

RESEARCH ON BOROPHANE, BORAZINE, AND PHOSPHORANE POLYMERS

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ABSTRACT

The synthesis of linear borophane polymers has been improved and expanded in terms of yields, molecular weights, and variety of substituent groