁾ although it has not been found to be generally useful for the synthesis of alkyl or perfluoroalkyl phosphonitriles. Only one example of the substitution of such a group is known in the chemistry of cyclic phosphonitriles,⁽⁴⁹⁾



TABLE 4

PHOSPHONITRILIC DERIVATIVES SYNTHESIZED FROM $[\text{PNCl}_2]_{3,4}$

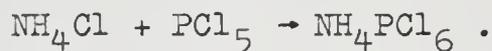
Starting Material	Reagent	Product	Reference
$[\text{PNCl}_2]_4$	PbF_4	$\text{P}_4\text{N}_4\text{Cl}_2\text{F}_6$	31
$[\text{PNCl}_2]_{3,4}$	KSO_2F	$[\text{PNF}_2]_{3,4}$	23
$[\text{PNCl}_2]_3$	KSO_2F	$\text{P}_3\text{N}_3\text{FCl}_{6-n}$; $n=2-4$	32
$[\text{PNCl}_2]_n$	$\text{KF}+\text{SO}_2$	$[\text{PNF}_2]_n$; $n=3-11$	33
$[\text{PNCl}_2]_{3,4}$	AgF	$[\text{PNF}_2]_{3,4}$	34
$[\text{PNCl}_2]_{3,4}$	NaF	$[\text{PNF}_2]_{3,4}$	35
$[\text{PNCl}_2]_{3,4}$	KSCN	$[\text{PN}(\text{SCN})_2]_{3,4}$	36, 37
$[\text{PNCl}_2]_3$	NaN_3	$[\text{PN}(\text{N}_3)_2]_3$	38
$[\text{PNCl}_2]_3$	$\text{C}_2\text{H}_5\text{ONa}$	$[\text{PN}(\text{OC}_2\text{H}_5)_2]_3$	39
$[\text{PNCl}_2]_3$	$\text{C}_4\text{H}_9\text{OH}$	$[\text{PN}(\text{OC}_4\text{H}_9)_2]_3$	40
$[\text{PNCl}_2]_3$	CH_3ONa	$[\text{PN}(\text{OCH}_3)_2]_3$	40
$[\text{PNCl}_2]_3$	RNH_2	$[\text{PN}(\text{NHR})_2]_3$; $\text{R}=\text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9,$ $\text{C}_5\text{H}_{11}, \text{C}_6\text{H}_{13}$	41

Table 4 (cont'd)

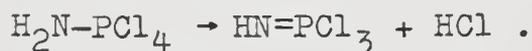
Starting Material	Reagent	Product	Reference
$[\text{PNCl}_2]_4$	NHRR'	$[\text{PN}(\text{NRR}')_2]_4$; R=CH ₃ , C ₂ H ₅ , C ₃ H ₇ , C ₄ H ₉ ; R'=H or R	42
$[\text{PNCl}_2]_{3,4}$	NH ₃	$[\text{PN}(\text{NH}_2)_2]_{3,4}$	27
$[\text{PNCl}_2]_3$	N ₂ H ₄	$[\text{PN}(\text{N}_2\text{H}_3)_2]_3$	43
$[\text{PNCl}_2]_3$	C ₆ H ₆ , AlCl ₃	P ₃ N ₃ Cl ₄ (C ₆ H ₅) ₂ , P ₃ N ₃ Cl ₂ (C ₆ H ₅) ₄ , P ₃ N ₃ (C ₆ H ₅) ₆	44, 45
$[\text{PNCl}_2]_3$	C ₆ H ₅ MgBr	$[\text{PN}(\text{C}_6\text{H}_5)_2]_3$	44
$[\text{PNCl}_2]_4$	C ₆ H ₅ MgBr	P ₄ N ₄ (C ₆ H ₅) ₄ Cl ₄ , $[\text{PN}(\text{C}_6\text{H}_5)_2]_4$, P ₃ N ₃ Cl ₄ (C ₆ H ₅) $[\text{NP}(\text{C}_6\text{H}_5)_3]$	46, 47

The above discussion refers only to cyclic phosphonitriles and their reactions. A renewal of interest in macromolecular phosphonitriles has occurred in recent years because of the possibility of finding products for military and space industry use.

As mentioned earlier, Stokes discovered the first highly polymeric phosphonitrilic "rubber" in 1897. Stokes found that by pyrolyzing the cyclic phosphonitrilic chlorides at about 300° C a rubbery material was formed which could be formulated as $[\text{PNCl}_2]_n$ where n is a large number. This material is thermally stable up to about 350° C where it begins to depolymerize yielding cyclic derivatives. In certain cases^(13,50) polymeric species of the type, $(\text{PNCl}_2)_n \cdot \text{PCl}_5$, or $\text{H}(\text{PNCl}_2)_n \text{Cl}$, were formed directly from the reaction of PCl_5 with NH_4Cl . It has been postulated⁽⁵¹⁾ that the first product of this reaction is ammonium hexachlorophosphate

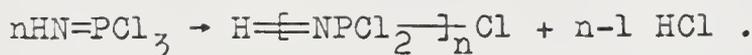


This salt could undergo a series of condensation reactions eliminating HCl

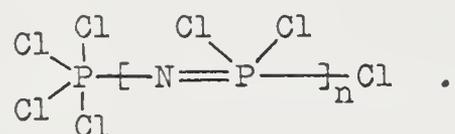


The new species, $\text{HN}=\text{PCl}_3$, has two possible courses available for further reaction. It can undergo intermolecular

condensation

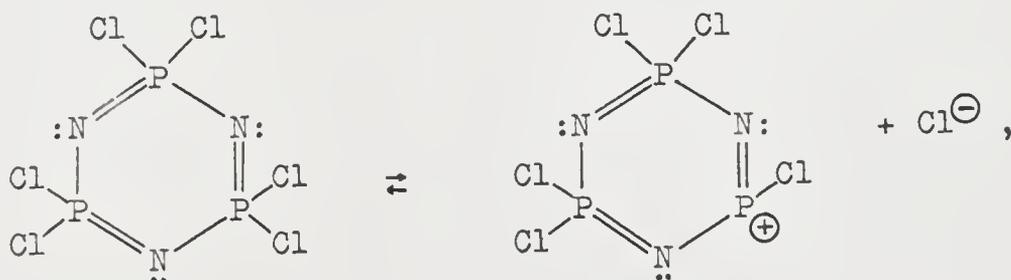


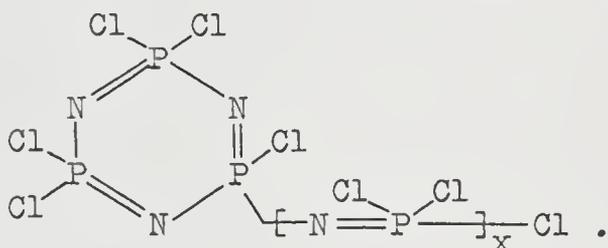
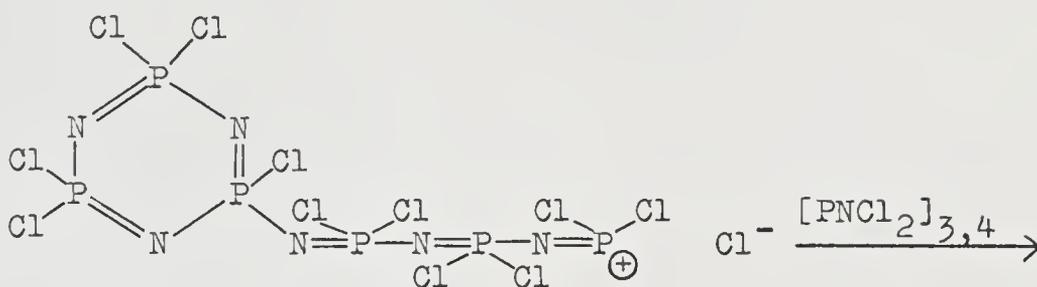
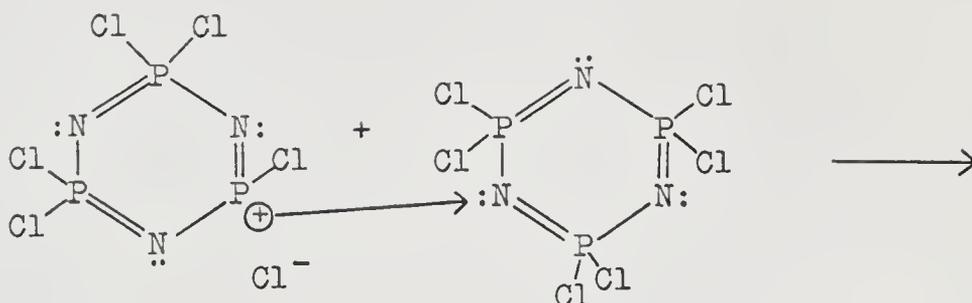
Or it can react with more PCl_5 to form the polymer,



Polymers in both these series are oils with n usually having values of from 10 to 20.

Strong evidence⁽⁵²⁾ provided by conductance and capacitance (dielectric constant) measurements and by electron paramagnetic resonance studies, indicates that the thermal polymerization of the cyclic phosphonitrilic chlorides takes place by ionization of a chlorine atom followed by an electrophilic attack by the positive phosphonium ion

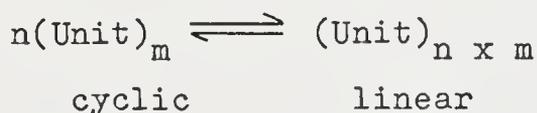




The other known halogen or pseudohalogen substituted phosphonitriles undergo a similar polymerization at high temperatures. The cyclic fluorides can be polymerized to rubbery materials by heating to 350°C .⁽⁵³⁾ The trimeric and tetrameric bromides give an elastomer when heated to $250\text{--}300^{\circ}\text{C}$.^(28,29) Likewise, the cyclic isothiocyanates polymerize when heated to 150°C .^(36,37) The average molecular weight of the polymeric chloride formed by thermal polymerization has been estimated to be as high as 300,000.

Although these halogen and pseudohalogen substituted phosphonitrilic high polymers are thermally stable, they all share the same disadvantage of being susceptible to hydrolysis. Thus, upon exposure to moisture, HX is evolved with the subsequent loss of rheologically interesting properties.

When the high polymers are heated considerably above the temperature of formation, a depolymerization reaction occurs and the cyclic derivatives are regenerated. One observes, therefore, the operation of a dynamic equilibrium,



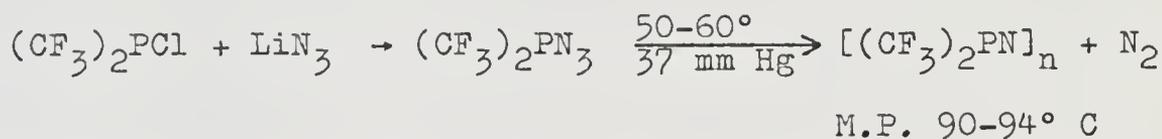
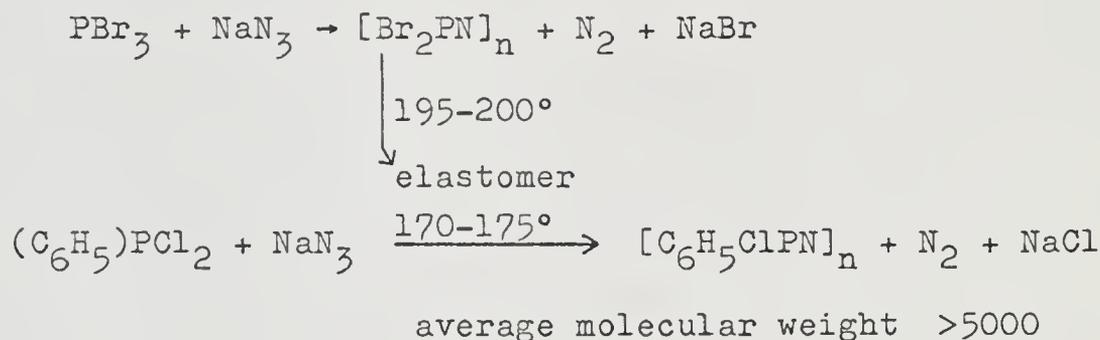
in which the products, or the average molecular weight of the system will depend on concentration, pressure and temperature. Depolymerization is favored thermodynamically at higher temperatures since, in the expression,

$$\Delta F = \Delta H - T\Delta S ,$$

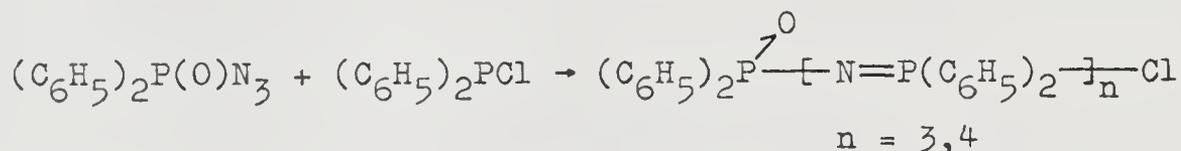
the enthalpy is constant because the number of bonds in many small molecules is approximately the same as the number of bonds in a few large molecules made of the same amount of material, and the entropy of many small molecules is greater than the entropy of a few large molecules of the same amount of material. (54)

Thermal polymerization has not been observed with the cyclic phosphonitriles which have groups other than

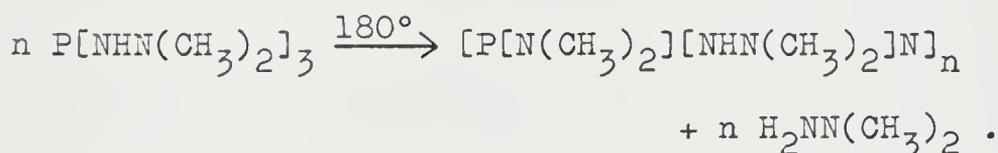
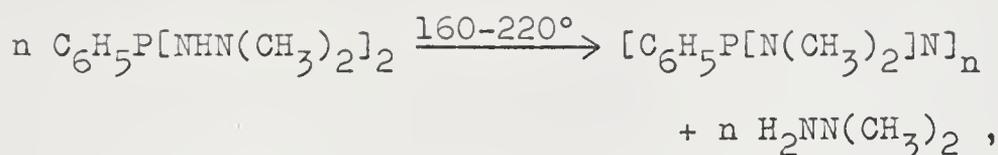
halogens or pseudohalogens on the phosphorus atoms. However, linear polymers with alkyl groups, aryl groups or N-substituted amines on phosphorus have recently been synthesized by several new procedures. It has been shown, for example, that lithium azide and sodium azide react with halophosphines to produce intermediates which undergo thermal polymerization giving high-molecular-weight phosphonitriles.^(55,56) The following reactions are illustrative



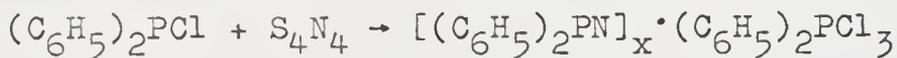
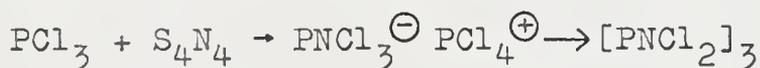
Diphenylphosphinyl azide undergoes a similar reaction.⁽⁵⁷⁾



Furthermore, recently published results⁽⁵⁸⁾ indicate that the pyrolysis of hydrazinophosphines produces polymeric phosphonitrilic species

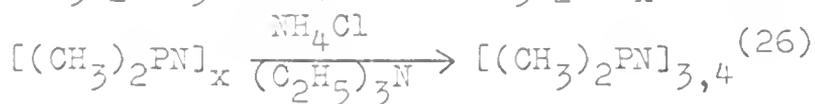
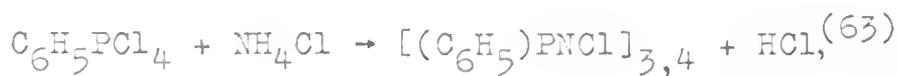


Halophosphines have been shown to undergo reaction with tetrasulfur tetranitride, S_4N_4 , giving phosphonitrilic polymers and precursors: (59,60,61)



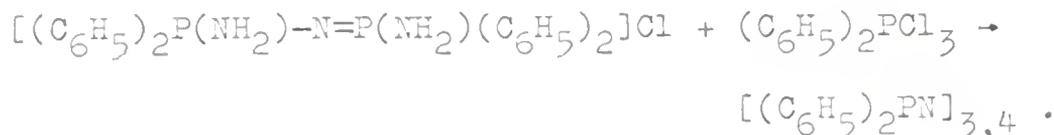
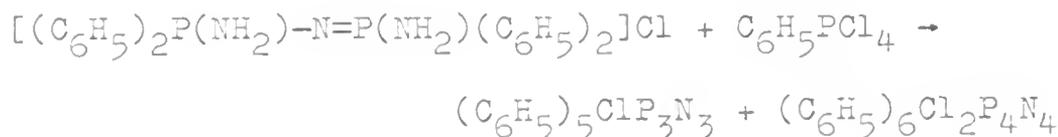
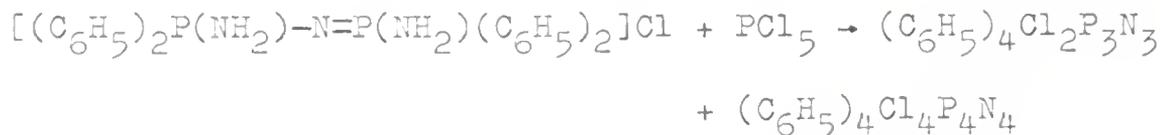
The only alkyl-substituted high polymer reported in the literature to date was synthesized by methylating polymeric phosphonitrilic chloride⁽⁶²⁾ by slurring the chloride with a solution of methylmagnesium bromide or methyl-lithium. A complete characterization of the products of this reaction has not yet appeared in the literature.

With the recent increase in interest in phosphonitrilic chemistry has come the development of several new methods of synthesizing these derivatives from non-phosphonitrilic starting materials. Some of these methods involve the ammonolysis of chlorophosphoranes and are quite similar to the original preparation using ammonium chloride or ammonia and PCl_5



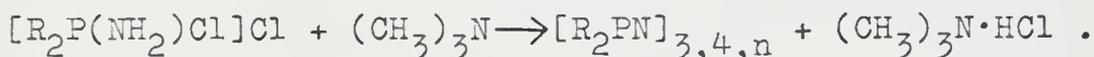
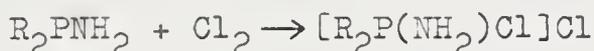
The phosphonitric precursor,

$[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)\text{-N} \text{P}(\text{NH}_2)(\text{C}_6\text{H}_5)_2]\text{Cl}$, has recently been shown to undergo ring closure reactions^(3,4) with a number of reagents producing a variety of cyclic derivatives

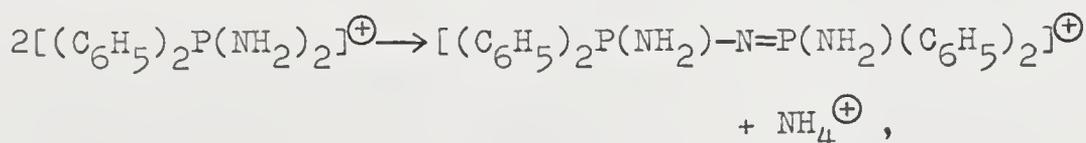


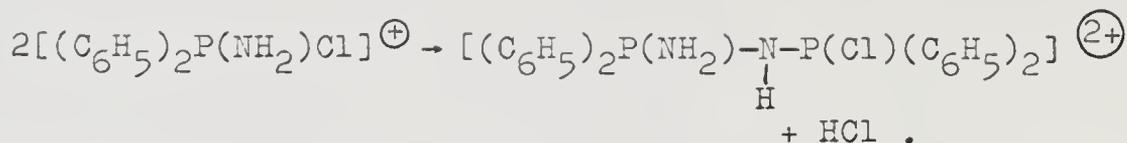
Mao, Dresdner and Young⁽⁶⁵⁾ have reported a unique method for the synthesis of $[\text{PNF}_2]_{3,4}$. In this procedure NF_3 or CF_3SF_5 is passed over P_3N_5 at 710°C , and the cyclic derivatives distill from the reaction zone.

Perfluoromethyl- and perfluoropropyl-derivatives have been synthesized by the chlorination of bis(perfluoromethyl)aminophosphine and bis(perfluoropropyl)aminophosphine.⁽⁶⁶⁾ This reaction is carried out at -30° C and it is postulated that the intermediate, $[R_2P(NH_2)Cl]Cl$, is first formed. Trimethylamine is added to the reaction mixture at the completion of the chlorination



This type of reaction is apparently quite general because it has been demonstrated by Sisler and coworkers^(1,67) that diphenylchlorophosphine produces phosphonitrilic derivatives and precursors when reacted with gaseous mixtures of anhydrous chloramine and ammonia,⁽⁶⁸⁾ with H_2NNH_3Cl and $H_3NNH_3Cl_2$, and with solutions of anhydrous, ammonia-free chloramine. As pointed out on page 2, the reactive intermediate postulated in the reaction sequence leading to phosphonitriles was the phosphonium ion, $[(C_6H_5)_2P(NH_2)_2]^{\oplus}$, when excess ammonia was used, or, $[(C_6H_5)_2P(NH_2)Cl]^{\oplus}$, when ammonia-free solutions of chloramine were used. These ions could undergo intermolecular condensation producing the precursors which were isolated





Indeed, the chloramination-ammonolysis of dialkylchloro-phosphines^(5,6) seems to follow a similar sequence and dialkyldiaminophosphonium chlorides were isolated from the reaction mixtures.

The Chloramination Reaction

Chloramine, NH_2Cl , was first prepared and used as a synthetic reagent by Raschig⁽⁶⁹⁾ in 1907. Raschig's method consists of the addition of ammonia to dilute, aqueous solutions of hypochlorite ion. Although this method has the disadvantage that only dilute solutions of chloramine can be obtained, and despite the difficulty in preparing the completely anhydrous reagent, this process has been widely used for many years for the commercial production of hydrazine from chloramine and ammonia. In 1951, Mattair and Sisler⁽⁷⁰⁾ found that anhydrous, gaseous chloramine could be produced in excellent yields from the gas phase reaction of ammonia and chlorine using an excess of NH_3 . The first synthetic application of this method was the production of anhydrous hydrazine



Subsequently, chloramine was used to synthesize substituted

hydrazines from primary and secondary amines,⁽⁷¹⁾ 1,1,1-trisubstituted hydrazinium salts from tertiary amines,⁽⁷²⁾ and aminophosponium salts from tertiary phosphines.⁽⁷³⁾

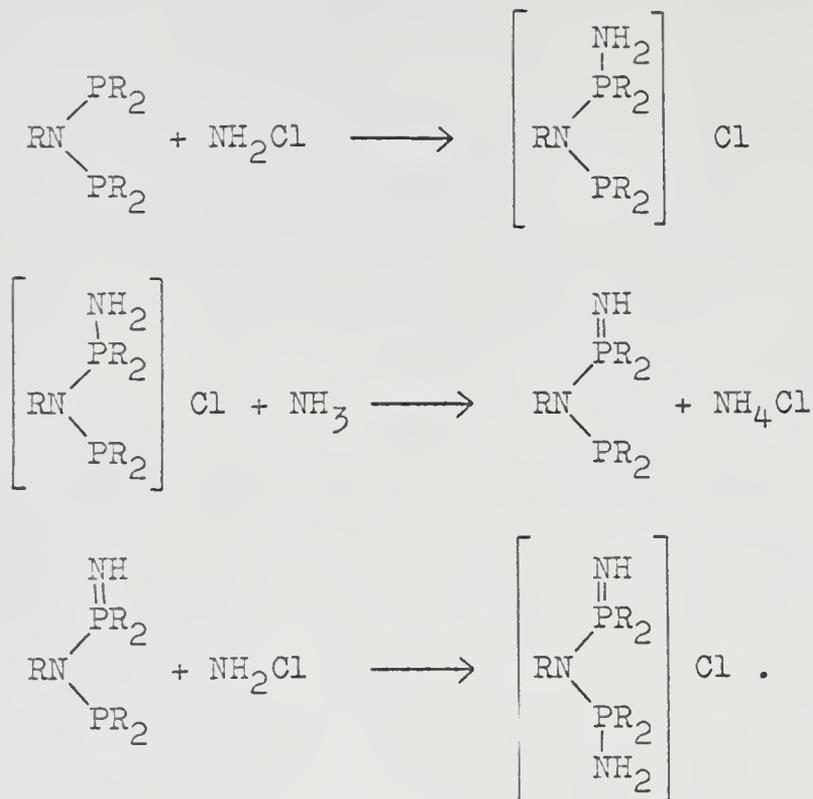
These reactions may be generalized as follows



Hart^(74,75) examined thoroughly the chloramination of aminophosphines and showed that chloramine attacks the phosphorus atom instead of the nitrogen atom attached to phosphorus, forming aminophosponium salts instead of hydrazinium salts



A similar study was undertaken by Clemens⁽⁷⁶⁾ using certain aminophosphines and bis(phosphino)amines. The results were analogous to those of Hart. With the bis(phosphino)amines the reaction was postulated to follow the general course,



The chloramination-ammonolysis of monochlorophosphines has been mentioned previously (pages 2, 28).

Since halophosphines can be synthesized by cleavage of diphosphines and polyphosphines with halogens, (77,78) it seems reasonable to expect chloramine to cleave the P-P bond in a similar manner. However, alkylation of diphosphines with alkyl halides, which is formally analogous to the chloramine reaction, (79) produces different results with different diphosphines. For example, tetramethyl-, tetraethyl-, and tetra-n-butylidiphosphine react with methyl and ethyl iodide to form diphosponium salts

CHAPTER III

REACTION OF THE CHLORAMINE-AMMONIA MIXTURE WITH SUBSTITUTED DIPHOSPHINES AND TETRAPHENYLCYCLOTETRAPHOSPHINE

Experimental

Manipulation of materials.-The diphosphines used in this study are extremely sensitive to oxygen, and detailed precautions were taken to prevent contamination by oxygen from the air. Similarly, some of the products formed in this study are sensitive to moisture, and precautions were taken to avoid contamination of solvents and other reagents by moisture.

Benzene was either obtained as the reagent grade product and stored over calcium hydride or obtained as the technical grade product and distilled and stored over calcium hydride. Petroleum ether and diethyl ether were obtained as reagent grade products and were stored over calcium hydride. Other solvents used were reagent grade.

Tri-n-butylphosphine was obtained from Food Machinery and Chemical Corporation and used as obtained. Phenyl-dichlorophosphine and diphenylchlorophosphine were obtained from Victor Chemical Works and used as obtained. These reagents were transferred by pipette under a stream of dry

nitrogen. Tetramethyldiphosphine and tetraethyldiphosphine are liquids at room temperature and were purified by distillation at reduced pressure. They were stored and transferred by pipette under nitrogen in a D. L. Herring Model HE-43 Dri Lab equipped with a Model HE-93 Dri Train. Tetraphenyldiphosphine and tetraphenylcyclotetraphosphine are solids and were stored and transferred under nitrogen in the dry box.

Infrared spectra.-Infrared spectra of the compounds produced in this study were determined using a Perkin-Elmer Model 337 grating infrared spectrometer. A summary of the spectral bands of these compounds between 2.5 and 25 microns is presented in Table 5.

Solid samples were examined between KBr disks as Nujol mulls, or, when the solid melted below 100°C, as a melt. In certain instances thin films could be obtained by carefully evaporating a chloroform solution of the sample on a KBr disk. Samples of substances which are sensitive to moist air were prepared for infrared analysis in the dry box.

Elemental analyses.-Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Several nitrogen analyses were carried out in these laboratories using a Coleman Model 29 Nitrogen Analyzer.

TABLE 5(a)

INFRARED ABSORPTION DATA (cm^{-1})

$[(\text{CH}_3)_2\text{P}(\text{NH}_2)_2]\text{Cl}$, Nujol Mull⁽⁶⁾

3920(w), 3850(w), 3260(vs,b), 2940(vs), 2850(vs),
2620(m), 2560(w,sh), 2530(w,sh), 2400(m), 2260(vw),
2200(w), 2160(w,b), 2100(w,sh), 2060(w), 2000(w),
1940(m), 1625(w), 1570(s), 1460(s), 1420(s), 1410(m,sh),
1375(m), 1310(m), 1300(s), 1070(sh), 1040(s), 990(s),
951(s), 885(m), 860(m), 835(m), 762(s), 695(s),
600(b), 527(b).

$[(\text{C}_2\text{H}_5)_2\text{P}(\text{NH}_2)_2]\text{Cl}$, Nujol Mull⁽⁶⁾

3940(w), 3160(vs), 3060(vs), 2940(vs,b), 2850(vs),
2640(w), 2550(w), 2330(w,sh), 2150(w), 2060(w),
1960(w,sh), 1920(w), 1870(w,sh), 1755(w,b), 1665(w,b),
1560(s), 1460(vs), 1395(s), 1380(s), 1275(s),
1240(m), 1160(w,b), 1075(s,sh), 1050(s), 1019(s),
980(s,sh), 968(s), 910(s), 761(s), 733(s), 721(s),
665(s), 625(s,b), 500(w,b), 447(m).

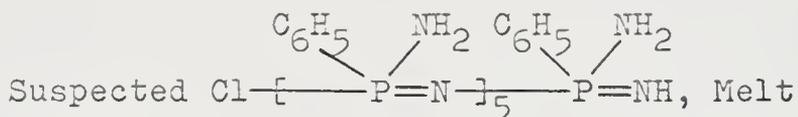
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{NH}_2$, Nujol Mull

3240(s,b), 3125(s), 2940(vs), 2860(vs), 1970(w),
1900(w), 1820(w), 1779(w), 1680(w), 1595(m),
1560(s), 1485(m), 1460(vs,b), 1440(vs,sh), 1439(vs),
1420(w,sh), 1380(s), 1365(m,sh), 1340(w), 1310(m),
1275(w), 1260(w), 1175(s), 1110(s), 1105(s),
1060(m), 1010(w), 990(m), 910(s), 858(w), 849(w),
752(s), 720(s), 695(s), 620(w), 532(s), 518(s),
488(m), 439(w).

$[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)_2]\text{Cl}$, Nujol Mull

3170(s), 3075(s), 2980(vs,sh), 2940(vs), 2860(vs),
2710(w), 2540(w,b), 2440(w), 1970(w), 1900(w),
1815(w), 1780(w), 1665(w,b), 1595(m), 1560(s),
1485(m), 1460(s), 1440(s), 1410(m), 1380(s),
1365(m,sh), 1340(w), 1320(w), 1280(w), 1190(w),
1160(w), 1110(s), 1075(w,sh), 1025(s,sh), 1010(s),
990(s,sh), 980(s), 922(m), 910(m), 855(w), 840(w),
756(s,sh), 751(s), 742(s), 720(s), 691(s), 638(w,b),
620(w), 549(w,b), 510(s), 505(s,sh), 472(m), 434(w),
413(m).

Table 5 (cont'd)



3400(s,sh), 3210(vs), 3060(vs), 2950(s), 2940(sh),
 2635(w), 2600(w), 2300(m), 2250(w), 1960(m),
 1900(m), 1820(m), 1770(w), 1720(w), 1670(m),
 1640(m), 1590(s), 1550(vs), 1480(s), 1440(vs),
 1280(s,sh), 1205(vs,vb), 1115(s), 1015(m), 910(m,b),
 799(m), 742(s), 692(s), 685(sh), 615(w), 502(s,vb).

$[(\text{C}_6\text{H}_5)\text{P}(\text{NH}_2)_3]\text{Cl}$, Nujol Mull

3375(m), 3250(s,sh), 3170(s), 3075(s), 2940(s,sh),
 2900(vs), 2850(s), 1590(w), 1559(m), 1460(s),
 1440(s), 1415(m), 1380(s), 1135(s), 1084(w),
 1070(w), 1025(w), 985(m), 925(w,sh), 875(m),
 798(w), 763(s), 721(w), 705(w), 692(m), 620(w,b),
 510(m), 474(m).

$(\text{C}_6\text{H}_5\text{P}(\text{O})(\text{NH}_2)_2)$, Nujol Mull

3350(s), 3275(s,sh), 3220(s), 3110(s,sh), 3055(m),
 2940(vs), 2850(vs), 2740(w), 1955(w), 1900(w),
 1770(w), 1590(m), 1560(m), 1460(s), 1440(s), 1410(m,b),
 1380(s), 1330(w), 1310(w), 1182(m), 1155(vs),
 1118(s), 1060(m), 1010(m), 939(s), 915(m,sh),
 885(m), 855(w), 745(s,sh), 740(s), 720(m), 694(s),
 620(w), 568(w,b), 520(s), 512(s), 494(w), 435(w,b).

(a) s, strong; m, medium; w, weak; b, broad; v, very;
 sh, shoulder.

Melting points were determined in a Thomas-Hoover capillary melting point apparatus and are uncorrected.

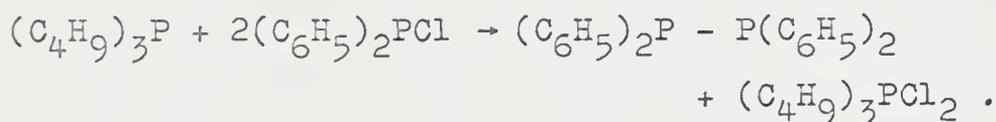
Preparation of substituted diphosphines and tetraphenylcyclotetraphosphine.-Tetramethyldiphosphine and tetraethyldiphosphine were prepared by the desulfuration of the corresponding diphosphine disulfide with tri-n-butylphosphine.⁽⁸⁴⁾ The diphosphine disulfides were synthesized by the Grignard method from PSCl_3 and RMgBr ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$). This method has been thoroughly discussed elsewhere.^(5,85,86) To the solid diphosphine disulfide under a nitrogen atmosphere was added by pipette, tri-n-butylphosphine according to the stoichiometry of the following general equation



It was convenient in this study to use from ten to fifteen grams of the diphosphine sulfide in each run and to mix the reagents in a 200 ml round-bottomed distillation flask. The mixture was then heated under reduced pressure. The tetraalkyldiphosphine was obtained by fractional distillation from the reaction mixture. The observed boiling point of tetramethyldiphosphine was 35°C at 16 mm Hg(Lit.⁽⁸⁴⁾): $\text{Bp}_{16} = 38-40^\circ \text{C}$). The observed boiling point of tetraethyldiphosphine was 67°C at 1.7 mm Hg(Lit.⁽⁸⁴⁾): $\text{Bp}_{740} = 220-3^\circ \text{C}$). Yields of tetraalkyldiphosphine from this reaction ranged between 50 and 80 per cent of theory based on the amount of diphosphine disulfide used. Distillation was

slow because of the difficulty in removing the diphosphines from $(C_4H_9)_3PS$ in which they are soluble.⁽⁸⁴⁾ At the completion of the distillation the diphosphines were placed in stoppered receivers under nitrogen and stored in the dry box until needed. The infrared spectra and nuclear magnetic resonance spectra of these tetraalkyldiphosphines have been treated thoroughly elsewhere⁽⁸⁴⁾ and need not be considered here.

Tetraphenyldiphosphine was prepared by the reaction of tri-n-butylphosphine with diphenylchlorophosphine⁽⁸⁷⁾ which can be represented by the following equation



In a typical experiment, 3.15 ml (14 mmoles) of tributylphosphine was pipetted into 5.0 ml (27 mmoles) of diphenylchlorophosphine in a Minilab reaction flask (Fig. 5) fitted with a stirrer and a nitrogen inlet and outlet. The mixture was stirred until it became homogenous. It was then allowed to stand under a nitrogen atmosphere for about three days. At the end of this time the reaction mixture had become a solid, crystalline mass. This crystalline mixture was extracted under a nitrogen flow with cool, freshly boiled, distilled water until the washings gave no chloride test with aqueous silver nitrate. The white, crystalline

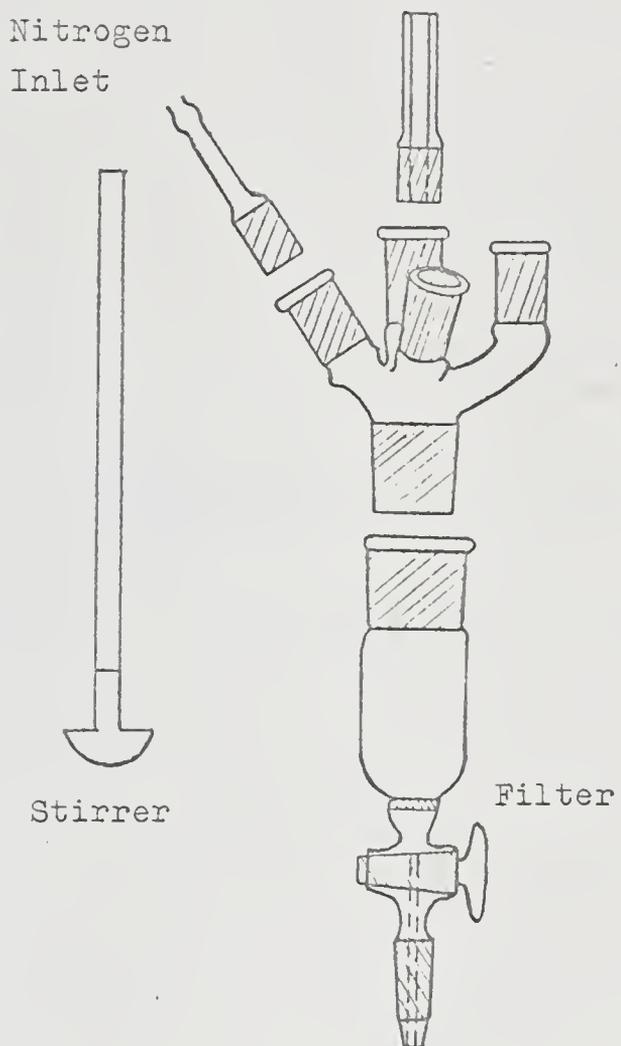
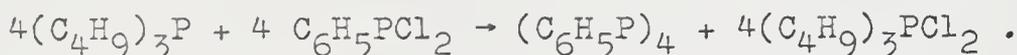


Fig. 5.-Minilab Reaction Flask.

residue was dried in vacuum and transferred to the dry box. M. P. 118-121° C (Lit.⁽⁷⁸⁾): M. P. 120.5° C). The average yield of tetraphenyldiphosphine produced by this method of synthesis was about 40 per cent of theory based on the amount of diphenylchlorophosphine used. Although strict precautions against oxidation of the diphosphine were taken, a small amount of tetraphenyldiphosphine monoxide⁽⁸⁸⁾ was probably present in each sample.

Tetraphenylcyclotetraphosphine was prepared by the reaction of tri-n-butylphosphine with phenyldichlorophosphine⁽⁸⁷⁾ as indicated by the following equation



In a typical experiment, 5.0 ml (36.6 mmoles) of phenyldichlorophosphine was pipetted into 8.24 ml of tri-n-butylphosphine in a Minilab reaction flask (Fig. 5) under nitrogen. Heat was evolved and after a few moments of stirring the reaction mixture became a solid, crystalline mass. When the mixture had cooled to room temperature, it was extracted with copious amounts of absolute ethanol. This extraction was continued until the acidified washings gave no precipitate with aqueous silver nitrate. The white, crystalline residue was dried in vacuum and transferred to the dry box. M. P. 153-155° C (Lit.⁽⁸⁹⁾): M. P. 153-155° C). The average yield of tetraphenylcyclotetraphosphine produced

by this method of synthesis was 50 per cent of theory based on the amount of phenyldichlorophosphine used. Strict precautions were taken to avoid oxidation of the product.

The infrared spectra of tetraphenyldiphosphine and tetraphenylcyclotetraphosphine are available in the literature.⁽⁷⁸⁾ However, a controversy exists in the current literature concerning the nature of tetraphenylcyclotetraphosphine.^(89,90) The material produced in this study has the melting point and infrared spectrum reported for "form A" which is considered to be one stereoisomeric form of $(C_6H_5P)_4$.

Preparation of chloramine.⁽⁷⁰⁾—The preparation of gaseous chloramine was carried out in a generator shown diagrammatically in Figure 6.⁽⁷⁰⁾ Anhydrous ammonia, chlorine and nitrogen were metered in rotameters and mixed in a glass reaction tube. The approximate rate of introduction of the gases was: Cl_2 , 0.1 mole/hr.; NH_3 , 1.2 mole/hr.; N_2 , 0.3 mole/hr. The approximate production rate of chloramine was 0.1 mole/hr. Since ammonia was present in a large excess of that required by the stoichiometry of the reaction



the effluent gases consisted of chloramine, ammonia and nitrogen. Glass wool plugs were placed in the reaction tube

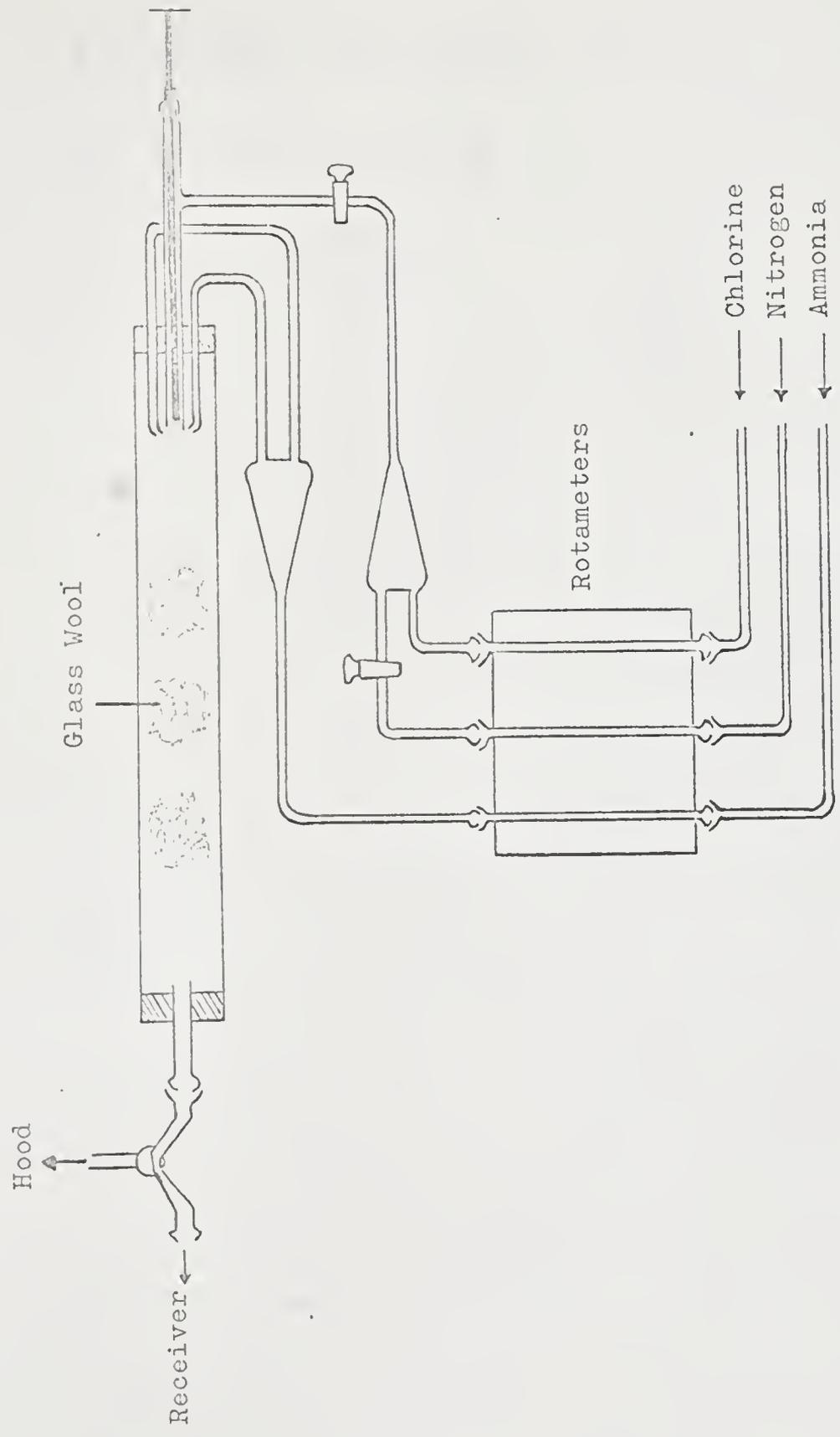
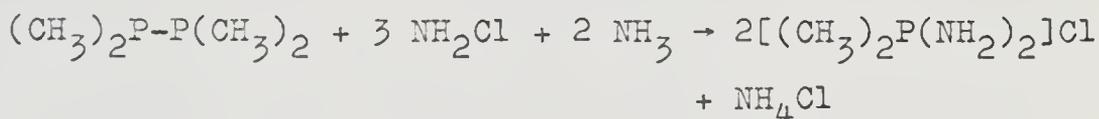


Fig. 6.-The Chloramine Generator.

to filter out the finely divided ammonium chloride produced in the reaction. The effluent gases were bubbled into a receiver containing the solution of the substance to be chloraminated.

The Reaction of the Chloramine-Ammonia Mixture
with Tetramethyldiphosphine

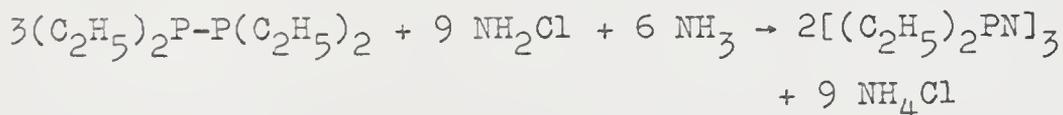
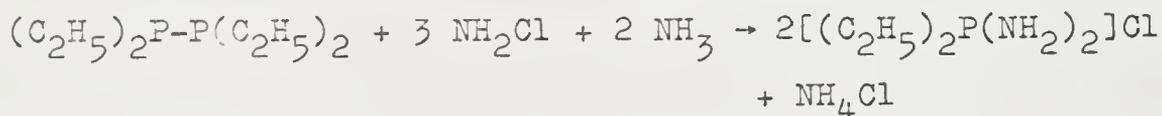


In a typical experiment, 1.0 ml (7.1 mmoles) of tetramethyldiphosphine was dissolved in 75 ml of dry benzene and exposed to the effluent gases of the chloramine generator. A reaction took place immediately. A white precipitate formed and the reaction mixture grew warm. After 10-15 minutes of chloramination the reaction appeared to be complete and the temperature of the mixture dropped to about 20° C because of evaporation of the solvent. Chloramination was continued for 5-10 minutes beyond this point to insure exposure of the reaction mixture to an excess of chloramine. At the completion of the chloramination the benzene was removed by filtration. The solids remaining on the filter were extracted with 60 ml of hot, 50/50 ethanol-acetone mixture. White crystals precipitated from the solution as it slowly cooled to room temperature. These crystals were removed by filtration and dried in vacuum. M.P. 191-194° C.

Anal. Found: N, 21.47. Calculated for $[(\text{CH}_3)_2\text{P}(\text{NH}_2)_2]\text{Cl}$: N, 21.79. The infrared spectrum of this material was identical with that of dimethyldiaminophosphonium chloride (M.P. 192-194° C) produced by chloramination-ammonolysis of dimethylchlorophosphine. (5,6)

Addition of petroleum ether to the mother liquor caused a larger portion of dimethyldiaminophosphonium chloride to precipitate. Yield: 1.08 g (63% of theory).

The Reaction of the Chloramine-Ammonia Mixture
with Tetraethyldiphosphine



Tetraethyldiphosphine (5 mmoles) was dissolved in 75 ml of dry benzene and exposed to the effluent gases of the chloramine generator. A white precipitate formed immediately and the solution became warm. After 10-15 minutes the temperature of the solution fell to about 20° C because of evaporation of the solvent, and the reaction appeared to be complete. Chloramination was continued, however, for 5-10 minutes longer until a relatively large excess of chloramine and ammonia had been added to the reaction mixture. The benzene solution was removed from the

precipitate by filtration and evaporated to dryness. A trace of oily crystals was observed. The crystalline material was separated from the oil by dissolving it in 30-60° petroleum ether. The oil was discarded. Evaporation of the petroleum ether yielded crystals which melted at 113-115° C and which sublimed readily at 30-40° C and 0.1 mm Hg. This material was identified by its infrared spectrum and melting point (see Chapter IV for a more complete description of the identification of this material) as diethylphosphonitrilic trimer⁽²⁵⁾ (Lit: M.P. 117-119° C). Yield: trace (1-5 millig.).

The solids remaining on the filter were extracted with three, 10 ml portions of absolute ethanol. This solution was evaporated to dryness and the resulting crystalline extract was dissolved in 10-15 ml of hot, 50/50 ethanol-acetone mixture. This solution was cooled with an ice bath and to it was added approximately 100 ml of 60-110° petroleum ether. The product crystallized from the solution as well formed, white needles. These crystals were filtered and dried in vacuum. M. P. 103-105° C. Anal. Found: N, 17.9. Calculated for $[(C_2H_5)_2P(NH_2)_2]Cl$: N, 17.89. The infrared spectrum of this material was identical with that of diethyldiaminophosphonium chloride (M. P. 106-108.5° C) produced by the chloramination-ammonolysis of diethylchlorophosphine.^(5,6) Yield: 1.07 g (68% of theory).

The Reaction of the Chloramine-Ammonia Mixture
with Tetraphenyldiphosphine

In a typical experiment, 1.05 g (2.8 mmoles) of tetraphenyldiphosphine was dissolved in 50-75 ml of dry benzene and exposed to the effluent gases of the chloramine generator. A white precipitate formed immediately and the reaction mixture grew warm. Chloramination was continued for about 20 minutes to insure exposure of the reactants to an excess of chloramine. At the completion of the reaction the temperature of the reaction mixture had fallen to about 20° C because of evaporation of the solvent. The benzene solution was removed from the white precipitate by filtration and the solids were washed with 25 ml of fresh benzene. The combined filtrate and washings were evaporated to dryness yielding 0.39 g of a white powder which melted in the range of 80-110° C. This solid was redissolved in 10 ml of boiling benzene. Upon cooling, white crystals precipitated from the benzene solution and were filtered and dried in vacuum. M. P. 158-160° C. Anal. Found: N, 6.6. Calculated for $(C_6H_5)_2P(O)NH_2$: N, 6.48. The infrared spectrum (Fig. 7) is consistent for the formulation, $(C_6H_5)_2P(O)NH_2$.⁽⁹¹⁾ Evaporation of the benzene solution to dryness yielded an oily foam. More crystalline $(C_6H_5)_2P(O)NH_2$ could be recovered from this foam by dissolving it in 2-4 ml of boiling benzene, adding hexane to

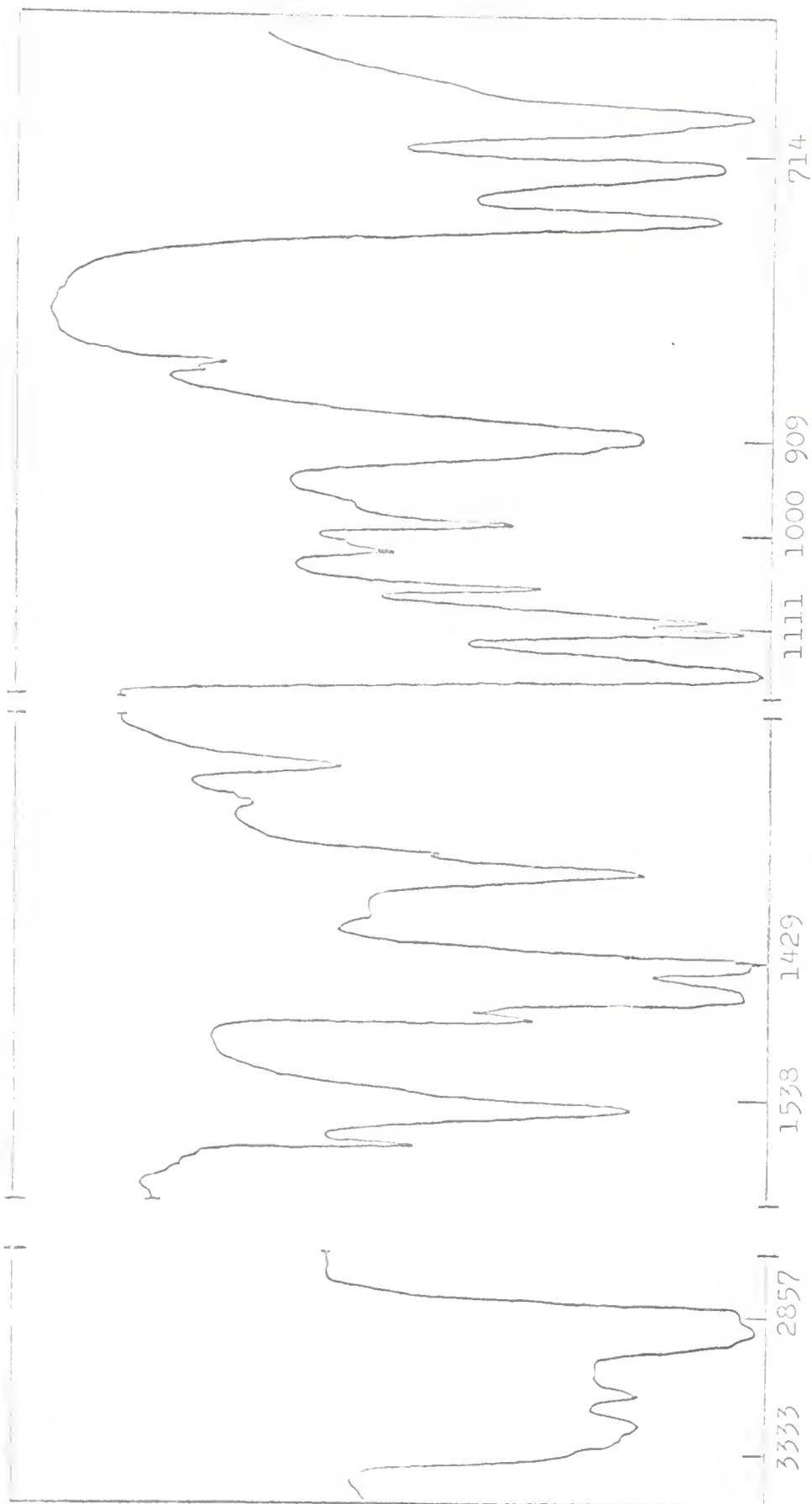


Fig. 7.--Infrared Spectrum of $(C_6H_5)_2P(O)NH_2$ (Nujol).

the hot solution until it became cloudy, and allowing this mixture to stand for several hours. By repeating this process several times, all but a trace of the sample was recrystallized and shown by its melting point and infrared spectrum to be $(C_6H_5)_2P(O)NH_2$. The noncrystalline residue was a yellow oil and was discarded.

In other experiments, evaporation of the benzene solution yielded a dark foam which appeared to be air sensitive, turning wet upon exposure. After recovery of the first crop of crystalline $(C_6H_5)_2P(O)NH_2$ from this mixture, further attempts at recrystallization resulted in the formation of oily products. The dark foam produced by evaporation of the benzene solution melted at 35-40° C. Its infrared spectrum is shown in Figure 8. Anal. Found: C, 65.54; H, 6.03; P, 12.67; N, 6.06; Mol. Wt. (cryoscopic in benzene), 450. The P:N ratio is 1:1. This implies the structural unit, $\begin{matrix} C_6H_5 & C_6H_5 \\ | & | \\ -P=N- \end{matrix}$, for which the calculated composition is: C, 72.4; H, 5.1; P, 15.6; N, 7.0. The analysis, however, is low and indicates that the material may consist also of oxygen-containing material.

The benzene-insoluble solids remaining on the filter were extracted with two, 10 ml portions of hot chloroform. The extracts were combined and concentrated to about half the original volume by evaporation. White crystals precipitated and were removed by filtration and dried in vacuum.

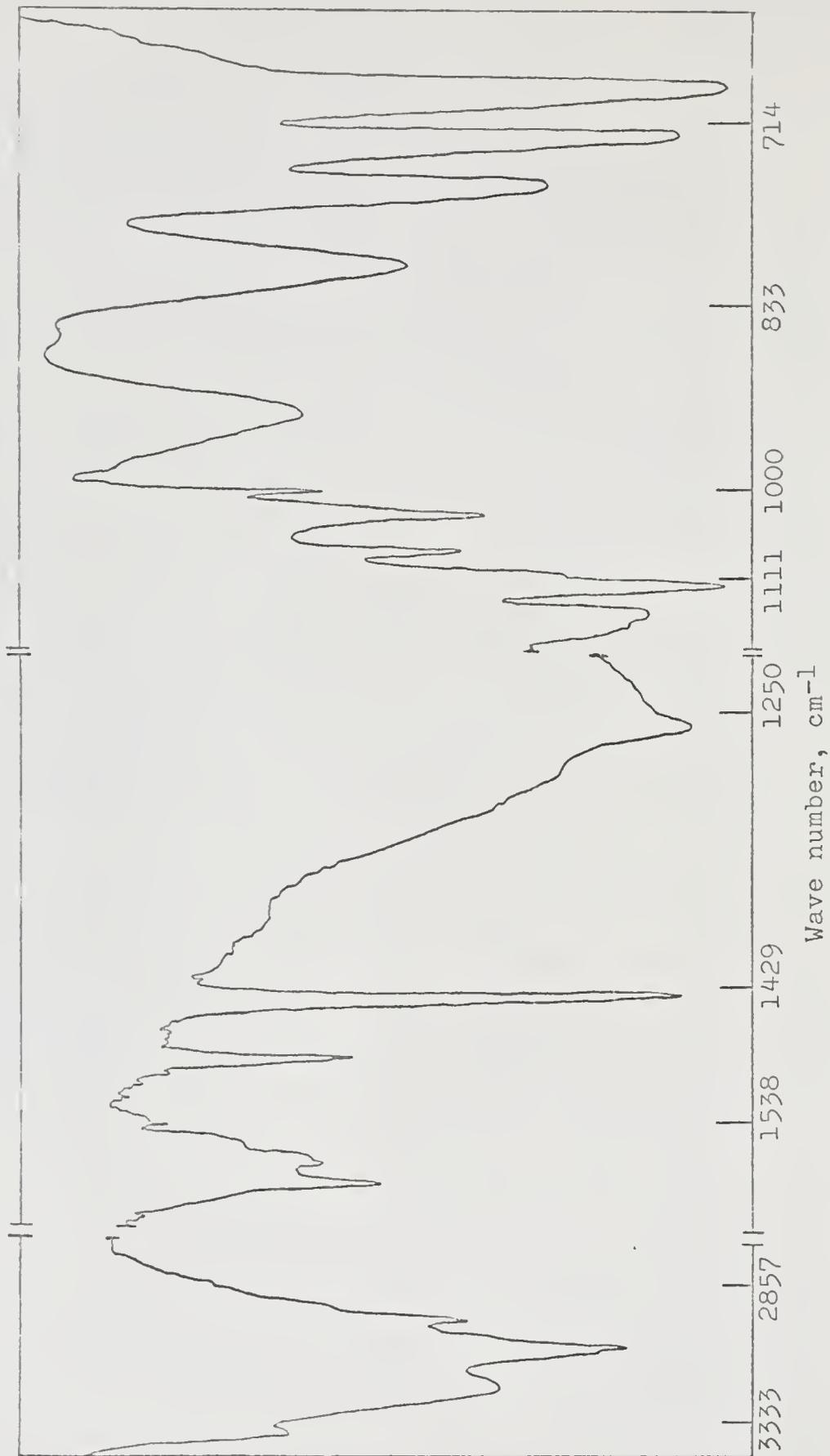


Fig. 8.--Infrared Spectrum of Intractable Chlorination Product of $(C_6H_5)_2P-P(C_6H_5)_2$ (Melt).

M.P. 230-232° C. Anal. Found: N, 8.9. Calculated for $[(C_6H_5)_2P(NH_2)-N=P(NH_2)(C_6H_5)_2]Cl$: N, 9.30. The infrared spectrum of this material was identical with that of $[(C_6H_5)_2P(NH_2)-N=P(NH_2)(C_6H_5)_2]Cl$ produced by the chloramination-ammonolysis of diphenylchlorophosphine.⁽¹⁾

Yield: 0.42 g (33% of theory based on tetraphenyldiphosphine used). If the vacuum drying process was not prolonged, the 1:1 chloroform adduct⁽²⁾ of the substance was obtained.

Anal. Found: N, 7.3. Calculated for $[(C_6H_5)_2P(NH_2)-N=P(NH_2)(C_6H_5)_2]Cl \cdot CHCl_3$: N, 7.36.

The chloroform-insoluble residue was extracted with 50 ml of hot, 50/50 acetone-ethanol mixture. Addition of diethyl ether to this solution caused a small amount of NH_4Cl to precipitate. The solution was filtered. Upon addition of a copious amount of diethyl ether more crystalline material precipitated. This material was filtered and dried in vacuum. M.P. 204-206° C (dec.). Anal. Found: C, 56.22; H, 5.84; P, 11.78; N, 10.69; Cl, 14.50. Calculated for $[(C_6H_5)_2P(NH_2)_2]Cl$: C, 57.04; H, 5.58; P, 12.26; N, 11.09; Cl, 14.03. This analysis indicates that the material may be slightly contaminated with ammonium chloride. The infrared spectrum of this material (Fig. 9) is consistent for the formulation $[(C_6H_5)_2P(NH_2)_2]Cl$, and shows that the amount of ammonium chloride present is too small to be detected by this infrared technique. Attempts to

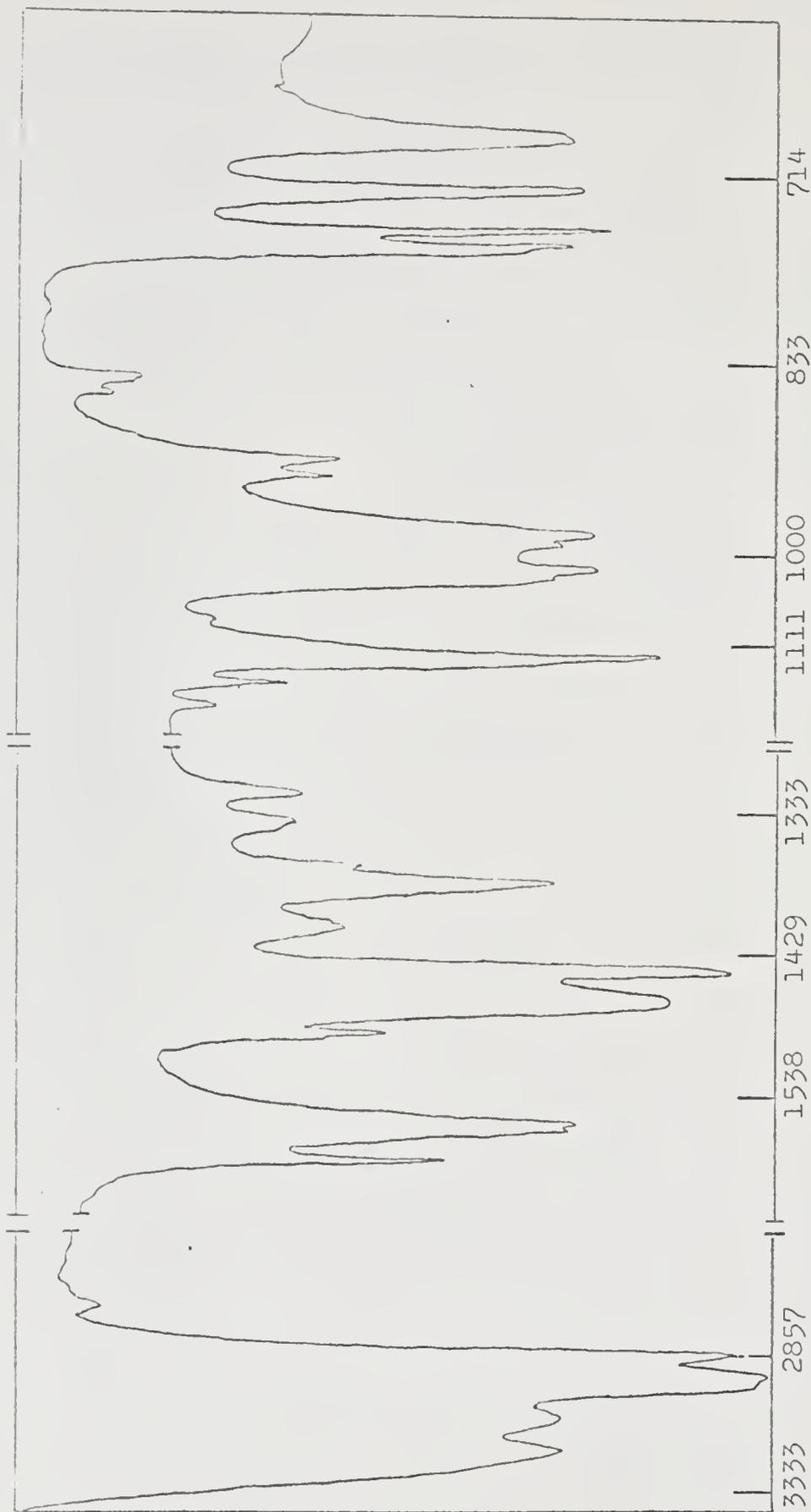


Fig. 9.—Infrared Spectrum of $[(C_6H_5)_2P(NH_2)_2]Cl$ (Nujol).

synthesize the hexafluorophosphate and tetraphenylborate derivatives of the diphenyldiaminophosphonium ion by meta-thesis in water failed. Yield of diphenyldiaminophosphonium chloride: 0.20 g (14% of theory based on tetraphenyldiphosphine used).

The remaining insoluble material was shown to be ammonium chloride.

The Reaction of the Chloramine-Ammonia Mixture
with Tetraphenylcyclotetraphosphine

In a typical experiment, 0.98 g (2.27 mmoles) of tetraphenylcyclotetraphosphine was dissolved in 50-75 ml of dry benzene and exposed to the effluent gases of the chloramine generator. A white precipitate formed immediately and the solution grew warm. The reaction was apparently complete when the temperature of the mixture dropped to about 20° C because of evaporation of the solvent. Chloramination was continued for 5-10 minutes longer to insure exposure of the reactants to an excess of chloramine and ammonia. The benzene solution was removed from the precipitate by filtration and the residue was washed with 25 ml of dry benzene. The filtrate and washings were combined and evaporated to dryness yielding 0.40 g of a white, air-sensitive solid. This solid melted to an opaque liquid at 68-72° C and the melt did not become clear when heated to above 200° C. The analytical data for

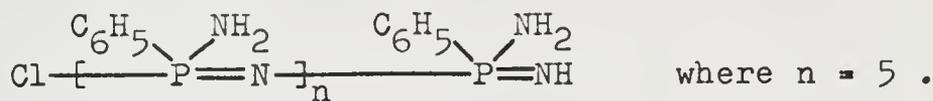
several samples of this material are summarized in the table below.

<u>Found</u>	<u>C</u>	<u>H</u>	<u>P</u>	<u>N</u>	<u>Cl</u>	<u>Mol. Wt.</u>
Sample 1	51.83	5.95	17.33	15.40	2.3	940 (in benzene)
Sample 2			20.31	17.13		
			20.41	17.18(Kjeldahl)		
Sample 3	49.74	5.21	21.43	19.20	4.08	870 (in benzene)

The P:N ratio in these samples is 1:2. This implies the

structural unit $\text{C}_6\text{H}_5\text{P}(\text{NH}_2)\text{N}$, and a likely structure

might be



The calculated elemental analysis for such a formulation is: C, 49.94; H, 4.97; P, 21.50; N, 19.42; Cl, 4.16; Mol. Wt. 865. The infrared spectrum (Fig. 10) is consistent for such a structure. Pyrolysis of the crude material at 200° C and 0.10 mm Hg produced ammonium chloride as a sublimate and an intractable residue which had a nitrogen content lower than the original material.

The benzene-insoluble precipitate was extracted with 50 ml of 50/50 ethanol-acetone mixture. The solution was removed from the insoluble ammonium chloride by filtration and a product was precipitated by the addition of copious amounts of diethyl ether. Upon filtration and drying in vacuum the crude material was found to melt with decomposition in the range 160-170° C. After recrystallization

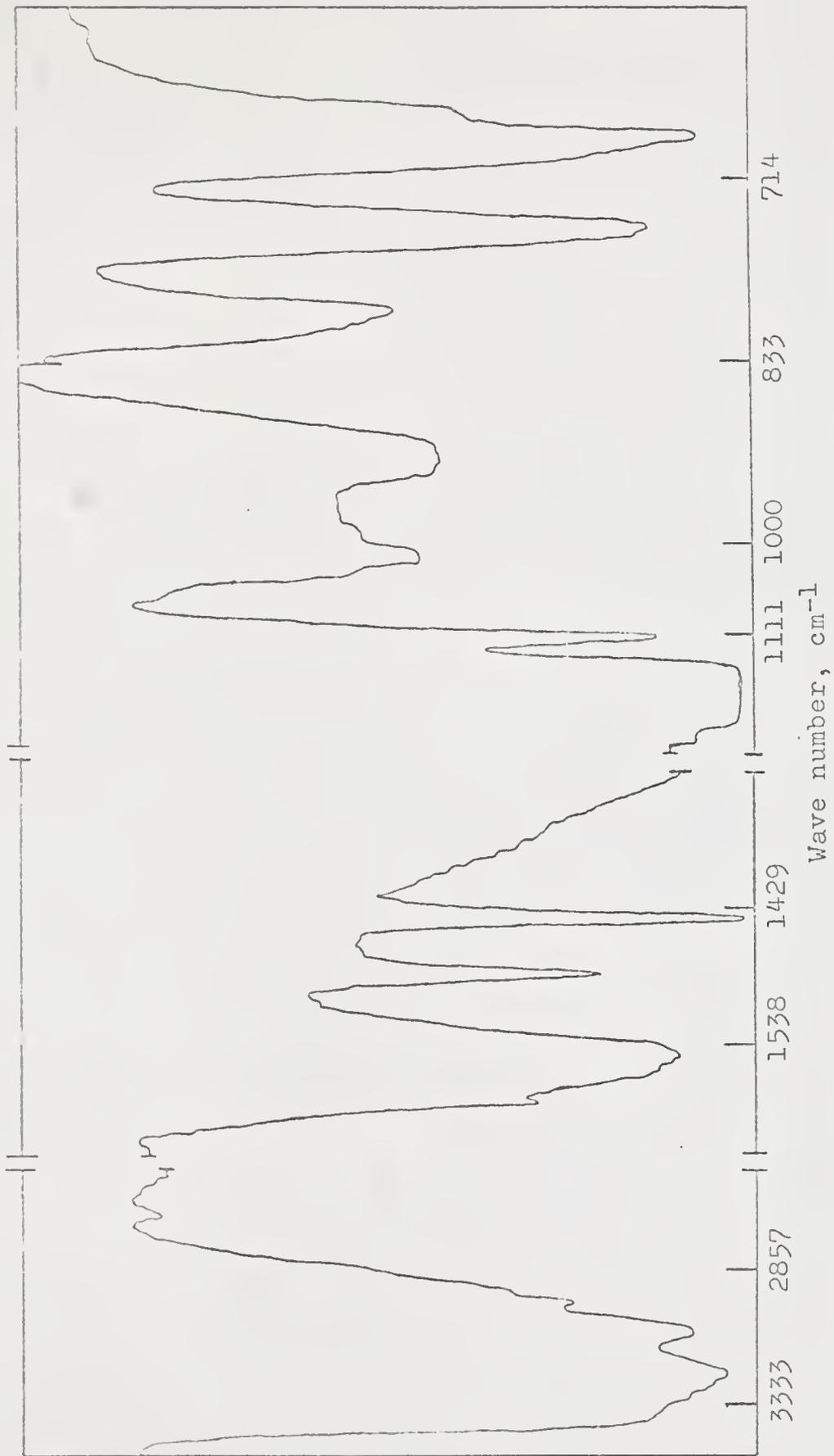


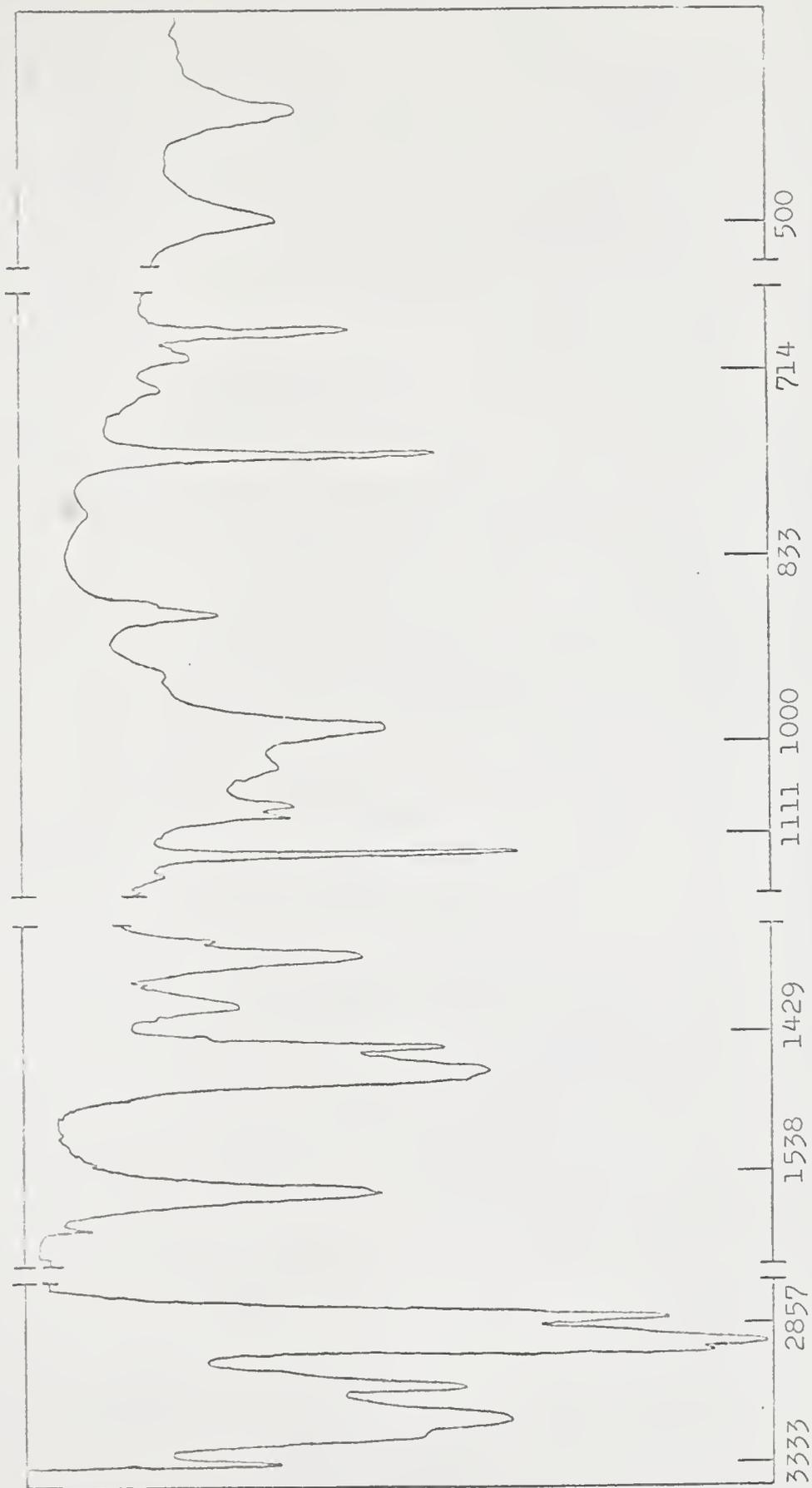
Fig. 10.-Infrared Spectrum of Intractable Chloramination Product of $(C_6H_5P)_4$ (Thin Film).

from 50/50 acetone-ethanol, the observed melting point was 164-165° C. Anal. Found: C, 38.24; H, 6.15; P, 16.37; N, 21.96; Cl, 17.35. Calculated for $[(C_6H_5)P(NH_2)_3]Cl$: C, 37.61; H, 5.79; P, 16.17; N, 21.93; Cl, 18.50. The infrared spectrum (Fig. 11) is consistent for the formulation $[(C_6H_5)P(NH_2)_3]Cl$. Attempts to synthesize the hexafluorophosphate and tetraphenylborate derivatives of the phenyltriaminophosphonium ion by metathesis in water failed. Yield: 0.24 g (14% of theory).

The phenyltriaminophosphonium chloride so prepared was quite sensitive to hydrolysis. Slow recrystallization of the product from alcohol exposed to the atmosphere produced the hydrolysis product, $C_6H_5P(O)(NH_2)_2$.⁽⁹²⁾ M.P. 180-181° C (dec.) (Lit.⁽⁹¹⁾: M.P. 189° C). Anal. Found: C, 45.47; H, 5.81; P, 19.86; N, 17.95; O (by difference), 10.43. Calculated for $C_6H_5P(O)(NH_2)_2$: C, 46.16; H, 5.81; P, 19.84; N, 17.94; O, 10.25. The infrared spectrum of phenylphosphinic diamide is shown in Figure 12.

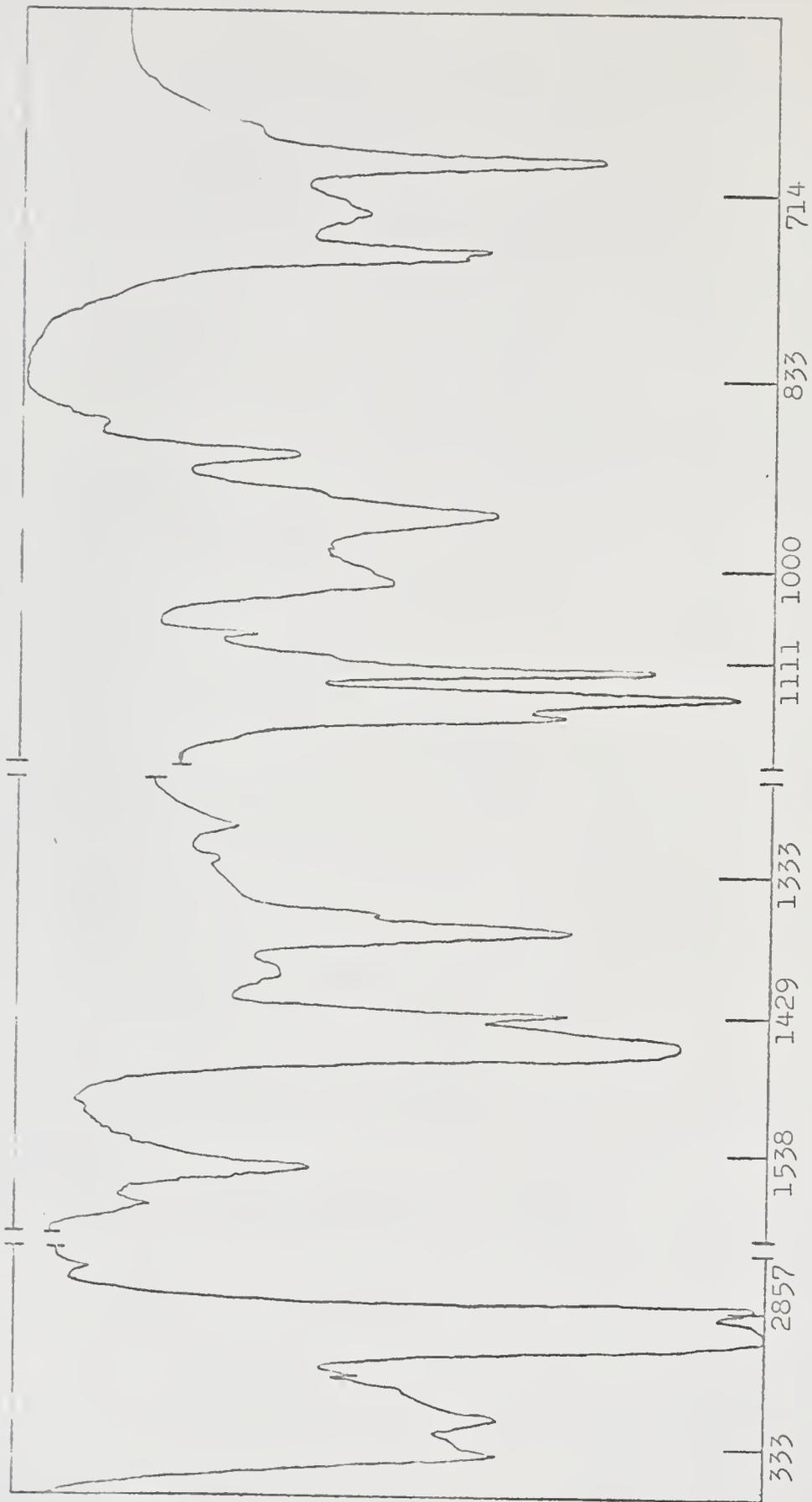
Discussion

The results of this study show that under the conditions of our experiment chloramine cleaves the phosphorus-phosphorus bond in tetramethyldiphosphine, tetraethyldiphosphine, tetraphenyldiphosphine and tetraphenylcyclotetra-



Wave number, cm^{-1}

Fig. 11.--Infrared Spectrum of $[(\text{C}_6\text{H}_5\text{P}(\text{NH}_2)_3)\text{Cl}]_3$ (Nujol).

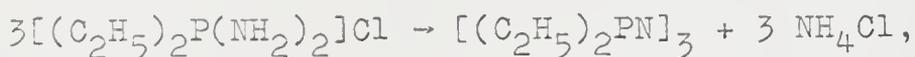


Wave number, cm^{-1}

Fig. 12.-Infrared Spectrum of $\text{C}_6\text{H}_5\text{P}(\text{O})(\text{NH}_2)_2$ (Nujol).

phosphine. The chloramination-ammonolysis of tetramethyldiphosphine yields dimethyldiaminophosphonium chloride as the only important product. Thus, this reaction appears to be quite analogous to the chloramination of dimethylchlorophosphine. (5,6)

Similarly, the chloramination-ammonolysis of tetraethyldiphosphine gives diethyldiaminophosphonium chloride in yields which average between 60 and 70 per cent of theory. Unlike in the chloramination of diethylchlorophosphine, however, the intermediate, $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$, is not produced. On the other hand, a trace of diethylphosphonitrilic trimer is observed. It is curious that only a trace of diethyldiaminophosphonium chloride undergoes complete condensation,



while no intermediate product of condensation, $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$, is observed. One might speculate that at some time during this exothermic reaction the complete condensation could momentarily become kinetically favored.

The chloramination-ammonolysis of tetraphenyldiphosphine is not so straightforward and simple as the chloramination-ammonolysis of tetraalkyldiphosphines. However, it is clear that cleavage of the phosphorus-phosphorus bond occurs. The principal product which could be isolated and

identified was the substance,

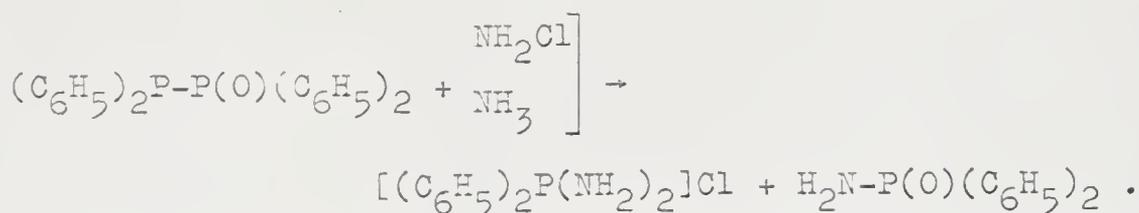
$[(C_6H_5)_2P(NH_2)-N=P(NH_2)(C_6H_5)_2]Cl$. This was also an important product of the chloramination-ammonolysis of diphenylchlorophosphine.⁽¹⁾ A more interesting result is the

identification of $[(C_6H_5)_2P(NH_2)_2]Cl$ as a product of the reaction. Diphenyldiaminophosphonium chloride or the diphenyldiaminophosphonium ion is the postulated reactive intermediate⁽¹⁾ in the formation of

$[(C_6H_5)_2P(NH_2)-N=P(NH_2)(C_6H_5)_2]Cl$ and $[(C_6H_5)_2PN]_3$ from $(C_6H_5)_2PCl$, NH_2Cl and NH_3 . Unfortunately, the yield of this material was small and it could not be purified from traces of ammonium chloride. The substance is soluble in polar solvents such as alcohol and water but is insoluble in chloroform and non-polar solvents such as benzene and n-hexane. Dissolved in water, it gives an immediate test for chloride ion with Ag^+ . However, it must hydrolyze rapidly in water for no metathetic derivative of PF_6^- or $(C_6H_5)_4B^-$ could be detected.

A third product which was isolated and identified was the amide of diphenylphosphinic acid, $(C_6H_5)_2P(O)NH_2$. This material was characterized by its melting point, nitrogen analysis and infrared spectrum. It is quite possible that during its preparation, the starting material, tetraphenyldiphosphine, became contaminated with the monoxide, $(C_6H_5)_2P-P(O)(C_6H_5)_2$. This material might undergo

chloramination-ammonolysis giving the amide as one product,



This is an interesting possibility and should be investigated further.

Alternatively, the amide may arise from the hydrolysis of diphenyldiaminophosphonium chloride,



Finally, in some experiments an intractable, benzene-soluble tar was isolated from the chloramination-ammonolysis of tetraphenyldiphosphine. This material melted at just above room temperature and contained no chlorine, but still appeared to be air sensitive, turning wet after a few minutes exposure to the atmosphere. Some structural features are evident from examination of the infrared spectrum (Fig. 8). This spectrum shows N-H stretching and deformation peaks in the region from 3380 cm^{-1} to 3180 cm^{-1} and at 1575 cm^{-1} , respectively. Phenyl C-H stretching peaks and "C=O" stretching peaks are observed at 3040 cm^{-1} and at 1590 cm^{-1} , 1480 cm^{-1} and 1439 cm^{-1} . A strong, broad peak is observed at 1260 cm^{-1} which is characteristic of "P=N" stretching in phosphonitrilic derivatives. A strong peak occurs at 1175 cm^{-1} , a region which is sometimes

associated with the phosphoryl group, $\text{>P}=\text{O}$. This peak appears as a shoulder on a strong peak at 1160 cm^{-1} which might be attributed to phenyl C-H in-plane bending. A sharp, strong peak occurs at about 1117 cm^{-1} . This peak is usually observed in compounds in which the phosphorus atom is tetracoordinate and bonded to at least one phenyl group.^(74,75) At 921 cm^{-1} a peak of medium intensity occurs which might be assigned to the P-NH-P grouping.⁽⁹³⁾ A similar peak occurs in the spectrum of $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)-\text{N}=\text{P}(\text{NH}_2)(\text{C}_6\text{H}_5)_2]\text{Cl}$.⁽¹⁾ Several sharp peaks appear in the region of $800-695\text{ cm}^{-1}$. Peaks in this region are usually attributed to C-H out-of-plane bending vibrations in the phenyl groups and to P-phenyl bonds. The observed molecular weight (450) of this substance is in the right range for the grouping, $[(\text{C}_6\text{H}_5)_2\text{P}-\text{N}-\text{P}(\text{C}_6\text{H}_5)_2]$; however, the analytical data obtained so far are not helpful in completing the characterization of this substance.

The infrared spectra of $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)_2]\text{Cl}$ and $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{NH}_2$ (Figs. 7 and 8) resemble each other closely. In fact, in the region from 4000 to 1200 cm^{-1} very little difference is noted in the placement and number of peaks in the two spectra. At 1175 cm^{-1} , however, the spectrum of $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{NH}_2$ has a strong absorption which is attributed to the phosphoryl group. This peak is absent in the spectrum of $[(\text{C}_6\text{H}_5)_2\text{P}(\text{NH}_2)_2]\text{Cl}$. The two spectra also differ

considerably in the region from 1105 to 695 cm^{-1} . This region contains the C-H bending peaks as well as the peaks attributed to P-phenyl bonding. In general, we can say that the infrared spectra confirm the identity of these compounds.

The chloramination-ammonolysis of tetraphenylcyclo-tetraphosphine produces a material which is apparently a linear phosphonitrilic derivative. An examination of its infrared spectrum (Fig. 10) shows a broad N-H stretching band which peaks at 3210 cm^{-1} , a strong N-H deformation band which peaks at 1550 cm^{-1} , a very broad band at 1250-1155 cm^{-1} which is very similar to the "P=N" stretching band in phosphonitrilics, and a sharp peak at 1115 cm^{-1} which is associated with tetracoordinate phosphorus bonded to phenyl. In addition the infrared spectrum contains peaks usually attributed to phenyl C-H stretching and bending vibrations, "C=C" stretching vibrations and P-phenyl bonds. Thus, the infrared spectrum is consistent for the

unit, $\text{C}_6\text{H}_5\text{-P(=N)-NH}_2$. The analytical data compiled on several samples of the same material indicate the same unit since, in all cases, the P:N ratio was almost exactly 1:2.

The average molecular weight of this material, determined cryoscopically on several samples, varied from 750 to 950 indicating an average of 5-7 P-N units. The

complete solubility of this substance in solvents such as benzene and chloroform indicates that the small amount of chlorine present is not caused by impurities such as ammonium chloride. Therefore, we postulate that the chlorine is bonded to the phosphorus atom of the molecule, perhaps as an end-stopping group. This postulate is supported somewhat by the broad, infrared peak at 510 cm^{-1} which is in the region of absorptions attributed to the P-Cl bond. The postulated structure is then,



This formulation is supported by infrared and analytical data as well as by consideration of the physical properties of the material. Clearly, however, the structure of this material is still a subject of speculation. Additional physical and chemical information should be obtained on this interesting substance. At the time of this writing a nuclear magnetic resonance investigation was being undertaken. However, the results of such a study are not yet available.

The second compound obtained from the chloramination-ammonolysis of tetraphenylcyclotetraphosphine was identified as phenyltriaminophosphonium chloride, $[(\text{C}_6\text{H}_5)\text{P}(\text{NH}_2)_3]\text{Cl}$. Although this material could not be isolated in absolute purity from ammonium chloride, there is little question of

its identity. The infrared spectrum (Fig. 11) contains the usual N-H stretching and deformation peaks and the peaks associated with phenyl C-H bonding, phenyl "C=C" bonding and P-phenyl bonding. A strong peak is observed at 1135 cm^{-1} which is attributed to tetracoordinate phosphorus bonded to phenyl. The absence of peaks in the region from 1300 cm^{-1} to 1150 cm^{-1} indicates that the material has neither a condensed P-N=P structure, nor is it contaminated with the amide, $\text{C}_6\text{H}_5\text{P}(\text{O})(\text{NH}_2)_2$. The amide was synthesized easily from phenyltriaminophosphonium chloride by exposing a solution of the chloride in alcohol to moist air. Indeed the infrared spectrum of the amide (Fig. 12) is quite similar to that of phenyltriaminophosphonium chloride. However, it contains a sharp peak at 1155 cm^{-1} attributed to the phosphoryl group.

Although portions of this study are incomplete, there are certain results which are significant. We can now state that chloramine cleaves the phosphorus-phosphorus bonds in substituted diphosphines and in tetraphenylcyclo-tetraphosphine. Although other reaction sequences may be possible, we feel that the first step in the chloramination of diphosphines involves the formation of an aminophosphine and a chlorophosphine,



This step is analogous to the first step in the reaction of certain diphosphines with methyl iodide (Chapter II), and is analogous to the first step in the halogenation of diphosphines. The aminophosphine and the chlorophosphine could then undergo further chloramination and ammonolysis to produce the observed products.

This study has provided a convenient new method for the synthesis of dialkyldiaminophosphonium salts. Previously, these derivatives were synthesized from dialkylchlorophosphines which are obtained with some difficulty. For example, instead of using dimethylchlorophosphine which has a short shelf-life and must be used as soon as it is obtained, we can now utilize tetramethyldiphosphine which can be stored indefinitely and used when desired. The convenience of this method for the preparation of dialkyldiaminophosphonium chlorides will be further appreciated in the discussion of Chapter IV which deals with the condensation reactions of these salts.

This method seems to favor the formation of diamino-phosphonium salts. Thus, using tetramethyldiphosphine and tetraethyldiphosphine, the corresponding diaminophosphonium salt was either the only product or the major product of the reaction. Chloramination-ammonolysis of diethylchlorophosphine, on the other hand, produces only a 20 per cent yield of the diaminophosphonium salt. Tetraphenyldiphosphine

gives diphenyldiaminophosphonium chloride, a material which was a postulated product in the chloramination of diphenylchlorophosphine but was never isolated. Likewise, tetraphenylcyclotetraphosphine produces phenyltriaminophosphonium chloride.

In view of the possible value of diamino- and triaminophosphonium salts as phosphonitrilic precursors (see Chapter IV), we feel that this reaction should be applied to a number of other diphosphines and polyphosphines. This would indicate the generality of the method and possibly make available a variety of diamino- and triaminophosphonium salts for further investigation. Some polyphosphines which should be chloraminated are $(CF_3P)_x$ and $(RP)_x$ where R is an alkyl group. It would also be interesting to examine the reaction of chloramine with amino-substituted diphosphines such as $C_6H_5(R_2N)P-P(R_2N)C_6H_5$ and $(R_2N)_2P-P(R_2N)_2$.

Summary

Chloramination-ammonolysis of tetramethyldiphosphine and tetraethyldiphosphine produces dimethyldiaminophosphonium chloride and diethyldiaminophosphonium chloride in good yields, and produces traces of diethylphosphonitrilic trimer. These materials were identified by chemical analysis and by comparison of their infrared spectra and

melting points with those of the authentic materials produced by other methods.

The chloramination-ammonolysis of tetraphenyldi-phosphine produces a new compound, diphenyldiaminophosphonium chloride, and its postulated condensation product, $[(C_6H_5)_2P(NH_2)-N=P(NH_2)(C_6H_5)_2]Cl$. In addition, the amide, $(C_6H_5)_2P(O)NH_2$, and an unresolved tar were produced in the reaction.

Chloramination-ammonolysis of tetraphenylcyclo-tetra-phosphine produces a material tentatively identified as



This reaction also produced a new compound, phenyltriaminophosphonium chloride. The identity of this material was established by elemental and infrared analysis and by synthesis of a derivative, $C_6H_5P(O)(NH_2)_2$.

Infrared data are presented and interpreted in terms of the structures of the compounds synthesized in this study.

The chemical evidence leads to the conclusion that the chloramination of diphosphines and polyphosphines causes cleavage of the phosphorus-phosphorus bonds. Further chloramination and ammonolysis of the fragments produces the same materials which arise from the chloramination of $RPCl_2$ or R_2PCl compounds. This reaction constitutes a new

method for the production of diamino- and triaminophosphonium chlorides. In this connection, the reaction is more convenient than the one which employs chlorophosphines because diphosphines and polyphosphines are easier to prepare and store.

CHAPTER IV

THE PYROLYTIC CONDENSATION OF DIALKYLDIAMINOPHOSPHONIUM CHLORIDES AND OF $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$

Experimental

Manipulation of materials.--The aminophosphonium salts used in this study were sensitive to atmospheric moisture, deliquescing and subsequently hydrolyzing after only a few minutes exposure. Therefore, the starting materials were stored and transferred in a D. L. Herring Model HE-43 Dri Lab equipped with a Model HE-93 Dri Train. The products of the condensation reactions were usually unreactive to moist air. However, in certain cases the products were hygroscopic in air. These materials were dried in a vacuum desiccator and stored in sealed vials in the desiccator.

Benzene and petroleum ether were obtained as reagent grade materials and were dried and stored over calcium hydride. Tri-n-butylphosphine was obtained from Food Machinery and Chemical Corporation and used as obtained. Phosphorus trichloride was obtained as the reagent grade material and used as obtained. All solvents and liquid reagents were transferred by pipette to minimize exposure to moisture.

Methods of analysis.-Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Some nitrogen analyses were also obtained using a Coleman Model 27 nitrogen analyzer.

Molecular weights were determined either by the cryoscopic method in benzene, or in benzene or chloroform solution using a Mecrolab Vapor Pressure Osmometer.

The infrared spectra of materials synthesized in this study were recorded on a Beckmann Model IR-10 spectrophotometer. Solid samples were either milled with Nujol, pressed into KBr disks, or melted on KBr plates and examined as thin films when the melting point was below 100° C. A summary of the spectral bands of new materials produced in this study between 3.4 and 30 microns is found in Table 6.

Melting points were obtained in capillary tubes using a Thomas-Hoover capillary melting point apparatus.

Preparation of dialkyldiaminophosphonium chlorides and $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$.-In the early stages of this investigation, dimethyldiaminophosphonium chloride and diethyldiaminophosphonium chloride were prepared by the chloramination-ammonolysis of dimethylchlorophosphine and diethylchlorophosphine,⁽⁵⁾ respectively. However, soon after this investigation was begun, a more convenient method was found, namely, the chloramination-ammonolysis of

TABLE 6^(a)INFRARED ABSORPTION DATA (Cm^{-1})

$[(\text{CH}_3)_2\text{PN}]_n$, KBr disk

2975(m), 2900(m), 1410(m), 1290(s), 1270(s), 1200(s,sh),
1160(vs), 1010(w,sh), 965(m), 940(m), 915(s),
880(s), 855(vs), 751(m), 720(s), 685(m),
630(w), 560(m), 490(m), 420(s), 368(w).

$[(n\text{-C}_4\text{H}_9)_2\text{PN}]_3$, melt

2945(s), 2920(s), 2855(m), 2300(w,b), 1459(w),
1450(w), 1400(w), 1362(w), 1300(w), 1260(w),
1224(m), 1155(vs), 1085(w), 1045(w,sh),
1000(w,b), 950(w,b), 913(w), 889(w), 785(w),
719(m), 660(m,b), 505(w), 280(vs,b).

(a) s, strong; m, medium; w, weak; b, broad; v, very;
sh, shoulder.

tetramethyldiphosphine and tetraethyldiphosphine. This method of preparation is discussed in detail in Chapter III.

The substance, $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$, was prepared by the chloramination-ammonolysis of diethylchlorophosphine.⁽⁵⁾ It was also obtained as a product of the condensation of diethyldiaminophosphonium chloride.

Di-n-butyldiaminophosphonium chloride was synthesized by the chloramination of di-n-butylchlorophosphine.⁽⁵⁾ This chlorophosphine was conveniently prepared by the method of V. M. Plets⁽⁹⁴⁾ which involves the decomposition of tri-n-butyldichlorophosphorane



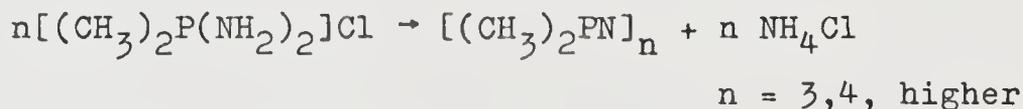
Tributyldichlorophosphorane can be readily synthesized by the reaction of tributylphosphine with PCl_3 :⁽⁸⁷⁾



In a typical experiment, 2.91 ml (33.3 mmoles) of phosphorus trichloride was dissolved in about 50 ml of dry benzene and placed under nitrogen in a Minilab reaction flask (Fig. 5). To this solution, 11.3 ml (50 mmoles) of tri-n-butylphosphine was added dropwise with stirring under a slow flow of dry nitrogen gas. The solution rapidly became deep, orange-red in color and heat was evolved. Near the end of the addition an orange-red, amorphous solid suddenly precipitated from the mixture. At the end of the addition the mixture

was stirred vigorously until it had cooled to room temperature (25° C). The benzene solution was removed from the precipitate by filtration and the precipitate was washed with 1-2, 25 ml portions of dry benzene and filtered, care being taken not to expose the solution to atmospheric moisture. The filtrate and washings were combined and evaporated to dryness in vacuum. The white, crystalline product, $(C_4H_9)_3PCl_2$, was obtained in almost quantitative yield. This material was transferred in the dry box to a 200 ml round bottomed distillation flask and heated under an atmosphere of nitrogen at about 140° C. Butyl chloride distilled from the mixture (b.p. 78° C) and some HCl was evolved. When the distillation of butyl chloride had ceased (1-3 hours) the mixture was cooled and distilled under vacuum. The product distilled at 37° C and 0.1 mm Hg (Lit.⁽⁶⁾: b.p. 0.25 = 39-47° C). The yield of dibutylchlorophosphine by this method was usually over 50 per cent of theory based on the amount of $(C_4H_9)_3PCl_2$ used.

The Pyrolytic Condensation of Dimethyldiaminophosphonium Chloride



In a typical experiment, 1.15 g (8.9 mmoles) of dimethyldiaminophosphonium chloride was placed in a semi-micro sublimation apparatus (Fig. 13) and heated at about

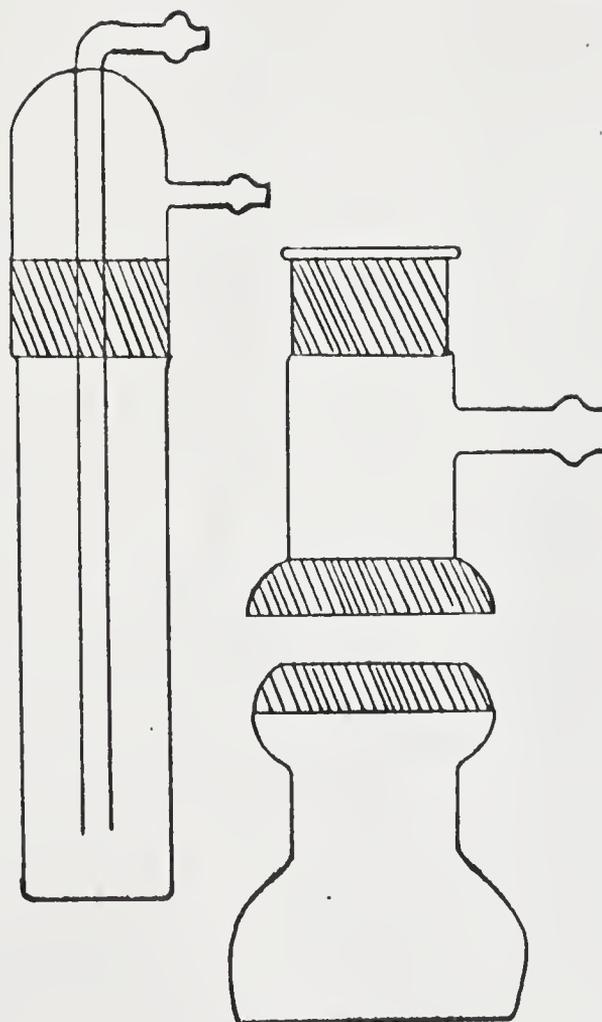


Fig. 13.-Semimicro Sublimation Apparatus.

200° C and 0.2 mm Hg for three days. The resulting sublimate was removed from the cold finger under nitrogen and extracted with several portions of hot, 30-60°, petroleum ether. The residue from this extraction was identified as ammonium chloride. Evaporation of the petroleum ether yielded a white, crystalline material with a melting range of 160-170° C. Anal. Found: C, 31.83; H, 7.98; P, 41.15; N, 18.73. Calculated for $[(\text{CH}_3)_2\text{PN}]_n$: C, 32.01; H, 8.06; P, 41.28; N, 18.66. Crude yield: 0.55 g (82% of theory). The mixture was separated into almost equal amounts of dimethylphosphonitrilic trimer and tetramer⁽²⁶⁾ by fractional crystallization from petroleum ether. The molecular weights (cryoscopic in benzene) were 220 (calculated: 225) and 311 (calculated: 300), respectively. The trimer melted with sublimation at 187-190° C (Lit:⁽²⁶⁾ M.P. 195-196° C) and the tetramer melted with sublimation at 157-160° C (Lit:⁽²⁶⁾ M.P. 163-164° C). The infrared spectra of these compounds agree with the assignments reported by Searle.⁽²⁶⁾

The Synthesis of Highly Polymeric Dimethylphosphonitrile

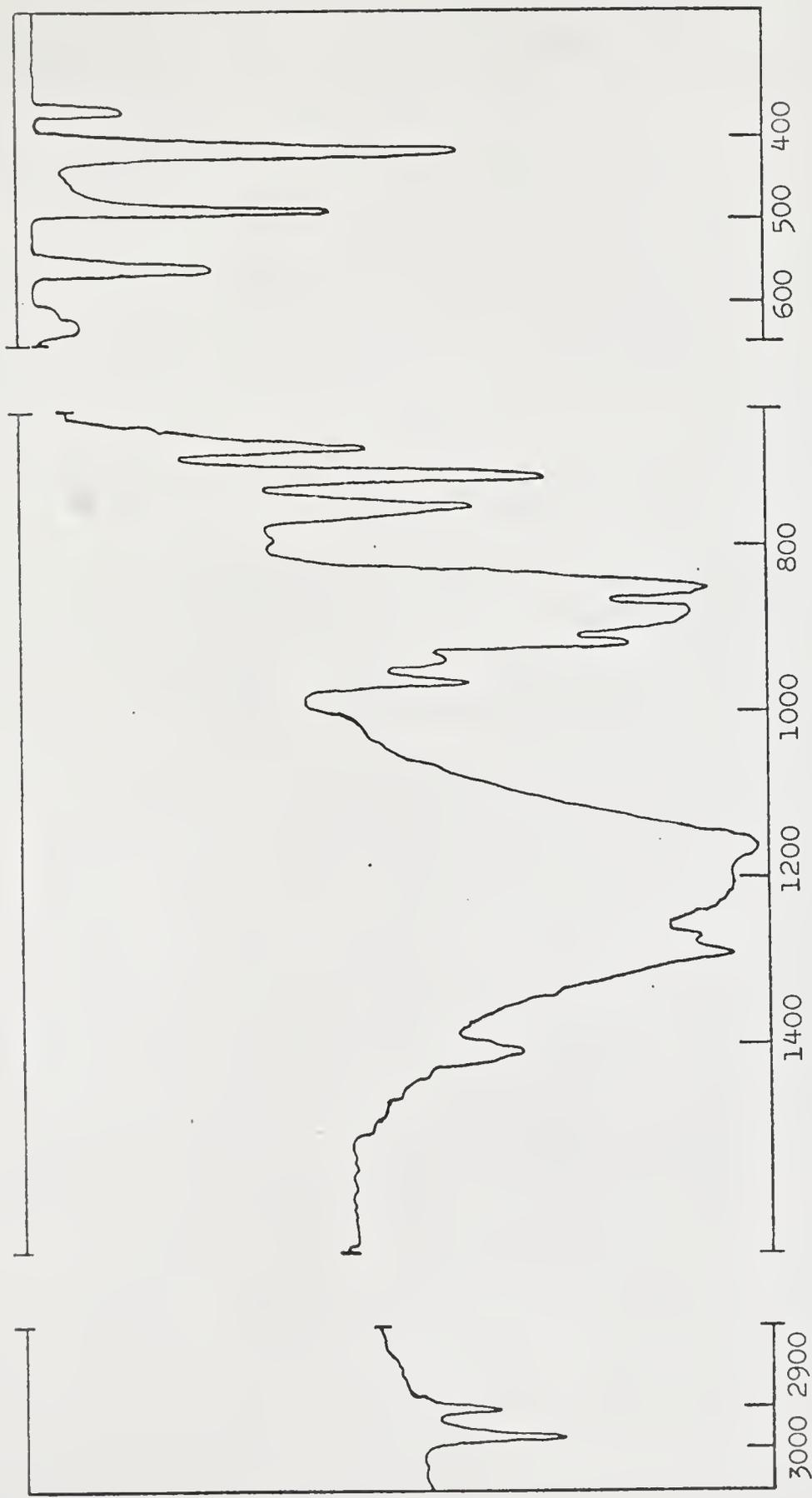
In several pyrolyses of dimethyldiaminophosphonium chloride, described above, a trace of a black, glassy residue was observed in the sublimation pot at the completion of the sublimation of ammonium chloride and $[(\text{CH}_3)_2\text{PN}]_{3,4}$. This material melted in the range of 136-146° C and was not visibly sensitive to moist air. Anal.

Found: C, 31.81; H, 8.16; N, 18.79; P, 41.14; Mol. Wt., 7640 (Mol. Wt. of a $(\text{CH}_3)_2\text{PN}$ -unit, 75). Thus, it was discovered that the pyrolytic condensation of dimethyldiaminophosphonium chloride produces trace amounts of $[(\text{CH}_3)_2\text{PN}]_n$ where n is a large number. The yield of high polymer could be increased considerably by mixing the starting phosphonium salt with finely divided ammonium chloride produced by the gas phase reaction of chlorine and ammonia. In a typical experiment the phosphonium salt and a weighed amount of ammonium chloride were thoroughly mixed in the dry box, placed in a semimicro sublimation apparatus and pyrolyzed as before. The dimethylphosphonitrilic trimer and tetramer and ammonium chloride sublimed to the cold finger and were separated as before. The high polymer remained in the sublimation pot and was either scraped from this vessel or removed by dissolving it in benzene. The effect of ammonium chloride on the distribution of products of this reaction is shown in Table 7. The infrared spectrum of the crude polymer is shown in Figure 14.

The high polymers so formed were usually soluble in hot benzene and chloroform. In some cases a residue was observed which swelled in benzene but did not dissolve. Extraction⁽⁹⁵⁾ of the crude material with cyclohexane produced, upon evaporation of the solvent, a white powder melting at 139-146° C and having a molecular weight of from

TABLE 7
EFFECT OF AMMONIUM CHLORIDE ON PRODUCT DISTRIBUTION

Wt. % of NH_4Cl in Starting Material	Recovered Yield of Polymer, %	Recovered Yield of $[(\text{CH}_3)_2\text{PN}]_{3,4}$ %
0	4.5	82
trace	4.2	82
trace	6.9	79
5.6	13.6	56
9.9	32	42
10.4	32	--
17.4	14.4	44
20	11.2	68



Wave number, cm^{-1}

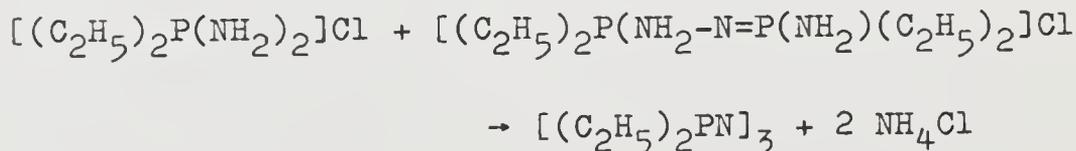
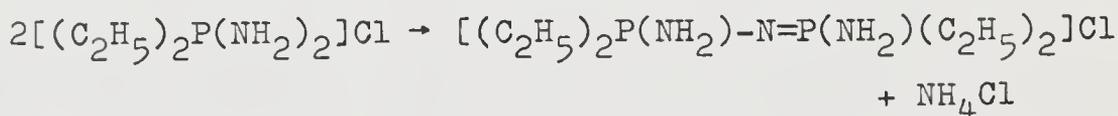
Fig. 14.-Infrared Spectrum of $[(\text{CH}_3)_2\text{PN}]_n$ (KBr).

3500 to 9000 depending on the sample used. The residue from the cyclohexane extraction was soluble in benzene, melted at 136-138° C and had a molecular weight of 12,500.

Thermal gravimetric analysis⁽⁹⁵⁾ (using an Aminco Thermograv, American Instrument Co.) of a sample with an average molecular weight between 8000 and 9000 was obtained using a 100 cc/min flow of helium at a rate of temperature increase of 3°/min. This analysis showed no weight loss up to 300° C, and a rapid loss of weight from 300° to 500° C during which essentially all of the sample sublimed from the apparatus as low-molecular-weight cyclic material, principally trimer and tetramer.

Differential thermal analysis was carried out on this material⁽⁹⁵⁾ in helium using a heating rate of 3°/min with Al₂O₃ as a reference. A sharp endotherm was observed at 142° C (M.P. of sample: 143-145° C) and a broad exotherm was observed starting at about 300° C, the latter presumably resulting from the onset of thermal decomposition.

The Pyrolytic Condensation of Diethyldiaminophosphonium Chloride



In a typical experiment, 0.99 g (6.3 mmoles) of diethylidiaminophosphonium chloride was placed in a semimicro sublimation apparatus and heated to about 180° C and 0.2 mm Hg for five days. This process produced a white sublimate as well as a substantial amount of light-colored residue. The residue was dissolved in boiling benzene and filtered. Upon evaporation of the benzene a white, crystalline material was recovered which melted at 61-64° C; yield, 0.30 g. This material is hygroscopic, water-soluble and gives a Cl- test with aqueous AgNO₃. Anal. Found: N, 16.3. Calculated for [(C₂H₅)₂P(NH₂)-N=P(NH₂)(C₂H₅)₂]Cl: N, 16.18. The infrared spectrum of this material was identical with that of [(C₂H₅)₂P(NH₂)-N=P(NH₂)(C₂H₅)₂]Cl (M.P. 58-61° C) produced by chloramination-ammonolysis of diethylchlorophosphine.⁽⁵⁾ The nuclear magnetic resonance data for [(C₂H₅)₂P(NH₂)-N=P(NH₂)(C₂H₅)₂]Cl, not included in the earlier reference,⁽⁵⁾ provides some interesting additional information about the structure of this substance. The proton magnetic resonance spectrum (Fig. 15) was run on a Varian high resolution spectrometer at 56.4 Mc using a CDCl₃ solution. The spectrum was obtained by sweeping slowly through the field and interchanging the reference, acetaldehyde, with the sample. Peak A refers to the NH₂ protons, peak B to the methylene protons and peak C to the methyl protons. The usual methylene quartet and methyl

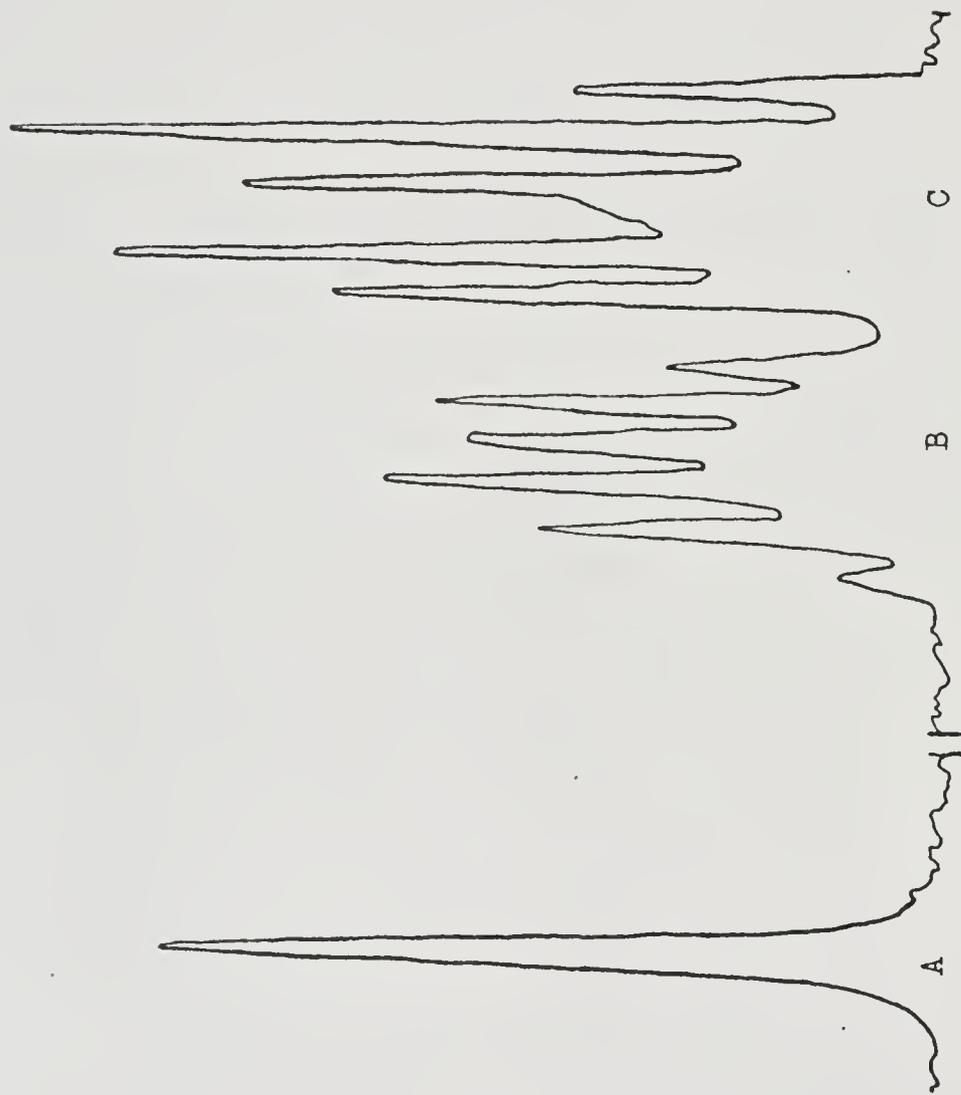
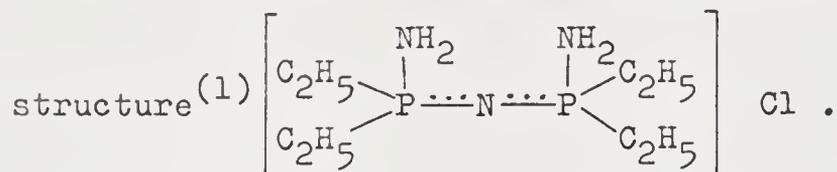


Fig. 15.-H' N.M.R. Spectrum of $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$.

triplet are further split by spin-spin coupling with the phosphorus atoms. The spectrum is consistent with the



Approximate τ values and average chemical shift values are listed in Table 8.

TABLE 8

N. M. R. SPECTRAL DATA FOR $[(\text{C}_2\text{H}_5)_2\text{P}(\text{NH}_2)\text{-N}=\text{P}(\text{NH}_2)(\text{C}_2\text{H}_5)_2]\text{Cl}$

Group	Chemical Shift, τ	Coupling, c.p.s.
NH ₂	5.18	H-H 8
CH ₂	7.98 (ave.)	P-CH ₂ 14
CH ₃	8.75 (ave.)	P-CH ₃ 18

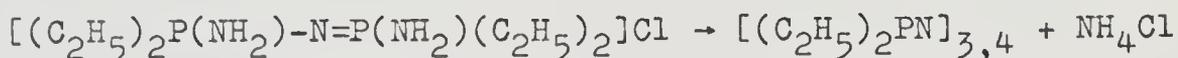
The ratio of areas under the NH₂ peak to those under the CH₂ and CH₃ peaks is approximately 1:5. When the nuclear magnetic resonance spectrum was run at 19.3 Mc a single, broad peak for phosphorus was observed corresponding to a chemical shift of 41 p.p.m. to low field in comparison to 85 per cent phosphoric acid.

The sublimate was dissolved in benzene and filtered to remove ammonium chloride. The benzene was removed by evaporation and the resulting white, crystalline material

was carefully resublimed at about 50° C and 0.1 mm Hg. The sublimate melted at 109-112° C. Anal. Found: C, 46.39; H, 9.92; P, 30.30; N, 13.49; Mol. Wt. 305. Calculated for $[(C_2H_5)_2PN]_3$: C, 46.60; H, 9.78; P, 30.04; N, 13.59; Mol. Wt. 309. Yield: 0.21 g (33% of theory). The infrared spectrum of this material agreed with the assignments listed in the literature⁽²⁵⁾ for diethylphosphonitrilic trimer. The literature value for the melting point of the trimer is 117.5-119° C.

The residue from this sublimation was recrystallized from benzene and identified as the intermediate, $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$. The total yield of this intermediate was 0.34 g (41% of theory).

The Pyrolytic Condensation of
 $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$



In a semimicro sublimation apparatus, 0.85 g (3.3 mmoles) of $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$ was heated at about 200° C and 0.15 mm Hg for 4-5 days. This process produced a white, oily sublimate and a trace of black residual ash. The sublimate was extracted with several portions of petroleum ether. The residue from this extraction was again extracted with several portions of hot

benzene. From the benzene solution, 0.25 g (0.96 mmoles) of unreacted starting material was recovered. From the petroleum ether solution, 0.36 g (75% of theory based on the starting material actually reacted) of a mixture of diethylphosphonitrilic tetramer and trimer was recovered by evaporation. The final residue of the solvent extractions consisted of ammonium chloride.

The mixture of diethylphosphonitrilic tetramer and trimer was separated by repeated fractional sublimation at 53° C and 0.1 mm Hg. By this method the mixture was found to consist of about 20 per cent trimer (M.P. 110-114° C) and 80 per cent tetramer (a viscous oil⁽²⁵⁾). Anal. Found: C, 46.36; H, 9.76; P, 29.84; N, 13.30; Mol. Wt. 401. Calculated for $[(C_2H_5)_2PN]_4$: C, 46.60; H, 9.78; P, 30.04; N, 13.59; Mol. Wt., 412. The infrared spectrum of this material agrees quite well with the assignments listed in the literature⁽²⁵⁾ for diethylphosphonitrilic tetramer.

The Pyrolytic Condensation of Di-n-butyl-diamino-phosphonium Chloride



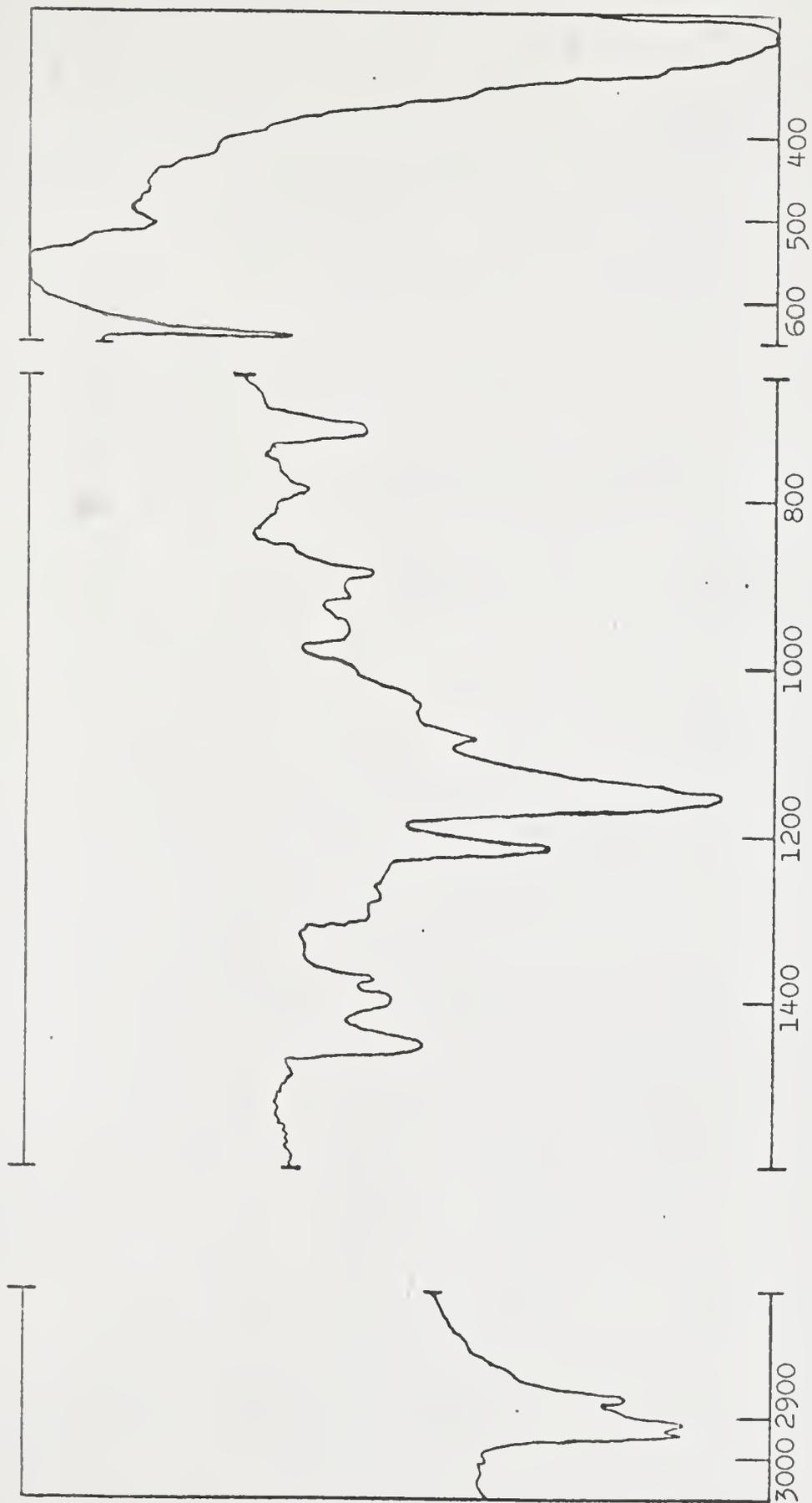
Di-n-butyl-diaminophosphonium chloride (1.08 g or 5 mmoles) was placed in a semimicro sublimation apparatus and heated at 190° C and 0.1 mm Hg for four days. A white sublimate was observed. Only a trace of black residue

remained in the pot at the completion of the reaction. The sublimate was extracted with 30-60° petroleum ether. The insoluble residue was shown to be ammonium chloride. Evaporation of the petroleum ether yielded a white wax which melted at 45-50° C and sublimed readily at 70° C and 0.1 mm Hg. Anal. Found: C, 60.09; H, 11.37; P, 19.23; N, 8.90; Mol. Wt., 470. Calculated for $[(C_4H_9)_2PN]_3$: C, 60.35; H, 11.40; P, 19.45; N, 8.80; Mol. Wt., 478. Yield: 0.77 g (95% of theory). The infrared spectrum of dibutylphosphonitrilic trimer is shown in Figure 16.

Discussion

The results of this study show that diamminophosphonium chlorides can be easily converted by pyrolytic condensation to phosphonitrilic derivatives. The yields observed in such a process are essentially quantitative.

The pyrolytic condensation of dimethyldiaminophosphonium chloride produces amounts of dimethylphosphonitrilic trimer and tetramer. These compounds were separated from the byproduct, ammonium chloride, by their solubility in petroleum ether, and the trimer/tetramer mixture was separated by fractional crystallization from petroleum ether. The materials were identified by elemental analysis, molecular weight determinations and comparison of their infrared spectra with published infrared data.⁽²⁶⁾ When finely



Wave number, cm^{-1}
Fig. 16.-Infrared Spectrum of $[(n\text{-C}_4\text{H}_9)_2\text{PN}]_3$ (Melt).

divided ammonium chloride was mixed with the starting material, pyrolysis produced a new compound identified as highly polymeric dimethylphosphonitrile. This material is

a polymer of the formula, $\left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad / \\ \text{P}=\text{N} \end{array} \right]_n$, where n varies from 50 to 150. It was characterized by elemental analysis, molecular weight determinations, infrared analysis, thermal gravimetric analysis and differential analysis. The infrared spectrum of this material (Fig. 14) is somewhat similar to that of the cyclic trimer or tetramer having C-H stretching and deformation peaks at 2970 cm^{-1} and at 1410 cm^{-1} , respectively. Two peaks occur at 1290 and 1270 cm^{-1} which are attributed to P-CH₃ bonding.⁽²⁶⁾ The "P=N" stretching band exhibits a broad, strong shoulder at about 1200 cm^{-1} and a strong peak at 1160 cm^{-1} . There are several peaks in the region from 850 cm^{-1} to 965 cm^{-1} and from 685 cm^{-1} to 755 cm^{-1} . Peaks in this region are generally attributed to "P=N" elongation and "P-N=P" deformation.^(24,25) Definite assignments for these peaks cannot be made at the present time. Yields of the polymer as high as 32 per cent of theory were obtained when mixtures of about 10 per cent finely divided ammonium chloride and 90 per cent dimethyldiaminophosphonium chloride were pyrolyzed.

The pyrolytic condensation of diethyldiaminophosphonium chloride produces the primary condensation product,

$[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$ which was recovered in about 40 per cent yield, and diethylphosphonitrilic trimer, $[(C_2H_5)_2PN]_3$ which was recovered in about 30 per cent yield. The first condensation product was shown by elemental analysis and infrared analysis to be identical with $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$ produced by the chloramination-ammonolysis of diethylchlorophosphine.⁽⁵⁾ Diethylphosphonitrilic trimer was identified by elemental analysis, molecular weight determination and comparison of its infrared spectrum with published infrared data.⁽²⁵⁾

The pyrolytic condensation of the intermediate, $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$, produces a mixture of diethylphosphonitrilic trimer and tetramer which was recovered in about 75 per cent yield. The phosphonitrilic mixture, consisting of about 80 per cent tetramer and 20 per cent trimer, was separated from the byproduct, ammonium chloride, by its solubility in petroleum ether. The trimer and tetramer were then separated from each other by repeated, fractional vacuum sublimation. In this case, the trimer was slightly more volatile than the tetramer and a separation could be made.

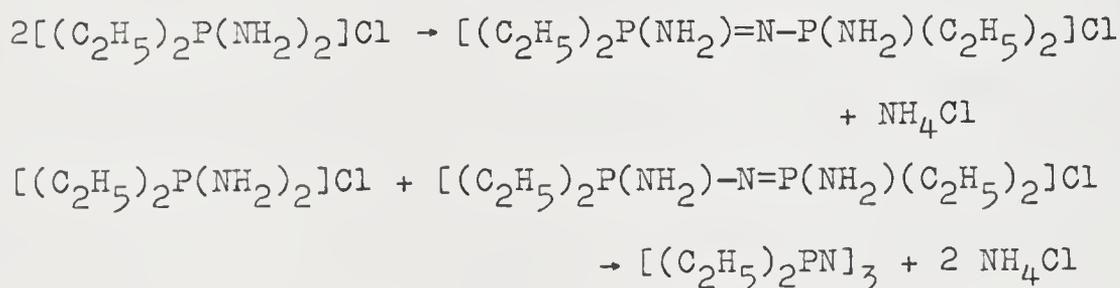
The pyrolytic condensation of di-n-butylldiaminophosphonium chloride produces a nearly quantitative yield of a new material identified as di-n-butylphosphonitrilic trimer, $[(n-C_4H_9)_2PN]_3$. This material was characterized by

elemental analysis, molecular weight determination and infrared analysis. The infrared spectrum of this material (Fig. 16) has the usual C-H stretching and deformation peaks in the region of 2950-2850 cm^{-1} and 1450-1370 cm^{-1} , respectively. Bands attributed to skeletal $-\text{CH}_2-$ vibrations occur at 1400 cm^{-1} , 1300 cm^{-1} and at 1260 cm^{-1} . A sharp peak is observed at 1215 cm^{-1} which may be attributed to P-C bonding. The "P=N" stretching peak occurs at 1155 cm^{-1} . Of all the phosphonitrilic derivatives for which this peak has been measured, it occurs at the lowest energy in this derivative. This is to be expected because the butyl groups have little, if any, electron attracting ability. Thus, they are unable to cause appreciable delocalization of the nitrogen lone-pair electrons into the region of the P-N bond. The remainder of the spectrum between 1155 cm^{-1} and 650 cm^{-1} contains several peaks of weak intensity, some of which may be attributed to skeletal vibrations of the butyl groups. Others lie in the region assigned to "P=N" deformation peaks, "P-N=P" stretching peaks and ring breathing vibrations. We can make no definite assignments in this region at this time.

This study establishes the fact that dimethyldiaminophosphonium chloride, diethyldiaminophosphonium chloride, di-n-butyldiaminophosphonium chloride and $[(\text{C}_2\text{H}_5)_2\text{P}(\text{NH}_2)-\text{N}=\text{P}(\text{NH}_2)(\text{C}_2\text{H}_5)_2]\text{Cl}$ are convenient phosphonitrilic precursors, giving excellent yields of cyclic

phosphonitrilics under pyrolytic conditions. Combined with the findings of Chapter III, this study constitutes an important part of a new method of synthesis of such derivatives from substituted diphosphines, chloramine and ammonia.

The results of this investigation have provided very convincing evidence in favor of the step-wise reaction sequence postulated⁽¹⁾ earlier in which the then unknown diamminophosphonium ion, $R_2P(NH_2)_2^{\oplus}$, was considered to be a reactive intermediate leading to phosphonitrilic derivatives. The case in point is the pyrolysis of diethyldiaminophosphonium chloride. The only products of this reaction are $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$ and $[(C_2H_5)_2PN]_3$. Indeed, these are the expected products if one assumes the following sequence



The pyrolysis of the intermediate,

$[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$, produces chiefly diethylphosphonitrilic tetramer. Some cleavage of the intermediate does occur, however, resulting in the formation of diethylphosphonitrilic trimer and some decomposed material.

One of the most interesting results of this study was the discovery and characterization of highly polymeric dimethylphosphonitrile. This discovery has attracted interest for several reasons. First of all, despite all the previous work in phosphonitrilic chemistry, there is a paucity of information concerning the synthesis of thermally stable and unreactive high polymers with the repeating unit

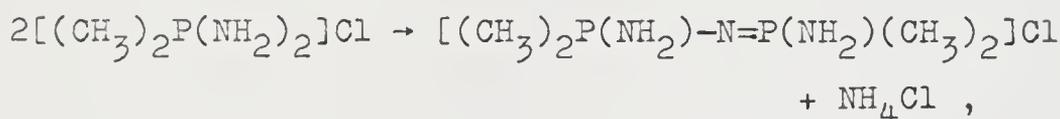
$\left[\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad / \\ \text{P} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \right]_n$ (See Chapter II). This method of synthesis is one of the few which results in a phosphonitrilic high polymer which is soluble in common solvents, which can be molded mechanically and which is relatively unreactive toward moisture and oxygen.

In addition to exciting academic interest, this method may also prove valuable in the synthesis of commercially useful polymers. Although the polymeric material synthesized in this study has some disadvantages in its ready solubility, low melting point and thermal instability above 300° C, films of the substance can be cast which have reasonable strength.⁽⁹⁵⁾ The dimethylphosphonitrile is

isoelectronic with dimethylsiloxane, $\left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad / \\ \text{Si} \\ \diagup \quad \diagdown \\ \text{O} \end{array} \right]_n$, the basic unit of an inorganic polymer system which has enjoyed such wide use in recent years that its parent, $(\text{CH}_3)_2\text{SiCl}_2$, is now produced commercially in large quantities. If the isoelectronic relationship is any indication of chemical

and physical similarities which may exist in these two systems of inorganic polymers, then there is a possibility that the process discovered in this study may become commercially important in the future.

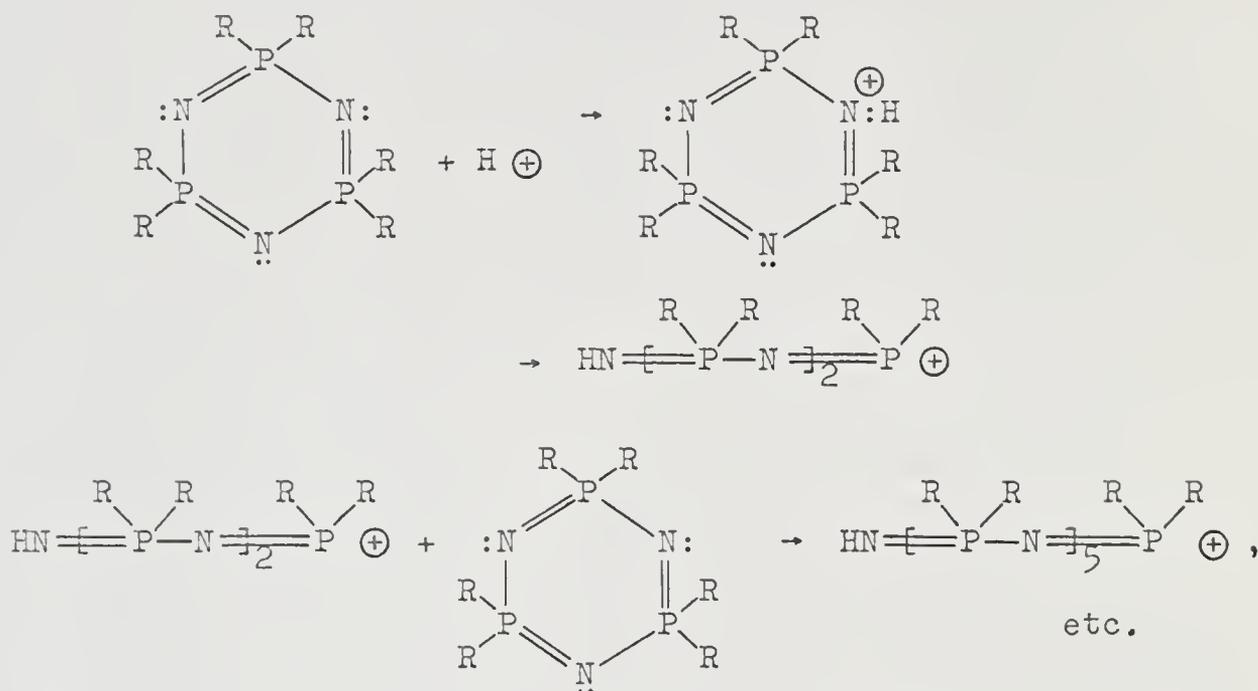
It is interesting to note that the yield of high polymers from the pyrolysis of dimethyldiaminophosphonium chloride seems to depend on the amount of ammonium chloride mixed with the starting material (Table 7), under similar conditions of temperature, pressure and time. The postulated first step of the condensation process,



has been confirmed in the pyrolysis of diethyldiaminophosphonium chloride. Since the actual mechanism of condensation is not clearly known, any statement concerning the mechanism of the effect of ammonium chloride on the first step or subsequent intermolecular condensations would be highly speculative.

However, in view of the fact that the cyclic dimethylphosphonitriles are weak bases,⁽¹⁹⁾ it is conceivable that in the molten reaction mixture a proton transfer could occur between ammonium chloride and a ring nitrogen. This could result in the breaking of a P-N bond and the formation of a $\overset{\text{N}}{\text{P}}^{\oplus}$ species which could attack other ring-nitrogen

atoms and lead to linear products. For instance, the attack could occur on a cyclic trimer



This is similar to the mechanism postulated by Allcock and Best⁽⁵²⁾ for the polymerization of $[\text{PNCl}_2]_{3,4}$ (see page 21). The polymer formed is not highly cross-linked and therefore undergoes almost complete depolymerization to cyclic derivatives in the 300-500° range.

There are two suggestions which we can make for further work in this area. Both suggestions are concerned with the formation of high polymers. The effect of ammonium chloride on the pyrolytic condensation of diamminophosphonium chlorides was investigated only in the case of dimethyl-diamminophosphonium chloride. This effect should be studied

with other diaminophosphonium chlorides in order to investigate its general applicability in the synthesis of an homologous group of $[R_2PN]$ polymers. Secondly, the effect of NH_4Cl on cyclic phosphonitrilic derivatives, $[R_2PN]_{3,4}$, should be investigated under various conditions in order to test the validity of the polymerization mechanism proposed above.

Summary

The pyrolytic condensation of dimethyldiaminophosphonium chloride produces in high yield the known phosphonitrilic derivatives, $[(CH_3)_2PN]_{3,4}$, and a new material identified by elemental analysis, molecular weight determination and infrared spectrum analysis as the substance,

$$\left[\begin{array}{c} CH_3 \quad CH_3 \\ \diagdown \quad / \\ P = N \\ \diagup \quad \diagdown \end{array} \right]_n$$
, where n varies from 50 to 150. When finely divided ammonium chloride is mixed with the starting material the yield of high polymer is increased. The highest yield of polymer (32%) was produced by a mixture consisting of about 10 per cent ammonium chloride and 90 per cent dimethyldiaminophosphonium chloride. A possible polymerization mechanism is put forward to explain the effect of ammonium chloride on this system.

The pyrolytic condensation of diethyldiaminophosphonium chloride produces the known compounds,

$[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$, and $[(C_2H_5)_2PN]_3$ in good yield. This reaction illustrates the step-wise nature of the reaction sequence leading from diaminophosphonium chlorides to phosphonitrilic derivatives.

The pyrolytic condensation of $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$ produces a mixture of the known phosphonitrilic derivatives, $[(C_2H_5)_2PN]_{3,4}$. This mixture consisted of about 80 per cent tetramer and 20 per cent trimer, and was recovered from the reaction in about 75 per cent yield.

The pyrolytic condensation of di-n-butyl-diamino-phosphonium chloride produces a new phosphonitrilic derivative, $[(n-C_4H_9)_2PN]_3$, in nearly quantitative yield. This material was characterized by elemental analysis, molecular weight determination and infrared analysis. The characteristic "P=N" stretching peak in this material occurs at 1155 cm^{-1} .

This study confirms the reaction sequence postulated earlier⁽¹⁾ for the formation of phosphonitrilic derivatives by condensation of diaminophosphonium chlorides. It also provides a new method for the formation of a highly polymeric phosphonitrile, and thus may become important as a general synthetic procedure for such inorganic polymers.

CHAPTER V

THE REACTION OF DIALKYLDIAMINOPHOSPHONIUM CHLORIDES WITH TRI-, TETRA-, AND PENTACHLOROPHOSPHORANES

Experimental

Manipulation of materials.-The dialkyldiaminophosphonium chlorides and the chlorophosphoranes used in this study are rapidly hydrolyzed in the presence of water and were stored and transferred in a D. L. Herring Model-43 Dri Lab equipped with a Model HE-93 Dri Train. Strict precautions were taken to avoid contamination of solvents and other reagents by moisture.

All solvents were obtained as the reagent grade products. Carbon disulfide was dried and stored over P_2O_5 . All other solvents were dried and stored over calcium hydride. Triethylamine was obtained as the technical product and dried and stored over calcium hydride.

Methyldichlorophosphine was obtained from Food Machinery and Chemical Corporation and was used as obtained. This material was stored and transferred by pipette in the dry box. Tetramethyldiphosphine was prepared by the desulfuration of tetramethyldiphosphine disulfide with tributyl phosphine, as described in Chapter III (page 36).

It was purified by distillation and stored in the dry box. Phosphorus pentachloride was obtained as the reagent grade product and was used as obtained. Dimethyldiaminophosphonium chloride and diethyldiaminophosphonium chloride were obtained by chloramination-ammonolysis of the corresponding diphosphines. This method is described in Chapter III.

Methods of analysis.-Infrared spectra of the materials produced in this study were obtained using either a Beckmann Model IR-10 grating infrared spectrometer or a Perkin-Elmer Model 337 grating infrared spectrometer. Solid samples were either mixed with KBr and pressed into pellets or mulled with Nujol and examined between KBr disks. In certain instances thin films of material could be obtained by carefully evaporating a chloroform solution of the sample on a KBr disk. Samples of substances which were sensitive to moist air were prepared for infrared analysis in the dry box. A summary of the spectral bands of these materials between 2.5 and 25 microns is presented in Table 9.

Elemental analyses and molecular weight determinations were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Several nitrogen analyses were carried out in these laboratories using a Coleman Model 29 Nitrogen Analyzer. For the compounds CH_3PCl_4 and $(\text{CH}_3)_2\text{PCl}_3$ the

TABLE 9(a)

INFRARED SPECTRAL DATA, Cm^{-1} CH_3PCl_4 , Nujol

2900(vs), 2840(vs), 1455(vs), 1375(s), 1298(w),
 1275(m), 1259(m), 1195(w), 1140(w,b), 1063(w),
 920(vs,b), 890(vs,b), 788(s), 733(w,sh),
 720(m), 605(vs,b), 542(m), 492(w,b), 474(m,sh),
 467(s).

 $(\text{CH}_3)_2\text{PCl}_3$, Nujol

3210(w), 3125(w), 2920(vs), 2850(vs), 2760(s),
 2700(w,sh), 2650(w,sh), 2575(w), 2370(w),
 2340(w), 2310(w), 2260(m), 2249(m), 2210(m),
 2170(w), 2040(w), 1659(s,b), 1580(vw), 1505(w,b),
 1455(vs), 1405(s), 1397(vs), 1379(vs), 1365(s,sh),
 1305(s), 1290(vs), 1250(w), 1140(w,b), 1065(w),
 966(vs), 940(vs), 900(vs), 880(w), 780(w,sh),
 760(m), 746(vs), 579(vs), 500(s).

 $(\text{CH}_3)_2\text{Cl}_4\text{P}_3\text{N}_3$, Nujol

2940(vs,b), 2850(vs), 2715(w), 2665(w,b),
 2299(w,b), 2245(w), 2175(w), 2144(w), 2085(w),
 2020(m), 1996(w,sh), 1960(w), 1939(w), 1874(w),
 1869(w), 1805(w), 1766(w), 1651(w), 1440(vs),
 1418(s), 1405(m), 1380(vs), 1365(s), 1308(vs),
 1295(vs), 1242(s,sh), 1220(vs), 1170(vs),
 962(s), 935(s), 905(w), 881(vs), 876(s),
 787(s), 758(s), 722(w), 694(s), 674(w),
 634(vs), 584(vs,b), 510(vs,b), 431(w), 404(vs).

 $[(\text{CH}_3)_2\text{PN} \cdot (\text{CH}_3)\text{ClPN}]_x$, Film

2899(vs,b), 2604(s), 1650(w,b), 1405(s),
 1305(vs,b), 1220(vs,b), 990(vs,sh), 971(vs,sh),
 935(vs,b), 881(vs), 819(s,b), 749(s), 682(w),
 678(w,sh), 662(m), 649(w,sh), 521(w,sh),
 488(b,sh), 467(s).

Table 9 (cont'd)



2959(m), 2920(m), 2890(w), 2860(m), 1455(m,sh),
1444(m), 1395(w), 1278(s), 1200(vs,b), 1150(vs),
1030(w), 1009(s), 821(s), 788(w), 750(w),
720(m), 677(w,sh), 665(w), 650(w), 610(s),
561(vs), 525(w), 489(vs), 407(w), 400(w,sh),
375(m).

(a) s, strong; m, medium; w, weak; b, broad; v, very;
sh, shoulder.

sampling technique of Galbraith Laboratories was not refined enough to prevent hydrolysis of the samples prior to analysis. Therefore, these materials could only be characterized by chloride analysis carried out in these laboratories. The samples were first transferred to weighed vials in the dry box. The weighed samples were then submerged, vials and all, in a hydrolyzing solution consisting of 25 ml of ethanol and 10 ml of 10 per cent NaOH. The analysis was then carried out by the usual Volhard procedure. This method was sufficient for the identification of the compounds; however, the values obtained were always slightly higher than theoretical.⁽⁵⁾

Melting points were determined in a Thomas-Hoover capillary melting point apparatus using tubes sealed with wax under nitrogen.

Preparation of CH_3PCl_4 and $(\text{CH}_3)_2\text{PCl}_3$.-The information to be found in the literature on these compounds is scant, and in certain cases, erroneous. Methyltetrachlorophosphorane, erroneously reported to arise from the chlorination of tetramethyldiphosphine disulfide,⁽⁸⁶⁾ was synthesized by chlorination of methyldichlorophosphine in CS_2 at about 0°C .⁽⁹⁶⁾ Similarly, dimethyltrichlorophosphorane was synthesized by the method suggested by Issleib and Seidel,⁽⁷⁷⁾ namely, the chlorination of tetramethyldiphosphine.

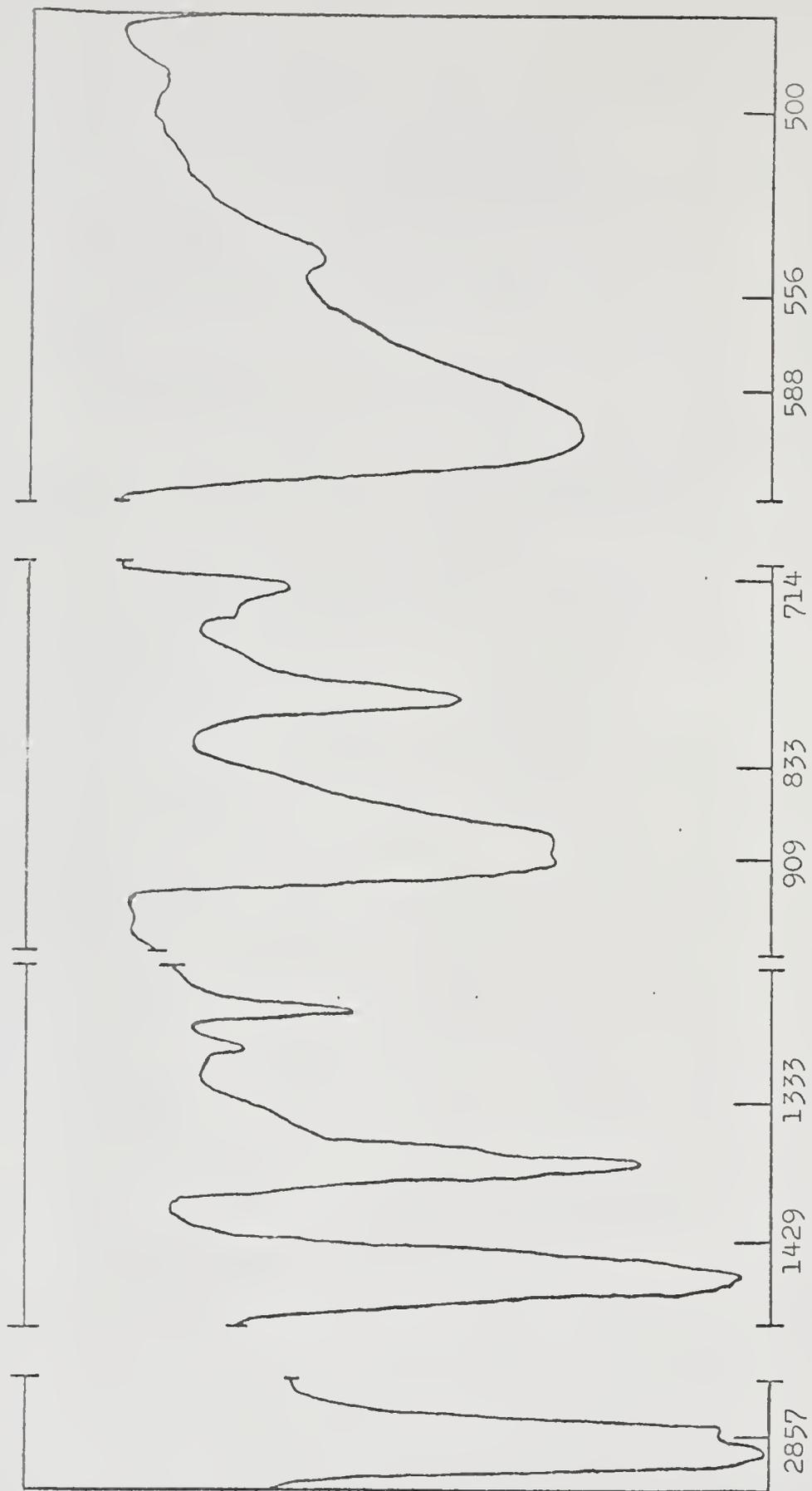
The same general procedure was used in the synthesis of both compounds. Into a 200 ml, 3-neck round-bottom flask equipped with a gas entry tube, a thermometer and a condenser leading through a liquid N₂ trap to the atmosphere, was placed the substance to be chlorinated and 50 ml of solvent. With this volume of material, the gas entry tube was well above the surface of the solution, thus avoiding dangerous plugging of the chlorine line. The solution was cooled with an ice and salt bath. Chlorine gas was introduced and metered with a previously calibrated rotameter at the rate of approximately 0.9 mmoles/min. The temperature of the magnetically stirred solution could be controlled somewhat by varying the rate of chlorine addition. The temperature was maintained at near 0° C and was never allowed to exceed 10° C. White, crystalline products formed immediately and precipitated from the respective solutions. The chlorination was stopped before the theoretical amount of chlorine had been introduced to prevent possible chlorination of the methyl groups which sometimes occurs with excess chlorine. The solution was then filtered in the dry box and the crystalline product was washed with additional, fresh solvent and dried in vacuum. Since both chlorophosphoranes react violently with water, they were stored in sealed vials in the dry box until needed.

In a typical experiment, 5 ml (50 mmoles) of methyl-dichlorophosphine was dissolved in 50 ml of CS_2 , cooled to about 0°C and chlorinated for 55 minutes. The white, crystalline product melted sharply with decomposition at 139.5°C . Anal. Found: Cl, 75.2. Calculated for CH_3PCl_4 : Cl, 75.5. Yield: 6.95 g (75% of theory based on chlorine used). The infrared spectrum of methyltetrachlorophosphorane is shown in Figure 17.

Similarly, 2 ml (14.2 mmoles) of tetramethyldiphosphine was dissolved in 50 ml of toluene, cooled to about 0°C , and chlorinated for 40 minutes. The white, crystalline product melted sharply with decomposition and sublimation at 194.5 - 195°C . Anal. Found: Cl, 66.7. Calculated for $(\text{CH}_3)_2\text{PCl}_3$: Cl, 63.5. Yield: 2.72 g (68% of theory based on chlorine used). The infrared spectrum of dimethyltrichlorophosphorane is shown in Figure 18.

The Reaction of Dimethyldiaminophosphonium
Chloride with PCl_5

In a typical experiment, 1.06 g (8.25 mmoles) of dimethyldiaminophosphonium chloride was mixed with 1.72 g (8.25 mmoles) of PCl_5 in a 100 ml round-bottom flask equipped with a reflux condenser and a side arm for introduction of nitrogen. Benzene (25 ml) was added as a solvent and the mixture was refluxed. A slow flow of dry nitrogen was



Wave number, cm^{-1}
Fig. 17.—Infrared Spectrum of CH_3PCl_4 (Nujol).

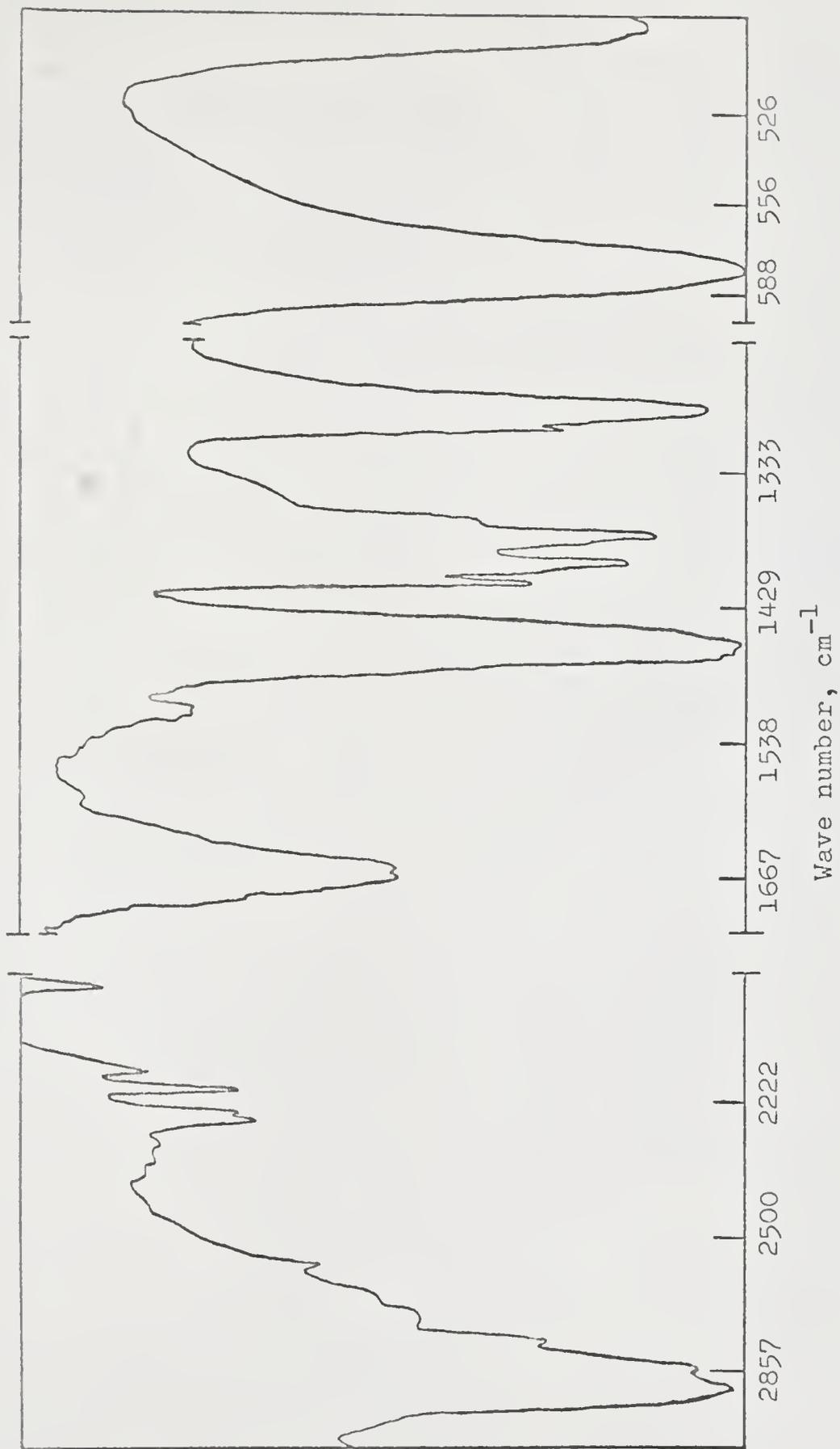


Fig. 18.--Infrared Spectrum of $(\text{CH}_3)_2\text{PCl}_3$ (Nujol).

passed over the mixture and then bubbled through a benzene solution of triethylamine at a rate of about 15-20 bubbles/min (less than 1 ℓ/min). HCl was evolved immediately from the refluxing mixture and collected in the triethylamine solution as the solid hydrochloride. After about three days of reaction, 3.86 g (85% of theory assuming all N-H hydrogen in $[(\text{CH}_3)_2\text{P}(\text{NH}_2)_2]\text{Cl}$ appears as HCl) of triethylamine hydrochloride had been recovered and the rate of evolution of HCl from the reaction mixture was negligible. The clear benzene solution was evaporated to dryness in vacuum, yielding 1.56 g of crude product. This material was highly hygroscopic giving off HCl readily in moist air. Sublimation of this material at about 50° C and 0.15 mm Hg yielded 0.75 g of white sublimate and 0.81 g of a hard, plastic residue. The sublimate was further purified by several recrystallizations from benzene and hexane and repeated sublimations at about 50° C and 0.1 mm Hg. M.P. 174-176° C (sub.). Anal. Found: C, 8.03; H, 2.20; N, 14.07; P, 29.53; Cl, 46.07; Mol. Wt., 308. Calculated for $(\text{CH}_3)_2\text{Cl}_4\text{P}_3\text{N}_3$: C, 7.83; H, 1.97; N, 13.70; P, 30.28; Cl, 46.22; Mol. Wt., 307. The infrared spectrum of this material is shown in Figure 19. The yield of this substance varied considerably in several experiments. The crude yields ranged from 25 per cent of theory to about 60 per cent of theory (based on PCl_5 used). The reaction was also

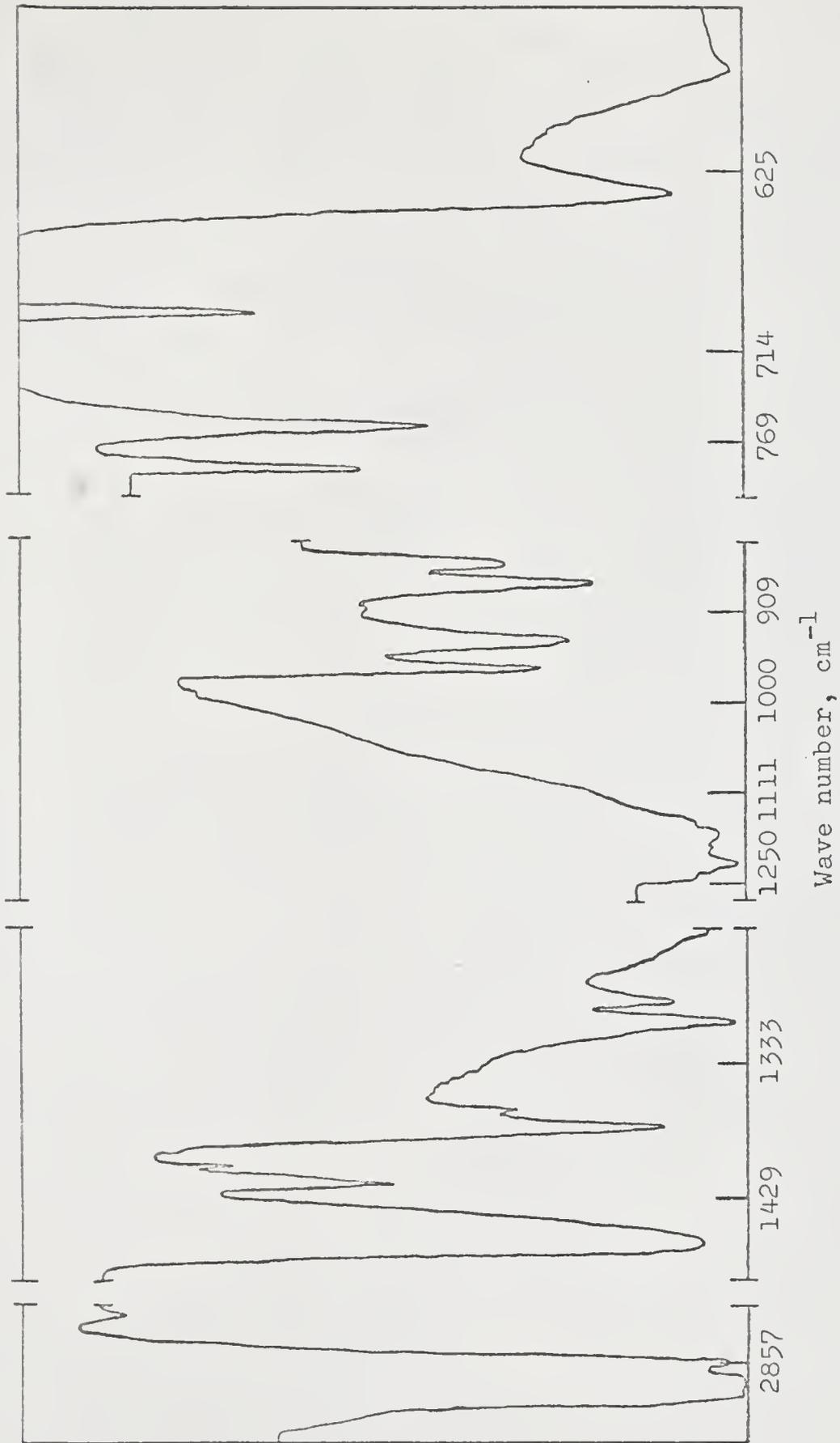


Fig. 19.-Infrared Spectrum of $(\text{CH}_3)_2\text{ClP}_3\text{N}_3$ (Nujol).

attempted with a 2:1 ratio of PCl_5 to $[(\text{CH}_3)_2\text{P}(\text{NH}_2)_2]\text{Cl}$. In this case the evolution of HCl was very rapid but only a 5 per cent yield of crystalline material could be extracted from the extremely air-sensitive, oily product.

The residue from the sublimation was a cream-colored, glassy substance which was extremely sensitive to moist air. In some cases this material was oily instead of solid. Vacuum pyrolysis of the crude reaction mixture at $180\text{--}190^\circ\text{C}$ and 0.1 mm Hg in a semimicro sublimation apparatus produced a sublimate as described above. The residue from this pyrolysis, however, was a grey-brown glass which did not appear to be affected by exposure to moist air. The glass was infusible up to 300°C and was insoluble in all solvents tried. The infrared spectrum of this material consisted of several broad bands, one of which occurred at 1250 cm^{-1} indicating that the material has phosphonitrilic "P=N" bonds. Analytical data indicate the following atomic ratios, C:H:P:N = 1.0:3.5:1.0:1.3. These numbers at least indicate the unit, $[(\text{CH}_3)_2\text{PN}\cdot\text{Cl}_2\text{PN}]_x$; however, the largest Cl:P ratio found was about 1:3 indicating a loss of chlorine, perhaps through cross-linking.

The Reaction of Diethyldiaminophosphonium
with PCl_5

In a typical experiment, 0.92 g (5.87 mmoles) of diethyldiaminophosphonium chloride was mixed with 1.22 g (5.87 mmoles) of PCl_5 in a 100 ml round-bottom flask equipped with a reflux condenser and a side arm for introduction of nitrogen. Benzene (25 ml) was added as a solvent and the mixture was refluxed. A slow flow of dry nitrogen was passed over the refluxing mixture and then bubbled through a benzene solution of triethylamine at a rate of 15-20 bubbles/min (less than 1 ℓ /min). After about five days of reflux, 2.53 g (18.4 mmoles; 78.4% of theory assuming all N-H hydrogen in $[(\text{C}_2\text{H}_5)_2\text{P}(\text{NH}_2)_2]\text{Cl}$ appears as HCl) of triethylamine hydrochloride had been recovered and the rate of evolution of HCl from the refluxing mixture had become negligible. The reaction was pushed to completion by the addition of 2-3 ml of dry triethylamine to the reaction mixture. Triethylamine hydrochloride precipitated from the solution and was removed by filtration. The clear benzene solution was then evaporated to dryness in vacuum yielding an oily solid which was extremely sensitive to moist air. This mixture was separated by sublimation at 40-50° C and 0.25 mm Hg. The white, crystalline sublimate so formed melted in the range of 120-125° C. Several recrystallizations of this material from acetonitrile and

benzene and repeated sublimation at 50° C and 0.1 mm Hg raised the melting range to 124-130° C (sub.). Anal. Found: C, 18.22; H, 4.08; P, 26.94; N, 12.52; Cl, 31.8; Mol. Wt., 386. Calculated for $[(C_2H_5)_2PN \cdot Cl_2PN]_2$: C, 21.94; H, 4.60; P, 28.29; N, 12.79; Cl, 32.4; Mol. Wt., 438. The infrared spectrum of this material is shown in Figure 20. The yields of this material in several experiments were quite low, ranging from 5 to 15 per cent of theory based on $[(C_2H_5)_2P(NH_2)_2]Cl$. The material seemed to be subject to slow hydrolysis in moist air, and further purification could not be accomplished.

The residue from the sublimation was a dark brown oil which fumed in air. In subsequent experiments the crude reaction mixture was pyrolyzed in a semimicro sublimation apparatus at 200-220° C and 0.1 mm Hg. The sublimate was similar to the sublimate described above, melting at 124-130° C and having a similar analysis. The residue, however, was a brown, glassy material which was apparently not affected by moist air. This material undergoes decomposition at 240-250° C and is insoluble in all solvents tried. Anal. Found: C, 24.31; H, 6.23; P, 31.22; N, 12.95. This analysis gives a C:P ratio of 2:1 and a P:N ratio of 1:0.9, indicating the formulation, $[(C_2H_5)_2PN \cdot Cl_2PN]_x$, for which the calculated analysis is: C, 21.94; H, 4.60; P, 28.29; N, 12.79. If the found

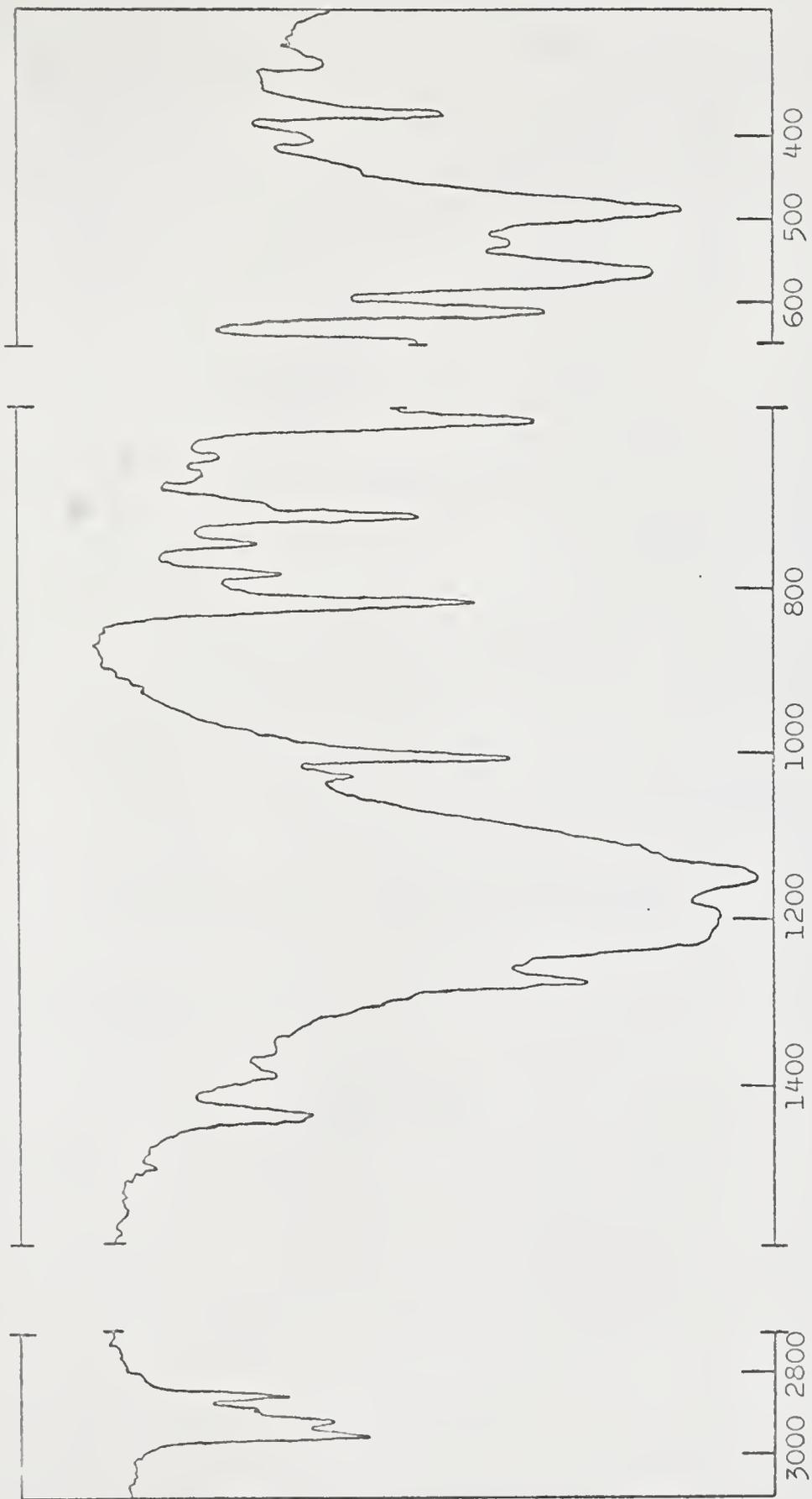


Fig. 20.-Infrared Spectrum of $[(C_2H_5)_2PN \cdot Cl_2PN]_2$ (KBr).

analysis is subtracted from 100 per cent and the difference is assumed to be percent Cl, the P:Cl ratio is 1:0.7. This is slightly less than the expected ratio of 1:1 and may indicate cross-linking. The infrared spectrum of this material is consistent for a polymeric material, consisting of several broad bands. One broad peak occurs at 1225 cm^{-1} and could be attributed to the phosphonitrilic "P=N" stretching. Another broad peak is observed at 460 cm^{-1} , the region associated with P-Cl vibrations.

The Reaction of Dimethyldiaminophosphonium Chloride
with Methyltetrachlorophosphorane

Dimethyldiaminophosphonium chloride (0.88 g; 6.82 mmoles) was mixed with 1.31 g (7.0 mmoles) of methyltetrachlorophosphorane in a 100 ml round-bottom flask equipped with a reflux condenser and a side arm for introduction of nitrogen. Benzene (25 ml) was added as a solvent and the mixture was refluxed for seven days. A slow stream of dry nitrogen was passed over the refluxing solution and bubbled into a benzene solution of triethylamine at the rate of 15-20 bubbles/min (less than 1 l/min). At the completion of the reaction, 26.8 mmoles (98% of theory assuming all N-H hydrogen from $[(\text{CH}_3)_2\text{P}(\text{NH}_2)_2]\text{Cl}$ appears as HCl) of triethylamine hydrochloride had been recovered. The clear benzene solution was cooled and evaporated to

dryness in vacuum. The product was a white solid which was extremely sensitive to moist air. This material was transferred in the dry box to a semimicro sublimation apparatus and heated at 170-185° C and 0.1 mm Hg for four days. The resulting sublimate was shown to be mostly ammonium chloride. The residue was a red-brown, glassy substance which melted at 97-107° C. This material was soluble in chloroform, insoluble in benzene and soluble in water, apparently hydrolyzing on contact with it. Upon exposure to moist air the material turned wet immediately and underwent hydrolysis. Thin, transparent films of the material could be cast by careful evaporation of chloroform solutions. The infrared spectrum of such a film is shown in Figure 21. Anal. Found: C, 20.24; H, 5.49; P, 31.92; N, 14.30; Cl, 21.23; Mol. Wt., 915. Calculated for $[(\text{CH}_3)_2\text{PN} \cdot (\text{CH}_3)\text{ClPN}]_x$: C, 21.13; H, 5.32; P, 36.33; N, 16.43; Cl, 20.79; Mol. Wt., 170.5/unit. Attempts to improve the P and N analyses by using the Kjeldahl method failed, presumably because the sample hydrolyzed prior to analysis. However, the P:N ratio was 1:1 indicating a phosphonitrilic structure. The other atomic ratios are close to those required by the formula postulated above: Cl:P = 1:1.7; C:P = 3:1.8; C:H = 1:3.2; Cl:C = 1:2.8. Yield: 0.81 g (70% of theory based on the formula $[(\text{CH}_3)_2\text{PN} \cdot (\text{CH}_3)\text{ClPN}]$).

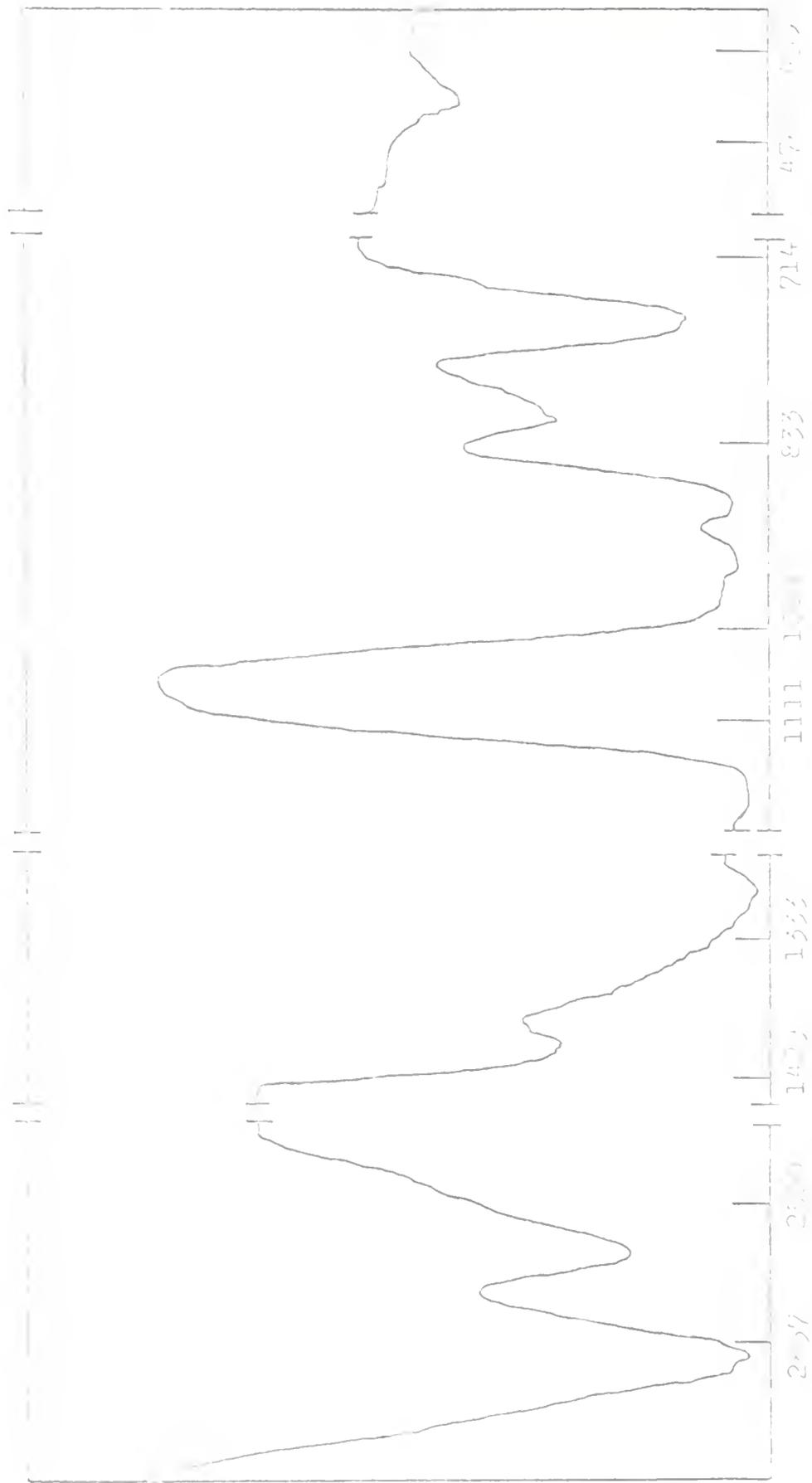


Fig. 11.—Infrared Spectrum of Bisphenol A $[(\text{CH}_3)_2\text{C}(\text{OH})\text{C}(\text{CH}_3)_2]_x$ (Thin Film).

The Reaction of Dimethyldiaminophosphonium Chloride
with Dimethyltrichlorophosphorane

Dimethyldiaminophosphonium chloride (0.67 g; 5.2 mmoles) was mixed with 0.90 g (5.4 mmoles) of dimethyltrichlorophosphorane in a 100 ml round-bottom flask equipped with a reflux condenser and a side arm for introduction of nitrogen. Benzene (25 ml) was added and the mixture was refluxed. A slow stream of dry nitrogen was passed over the refluxing mixture and bubbled through a solution of triethylamine in benzene at a rate of 15-20 bubbles/min (less than 1 l/min). After about four days of refluxing, only 70 per cent of the theoretical HCl had been evolved and reaction had ceased. The solvent was evaporated to dryness in vacuum and replaced by dry chlorobenzene (B.P. 130° C). Refluxing in this solvent did not produce more HCl, however. Finally 0.9 ml (about 6 mmoles) of dry triethylamine was added to the reaction mixture and refluxed for one hour to push the reaction to completion. Triethylamine hydrochloride precipitated and was removed from the benzene solution by filtration. The total amount of triethylamine hydrochloride recovered was 2.66 g (18.6 mmoles; 90% of theory assuming all N-H on $[(\text{CH}_3)_2\text{P}(\text{NH}_2)_2]\text{Cl}$ appears as HCl). The clear solution was then evaporated to dryness yielding an oily solid. This mixture was separated by sublimation at 50° C and 0.1 mm Hg. The crude

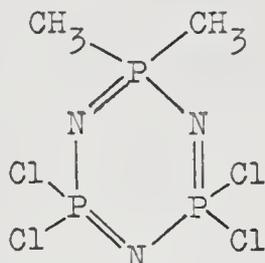
sublimate (0.69 g) was extracted with petroleum ether. Careful recrystallization from this solvent followed by re-sublimation at 50° C and 0.1 mm Hg yielded 0.36 g (46% of theory) of dimethylphosphonitrilic tetramer, M.P. 159-162° C. The infrared spectrum of this material was identical with that of dimethylphosphonitrilic tetramer reported in the literature.⁽²⁶⁾ The "P=N" stretching frequency occurs at 1220 cm^{-1} . A shoulder occurs at 1160 cm^{-1} indicating the presence of trimer. The concentration of trimer, however, was very low because no separation could be made by repeated fractional crystallization from petroleum ether.

The residue from the sublimation and the petroleum ether extractions were clear oils which were insoluble in petroleum ether and benzene. This material was soluble in water and its water solution gave a strong test for chloride ion with aqueous silver nitrate. The infrared spectrum of this substance has strong peaks in the regions associated with O-H bonding and has P-CH₃ peaks. Therefore, it was postulated that this oil was a product of partial hydrolysis of dimethyltrichlorophosphorane or of some chlorine-containing intermediate formed in the early stages of the reaction. The product, $[(\text{CH}_3)_2\text{PN}]_{3,4}$, was quite soluble in this oil and some loss occurred when the oil was discarded.

Discussion

The results of this study show that, in general, phosphonitrilic derivatives result from the reactions of diaminophosphonium salts with tri-, tetra- and pentachlorophosphoranes. This, then, indicates another procedure in which diaminophosphonium salts can be used to obtain a variety of phosphonitriles. As a direct result of this study, some interesting new derivatives were formed. For instance, the reaction of dimethyldiaminophosphonium chloride with PCl_5 has produced the "trimer," $(\text{CH}_3)_2\text{Cl}_4\text{P}_3\text{N}_3$ in moderate yields. This material was characterized by elemental analysis, molecular weight determination and infrared analysis. Its infrared spectrum (Fig. 19) has a strong peak at 1420 cm^{-1} which may be attributed to C-H bending vibrations, and a doublet at about 1300 cm^{-1} which is attributed to P- CH_3 bonding. In the region characteristic of "P=N" stretching, two peaks occur, one at 1220 cm^{-1} and the other at 1165 cm^{-1} and from 865 cm^{-1} to 960 cm^{-1} . Peaks in this region have been attributed to P-C stretching and to methyl C-H vibrations as well as to "P=N" elongation and "P-N=P" ring vibrations. Not enough information is available yet for us to make definite assignments in these regions. Several strong peaks occur between 510 and 632 cm^{-1} . Daasch⁽²⁴⁾ attributes peaks in this region to PCl_2 vibrations and to phosphonitrilic ring vibrations.

Considering the method of synthesis, this "trimer" probably has the structure,



with both methyl groups on the same phosphorus. Such a derivative cannot be synthesized by substitution reactions starting with $(\text{PNCl}_2)_3$.

The byproduct of this reaction was an air-sensitive, glassy material, which when pyrolyzed at 180-190° C in vacuum, yielded a glassy substance which seemed to be a cross-linked polymer derived from the grouping, $[(\text{CH}_3)_2\text{PN}\cdot\text{Cl}_2\text{PN}]$.

The reaction of diethyldimainophosphonium chloride with PCl_5 produces low yields of a substance tentatively identified as the tetramer, $[(\text{C}_2\text{H}_5)_2\text{PN}\cdot\text{Cl}_2\text{PN}]_2$. The infrared spectrum of this material (Fig. 20) has C-H stretching and deformation peaks at 2960, 2920 and 2860 cm^{-1} and at 1450 and 1400 cm^{-1} , respectively. A strong peak occurs at 1279 cm^{-1} which is usually associated with P-C bonding. Two peaks characteristic of the phosphonitrilic "P=N" stretching vibrations occur at 1200 cm^{-1} and at 1150 cm^{-1} . A number of peaks occur in the region from 600 cm^{-1} to 1030 cm^{-1} . Peaks in this region are often attributed to

C-H vibrations of the ethyl groups and to various vibrations of the phosphonitric ring. Definite assignments are difficult to make, however, the peak at 788 cm^{-1} can probably be attributed to P-C asymmetric stretching,⁽⁹⁷⁾ and the peak at 610 cm^{-1} can probably be attributed to P-Cl bonds. Several peaks occur between 400 and 565 cm^{-1} , but no definite assignments of these peaks can be made.

The main product of this reaction was a dark, air-sensitive oil. By pyrolysis at $200\text{-}220^\circ\text{ C}$ this substance was converted to a brown, glassy solid which was apparently unreactive in air. The analysis of this material indicates the formula, $[(\text{C}_2\text{H}_5)_2\text{PN}\cdot\text{Cl}_2\text{PN}]$. The P:Cl ratio is 1:0.7 and this deviation from the theoretical ratio of 1:1 is attributed to cross-linking. The substance has the properties of a cross-linked polymer, being insoluble in all solvents tried and decomposing slowly in the range of $240\text{-}250^\circ\text{ C}$.

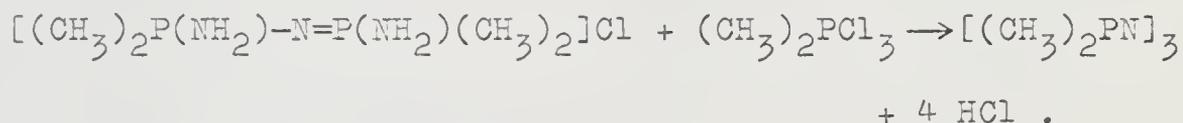
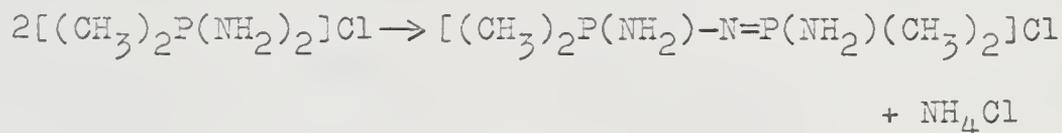
The reaction of dimethyldiaminophosphonium chloride with methyltetrachlorophosphorane produces a white, air-sensitive solid which, upon pyrolysis at about 180° C , gives a light-brown, glassy substance with an average molecular weight of 915. This material is still moisture sensitive. The analysis indicates the formula, $[(\text{CH}_3)_2\text{PN}\cdot(\text{CH}_3)\text{ClPN}]_x$. The infrared spectrum of a thin film of this material (Fig. 21) has broad C-H stretching deformation peaks at 2900 cm^{-1}

and at 1400 cm^{-1} , respectively. A broad peak occurs at 1305 cm^{-1} and can be attributed to P-CH₃ bonds. The usual phosphonitrilic "P=N" stretching peak occurs at about 1220 cm^{-1} and is quite broad. Several peaks occur in the region from 662 cm^{-1} to 980 cm^{-1} . No definite assignments can be made for peaks in this region. A broad peak occurs at 466 cm^{-1} which might be attributed to P-Cl bonds. On the basis of the elemental analysis, molecular weight determination and infrared spectrum this material appears to be a linear polymer of the unit, $\left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{Cl} \\ \diagdown \quad / \quad \diagdown \quad / \\ \text{---P=N---P=N---} \end{array} \right]_n$.

The reaction of dimethyldiaminophosphonium chloride with dimethyltrichlorophosphorane produces 0.69 g (88% of theory) of crude $[(\text{CH}_3)_2\text{PN}]_{3,4}$. This material was purified by fractional crystallization from petroleum ether and re-sublimation, and was identified by its melting point and by comparison of its infrared spectrum with published data. The product consisted chiefly of tetramer (M.P. $159\text{--}162^\circ\text{ C}$) and attempts to separate the small amount of trimer present by careful fractional crystallization from petroleum ether failed. The presence of trimer was indicated by the infrared spectrum which shows a shoulder at 1160 cm^{-1} , the position of the characteristic "P=N" stretching band in the trimer.

In predicting the course of these reactions, we had considered it possible that diaminophosphonium salts would

The results of this study generally confirm the predictions which were made considering the reaction sequence postulated above. In the reaction of dimethyldiaminophosphonium chloride with dimethyltrichlorophosphorane the principal product was the tetramer, $[(CH_3)_2PN]_4$. Traces of trimer which were detected might have resulted from self-condensation of the phosphonium salt,



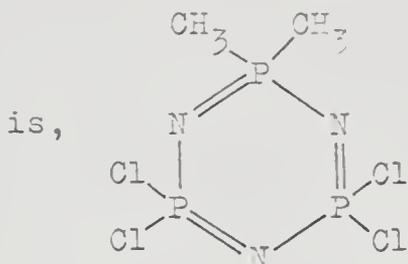
The reaction of diethyldiaminophosphonium chloride with PCl_5 also produces a tetrameric species tentatively identified as $[(C_2H_5)_2PN \cdot Cl_2PN]_2$. The structure of this material was not determined. Such a determination would be interesting and would perhaps provide additional information about the course of the reaction.

A material assumed to be a linear polymer of the unit, $\left[\begin{array}{c} CH_3 \quad CH_3 \quad CH_3 \quad Cl \\ \diagdown \quad / \quad \diagdown \quad / \\ P = N - P = N \end{array} \right]_n$, was obtained from the reaction of dimethyldiaminophosphonium chloride with methyl-tetrachlorophosphorane. The average molecular weight was 915 giving n an average value of about 5 (or 10 P-N units). The properties of the material are consistent with this

assumption. In addition, materials which appear to be cross-linked polymers derived from the units, $[(\text{CH}_3)_2\text{PN}\cdot\text{Cl}_2\text{PN}]$ and $[(\text{C}_2\text{H}_5)_2\text{PN}\cdot\text{Cl}_2\text{PN}]$ are formed in the reactions of PCl_5 with dimethyldiaminophosphonium chloride and diethyldiaminophosphonium chloride, respectively.

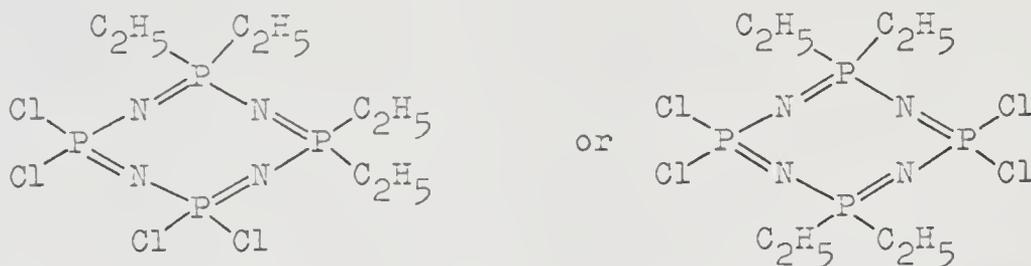
The only product of this study which cannot be easily rationalized by the sequence postulated above is the "trimer," $(\text{CH}_3)_2\text{Cl}_4\text{P}_3\text{N}_3$, which results from the reaction of PCl_5 with dimethyldiaminophosphonium chloride. The formation of this "trimer" implies the formation of the substances $\text{NH}_2\text{-PCl}_4$, HN=PCl_3 and $\text{Cl}_3\text{P=N-PCl}_4$. The latter species could condense with dimethyldiaminophosphonium chloride giving the observed "trimer." The nitrogen atom in the intermediate, $\text{Cl}_3\text{P=N-PCl}_4$, might come from the possible contaminant, NH_4Cl , since this intermediate is known to form in the reaction of NH_4Cl and PCl_5 . It might also come from the diaminophosphonium salt by some complex mechanism which cannot be predicted. Only one reaction sequence has been considered here. Of course, other sequences might be postulated which could account for this product as well as the other products of the reaction.

The "trimer," $(\text{CH}_3)_2\text{Cl}_4\text{P}_3\text{N}_3$, is an interesting derivative. Since, under the conditions of the reaction, migration of the methyl groups is not expected, the structure



This derivative cannot be prepared by substitution reactions starting with $[\text{PNCl}_2]_3$ because substitution in such derivatives occurs evenly, one chlorine on each phosphorus undergoing substitution before the second chlorine atom is substituted. Therefore, this is presently the only known method of preparation of this derivative. Likewise, the derivative, $[(\text{C}_2\text{H}_5)_2\text{PN}\cdot\text{Cl}_2\text{PN}]_2$ cannot be synthesized by substitution starting with $[\text{PNCl}_2]_4$.

The question of the structure of the tetramer, $[(\text{C}_2\text{H}_5)_2\text{PN}\cdot\text{Cl}_2\text{PN}]_2$, is also an interesting one. The material could be either



Thus, a complete structural investigation is necessary to fully characterize this compound.

Although this study has resulted in the synthesis of some interesting phosphonitric derivatives, the experimental difficulties involved preclude its classification as a "convenient" method. However, a more thorough

study of these reactions using different solvents and different mole ratios of reactants might further clarify the results obtained in this study and might reveal some advantages in using this method for phosphonitrilic synthesis.

Summary

The reaction of dimethyldiaminophosphonium chloride with PCl_5 in refluxing benzene has produced the new phosphonitrilic "trimer," $(\text{CH}_3)_2\text{Cl}_4\text{P}_3\text{N}_3$, in good yield. The byproduct of this reaction is an air-sensitive solid which, upon pyrolysis at about 180°C , yields a material tentatively identified as a cross-linked polymer derived from the unit, $[(\text{CH}_3)_2\text{PN}\cdot\text{Cl}_2\text{PN}]$.

The reaction of diethyldiaminophosphonium chloride with PCl_5 in refluxing benzene has produced the tetramer, $[(\text{C}_2\text{H}_5)_2\text{PN}\cdot\text{Cl}_2\text{PN}]_2$, in low yield. The principal product in this reaction is an air-sensitive, oily material which gives an insoluble glass when pyrolyzed at about 200°C . This glass has been tentatively identified as a cross-linked polymer derived from the unit, $[(\text{C}_2\text{H}_5)_2\text{PN}\cdot\text{Cl}_2\text{PN}]$.

The reaction of dimethyldiaminophosphonium chloride with methyltetrachlorophosphorane in refluxing benzene produces a white solid which is air-sensitive. Pyrolysis of this solid at 180°C produces an air-sensitive glass

which was tentatively identified as a linear polymer of the unit, $[(\text{CH}_3)_2\text{PN} \cdot (\text{CH}_3)\text{ClPN}]$. The average number of units per chain, as indicated by molecular weight determination, is about 5. This material is produced in good yield.

The reaction of dimethyldiaminophosphonium chloride with dimethyltrichlorophosphorane has produced principally dimethylphosphonitrilic tetramer in good yield.

All products synthesized in this study were characterized by melting point determination, elemental analysis, molecular weight determination (except for insoluble polymers) and infrared analysis. The results are discussed in terms of a postulated reaction sequence.

CHAPTER VI

GENERAL CONCLUSIONS AND SUMMARY

In general, this study has shown that (1) diamino- and triaminophosphonium chlorides can be conveniently synthesized by the chloramination-ammonolysis of substituted diphosphines and cyclotetraphosphines; (2) diamino-phosphonium chlorides are phosphonitrilic precursors giving phosphonitrilic derivatives in good yield by pyrolytic condensation; (3) under certain conditions highly polymeric, linear, dimethylphosphonitrile can be synthesized in good yield from dimethyldiaminophosphonium chloride; and (4) diaminophosphonium salts undergo condensation reactions with PCl_5 and substituted tetra- and trichlorophosphoranes to give phosphonitrilic derivatives.

In particular, it has been shown that chloramination-ammonolysis of tetramethyldiphosphine and tetraethyldiphosphine produces the corresponding diaminophosphonium chlorides in good yield. This method is presently the most convenient one known for the production of these substances. The chloramination-ammonolysis of tetraethyldiphosphine also produces a trace amount of diethylphosphonitrilic trimer.

Chloramination-ammonolysis of tetraphenyldiphosphine produces the new compound, diphenyldiaminophosphonium chloride and its first condensation product, $[(C_6H_5)_2P(NH_2)-N=P(NH_2)(C_6H_5)_2]Cl$. When carried out at room temperature in benzene the yield of diphenyldiaminophosphonium chloride is low. Further study of this reaction might reveal conditions under which the yield of this diaminophosphonium salt could be optimized.

The chloramination-ammonolysis of tetraphenylcyclo-tetraphosphine has produced the new compound, phenyltri-aminophosphonium chloride, and a substance tentatively identified as the linear polymer,

$Cl-[\begin{array}{c} C_6H_5 \quad NH_2 \\ \diagdown \quad / \\ P \\ \diagup \quad \backslash \\ C_6H_5 \quad NH_2 \end{array} = N]_5 \begin{array}{c} C_6H_5 \quad NH_2 \\ \diagdown \quad / \\ P \\ \diagup \quad \backslash \\ C_6H_5 \quad NH_2 \end{array} = NH$. Even though this reaction was carried out at room temperature, the yield of the tri-aminophosphonium salt was sometimes as high as 25 per cent of theory. Further study might reveal conditions under which the yield of this salt might be even higher.

The study of the pyrolytic condensation of diamino-phosphonium chlorides has demonstrated thoroughly the value of the reaction sequence postulated earlier,⁽¹⁾ and has shown that these salts are indeed precursors of phospho-nitrilic polymers. Thus, dimethyldiaminophosphonium chloride undergoes pyrolytic condensation to produce excellent yields of dimethylphosphonitrilic trimer and tetramer. Diethyldi-aminophosphonium chloride undergoes condensation in steps

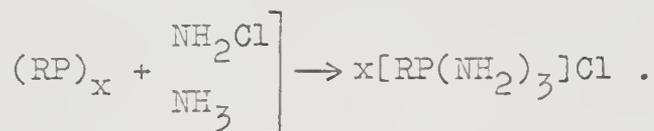
giving the first condensation product, $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$, and diethylphosphonitrilic trimer. The intermediate, $[(C_2H_5)_2P(NH_2)-N=P(NH_2)(C_2H_5)_2]Cl$, undergoes pyrolytic condensation to give excellent yields of diethylphosphonitrilic trimer and tetramer. The tetramer is the predominant product of this reaction. The pyrolytic condensation of di-n-butylldiaminophosphonium chloride produces the new compound, $[(n-C_4H_9)_2PN]_3$ in excellent yield.

One of the most important results of this work was the discovery of the conditions under which dimethyldiaminophosphonium chloride could be polymerized to give a highly polymeric, linear dimethylphosphonitrile. Yields of crude polymer as high as 30 per cent of theory were obtained by varying the concentration of ammonium chloride in the pyrolysis mixture. This material contains polymers of the unit, $[(CH_3)_2PN]$ with molecular weights which average from 3500 to 12,500, indicating molecules in which the average number of units varied from 50 to 150.

The discovery of polymeric dimethylphosphonitrile leads one to speculate about the possibility of developing a useful, unreactive, thermally stable phosphonitrilic polymer system. The dimethylphosphonitrilic polymer synthesized in this study has been demonstrated to be unreactive to moist air, and has been shown to have potential uses in the fabrication of films. However, the material is

thermally degraded to cyclic derivatives, $[(\text{CH}_3)_2\text{PN}]_{3,4}$, upon heating above 300°C . The answer to this problem is to build into the polymer molecules end-stopping groups and branching or cross-linking groups to lock the linear chains in position and to prevent cyclization. An analogous situation occurs in the isoelectronic dimethylsiloxane derivatives which have the unit, $[(\text{CH}_3)_2\text{Si-O}]$.⁽⁹⁸⁾ Cyclic derivatives and not linear polymers are favored at high temperatures unless some end-stopping groups, $[(\text{CH}_3)_3\text{Si-O}]$, and branching groups, $\left[\begin{array}{c} \text{O} \\ | \\ (\text{CH}_3)_3\text{Si-O} \\ | \\ \text{O} \end{array} \right]$, are incorporated in the high polymer. This study has shown that dimethyldiaminophosphonium chloride is the starting material for the chain-

making units, $[-\text{N}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{P}}}-\text{N}-]$. We have also indicated a method of synthesizing the starting materials for the branching units, $\left[\begin{array}{c} \text{N} \\ | \\ \text{RP-N-} \\ | \\ \text{N} \end{array} \right]$, namely, the chloramination-ammonolysis of cyclopolyphosphines,



And the synthetic procedure for compounds which lead to end groups, $[\text{R}_3\text{P-N-}]$, is the well-known⁽⁷³⁾ chloramination of tertiary phosphines. The basic structural units for the

phosphonitrilic polymer system are therefore available. We feel that the synthesis of polymers utilizing these units would make a very interesting study for further work in this area.

The reactions of dimethyldiaminophosphonium chloride and diethyldiaminophosphonium chloride with PCl_5 , methyltetrachlorophosphorane and dimethyltrichlorophosphorane also produce phosphonitrilic derivatives. Dimethyldiaminophosphonium chloride reacts with PCl_5 to produce good yields of the "trimer," $(\text{CH}_3)_2\text{Cl}_4\text{P}_3\text{N}_3$. A second product of this reaction is an air-sensitive oil which can be pyrolyzed to yield a material that appears to be a cross-linked polymer derived from $[(\text{CH}_3)_2\text{PN}\cdot\text{Cl}_2\text{PN}]$. Similarly, diethyldiaminophosphonium chloride reacts with PCl_5 to form the tetramer, $[(\text{C}_2\text{H}_5)_2\text{PN}\cdot\text{Cl}_2\text{PN}]_2$, and an air-sensitive substance which can be pyrolyzed to yield a material that appears to be a cross-linked polymer derived from $[(\text{C}_2\text{H}_5)_2\text{PN}\cdot\text{Cl}_2\text{PN}]$.

The reaction of dimethyldiaminophosphonium chloride with methyltetrachlorophosphorane produces an extremely air-sensitive material which was pyrolyzed to yield a material that appears to be a low-molecular-weight linear polymer of the unit, $[(\text{CH}_3)_2\text{PN}\cdot(\text{CH}_3)\text{ClPN}]$.

The reaction of dimethyldiaminophosphonium chloride with dimethyltrichlorophosphorane produces, predominantly, dimethylphosphonitrilic tetramer.

The reactions studied in Chapter V are somewhat analogous to the so-called ring-closure reactions observed with $[(C_6H_5)_2P(NH_2)-N=P(NH_2)(C_6H_5)_2]Cl$ and PCl_5 , $RPCl_4$ and R_2PCl_3 .^(3,4) However, the reactions studied here differ by the important distinction that linear and cross-linked polymers are formed, sometimes in high yield.

BIBLIOGRAPHY

1. H. H. Sisler, H. S. Ahuja and N. L. Smith, *Inorg. Chem.*, 1, 84(1964).
2. I. I. Bezman and J. H. Smally, *Chem. and Ind.*, 839 (1960).
3. C. D. Schmulbach and C. Derderian, *J. Inorg. Nucl. Chem.*, 25, 1395(1963).
4. D. L. Herring and C. M. Douglas, *Inorg. Chem.*, 3, 428 (1964).
5. S. E. Frazier, Master's Thesis, University of Florida, December, 1963.
6. H. H. Sisler and S. E. Frazier, *Inorg. Chem.*, 4, 1204(1965).
7. J. Liebig, *Ann.*, 11, 139(1834).
8. J. H. Gladstone and J. K. Holmes, *J. Chem. Soc.*, 17, 225(1864).
9. H. N. Stokes, *Am. Chem. J.*, 17, 275(1895); 18, 629 (1896); 19, 782(1897); 20, 740(1898).
10. R. A. Shaw, B. W. Fitzsimmons and B. C. Smith, *Chem. Rev.*, 3, 247(1962).
11. N. L. Paddock, *Quart. Rev.*, 18, 168(1964).
12. C. P. Haber, *Inorganic Polymers*, *Chem. Soc. Special Publ.*, 15, The Chemical Society (London), 115(1961).
13. L. G. Lund, *et al.*, *J. Chem. Soc.*, 2542(1960).
14. D. P. Craig, *J. Chem. Soc.*, 997(1959).
15. M. J. S. Dewar, E. C. A. Lucken and M. A. Whitehead, *J. Chem. Soc.*, 2423(1960).
16. D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 4118(1962).

17. D. P. Craig, Chem. and Ind., 3(1958).
18. B. Lakatos, et al., Naturwiss., 21, 493(1962).
19. D. Feakins, W. A. Last, N. Neemuchwala and R. A. Shaw, J. Chem. Soc., 2804(1965).
20. D. Feakins, W. A. Last and R. A. Shaw, J. Chem. Soc., 4464(1964).
21. L. Pauling, The Nature of the Chemical Bond, Third Edition, Cornell University Press, 1960.
22. E. Constantinides, Proc. Chem. Soc., 290(1964).
23. F. Seel and J. Lange, Z. anorg. Chem., 295, 316(1958).
24. L. W. Daasch, J. Am. Chem. Soc., 76, 3403(1954).
25. A. J. Bilbo, Z. Naturforsch., 15b, 330(1960).
26. H. T. Searle, Proc. Chem. Soc., 7(1959).
27. L. F. Audrieth and D. B. Sowerby, Chem. and Ind., 748(1959).
28. K. John and T. Moeller, J. Am. Chem. Soc., 82, 2647 (1960).
29. N. E. Bean and R. A. Shaw, Chem. and Ind., 1189(1960).
30. R. G. Rice, et al., J. Inorg. Nucl. Chem., 5, 190(1958).
31. O. Schmitz-Dumont and H. Kulkens, Z. anorg. Chem., 238, 189(1938).
32. A. C. Chapman, et al., J. Chem. Soc., 1768(1961).
33. A. C. Chapman, et al., J. Chem. Soc., 3608(1960).
34. R. Ratz and Ch. Grundmann, J. Inorg. Nucl. Chem., 16, 60(1960).
35. T. Moeller, K. John and F. Tsang, Chem. and Ind., 347(1961).
36. R. J. A. Otto and L. F. Audrieth, J. Am. Chem. Soc., 80, 5894(1958).

37. G. Tesi, et al., J. Am. Chem. Soc., 82, 528(1960).
38. G. Grundmann and R. Ratz, Z. Naturforsch., 10b, 116(1955).
39. R. Ratz and M. Hess, Chem. Ber., 84, 889(1951).
40. B. Dishon, J. Am. Chem. Soc., 71, 2251(1949).
41. S. G. Kokalis, et al., J. Inorg. Nucl. Chem., 19, 191(1961).
42. S. K. Ray, R. A. Shaw, B. C. Smith, J. Chem. Soc., 3236(1963).
43. R. J. A. Otto and L. F. Audrieth, J. Am. Chem. Soc., 80, 3575(1958).
44. H. Bode and H. Bach, Chem. Ber., 75B, 215(1942).
45. R. A. Shaw and F. B. G. Wells, Chem. and Ind., 1189(1960).
46. H. Bode and R. Thamer, Chem. Ber., 76B, 121(1943).
47. R. A. Shaw and M. Biddlestone, Chem. Comm., 205(1965).
48. M. Becke-Goehring and K. John, Angew. Chem., 70, 657(1958).
49. G. Tesi and P. J. Slota, Jr., Proc. Chem. Soc., 404(1960).
50. M. Becke-Goehring and G. Koch, Chem. Ber., 92, 1188(1959).
51. N. L. Paddock and H. T. Searle, Adv. Inorg. Chem. Radiochem., Academic Press, New York, Vol. I, p. 352, 1959.
52. H. R. Allcock and R. J. Best, Can. J. Chem., 42, 447(1964).
53. F. Seel and J. Langer, Angew. Chem., 68, 461(1956).
54. A. B. Lurg, J. Chem. Ed., 37, 482(1960).
55. D. L. Herring, Chem. and Ind., 717(1960).

56. G. Tesi, C. P. Haber and C. M. Douglas, Proc. Chem. Soc., 219(1960).
57. K. L. Paciorek, Inorg. Chem., 3, 96(1964).
58. N. Winyall and H. H. Sisler, Inorg. Chem., 4, 655(1965).
59. M. E. Cohen, et al., U. S. Dept. Comm. Office Tech. Serv., PH Rept. 161,883(1960).
60. W. D. Groeneveld, et al., J. Inorg. Nucl. Chem., 8, 245(1958).
61. N. Goehring and J. Heinke, Z. anorg. Chem., 278, 53(1955).
62. C. F. Lui and R. L. Evans, U. S. Patent #3,169,933 (Feb. 13, 1965).
63. R. A. Shaw and C. Stratton, J. Chem. Soc., 5004(1962).
64. C. P. Haber, D. L. Herring and E. A. Lawton, J. Am. Chem. Soc., 80, 2113(1958).
65. T. J. Rao, R. D. Dresner and J. A. Young, J. Am. Chem. Soc., 81, 1020(1959).
66. G. Tesi and C. M. Douglas, J. Am. Chem. Soc., 84, 543(1962).
67. I. T. Gilson and H. H. Sisler, Inorg. Chem., 4, 273(1965).
68. H. H. Sisler, F. T. Neth, R. S. Drago and D. Young, J. Am. Chem. Soc., 76, 3906(1954).
69. F. Raschig, Chem. Ber., 40, 4586(1907).
70. R. Mattair and H. H. Sisler, J. Am. Chem. Soc., 73, 1619(1951).
71. G. M. Omietanski, et al., J. Am. Chem. Soc., 78, 337-(1956).
72. G. M. Omietanski and H. H. Sisler, J. Am. Chem. Soc., 78, 1211(1956).
73. H. H. Sisler, et al., J. Am. Chem. Soc., 81, 2982(1959).

74. W. A. Hart, Studies of the Chloramination of Amino-phosphine Derivatives. Ph.D. Dissertation, University of Florida, August, 1963.
75. W. A. Hart and H. H. Sisler, *Inorg. Chem.*, 3, 617(1964).
76. D. F. Clemens and H. H. Sisler, *Inorg. Chem.*, 4, 1222(1965).
77. K. Issleib and W. Seidel, *Chem. Ber.*, 92, 2681(1959).
78. W. Kuchen and H. Buchwald, *Chem. Ber.*, 91, 2871(1958); 91, 2296(1958).
79. H. H. Sisler and N. L. Smith, *J. Org. Chem.*, 26, 4733(1961).
80. A. B. Burg, *J. Inorg. Nucl. Chem.*, 11, 258(1959).
81. K. Issleib and A. Tzschach, *Chem. Ber.*, 92, 1397(1959).
82. H. Hoffmann, R. Grunewald and L. Horner, *Chem. Ber.*, 93, 861(1960).
83. A. B. Burg, *J. Am. Chem. Soc.*, 83, 2226(1961).
84. L. Maier, *J. Inorg. Nucl. Chem.*, 24, 275(1962).
85. H. Niebergall and B. Langenfeld, *Chem. Ber.*, 90, 1657(1957).
86. H. Reinhart, D. Bianchi and D. Moelle, *Chem. Ber.*, 90, 1657(1957).
87. S. E. Frazier, R. P. Nielsen and H. H. Sisler, *Inorg. Chem.*, 3, 292(1964).
88. J. McKechnie, D. S. Payne and W. Sim, *J. Chem. Soc.*, 3500(1965).
89. W. A. Anderson, M. Epstein and F. S. Seichter, *J. Am. Chem. Soc.*, 85, 2462(1963).
90. R. L. Amster, W. A. Anderson and N. B. Colthup, *Can. J. Chem.*, 42, 2577(1964).
91. I. N. Zhmurova, I. Yu. Voitsekhovskarya and A. V. Kirsonov, *Zhur. Obshchei Khim.*, 29, 2083(1959); C.A. 54:8681h.

92. A. Michaelis, *Ann.*, 293, 193(1896); 294, 1(1896).
93. E. Steger, *Chem. Ber.*, 94, 266(1961).
94. V. M. Plets, Dissertation, Kazan, 1938; G. M. Kosolapoff, Organophosphorus Compounds, John Wiley and Sons, Inc., New York, 1950.
95. Rip G. Rice, Private Communication.
96. I. P. Komkov, et al., *Z. Obshchei Khim.*, 32, 301(1962); *C.A.* 57:16649b.
97. G. B. Deacon, R. A. Jones and P. E. Rogasch, *Austral. J. Chem.*, 16, 360(1963).
98. E. G. Rochow, An Introduction to the Chemistry of the Silicones, Second Edition, John Wiley and Sons, Inc., New York, 1951.

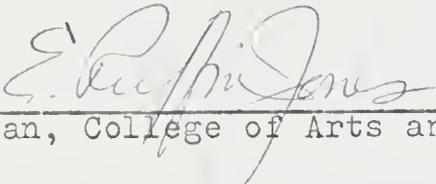
BIOGRAPHICAL SKETCH

Stephen Earl Frazier was born October 21, 1939, at Spencer, West Virginia. In June, 1957, he was graduated from Tarpon Springs High School in Tarpon Springs, Florida. From September, 1958, until June, 1961, he worked as a laboratory assistant in the Department of Chemistry at Florida Southern College. He received the degree of Bachelor of Science from Florida Southern College in June, 1961. Upon graduation he enrolled in the Graduate School of the University of Florida. He received the degree of Master of Science in December, 1963. He worked as a teaching assistant until January, 1962, and as a research assistant in the Department of Chemistry while pursuing his graduate degrees.

Mr. Frazier is a member of the American Chemical Society, Omicron Delta Kappa, Gamma Sigma Epsilon and Who's Who Among Students in American Universities and Colleges (1960-1961).

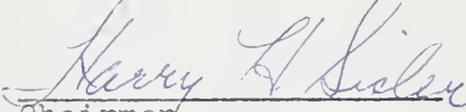
This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 18, 1965

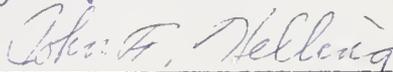

Dean, College of Arts and Sciences

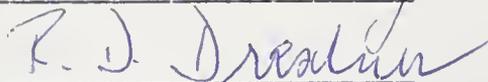
Dean, Graduate School

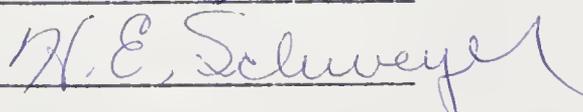
Supervisory Committee:


Chairman









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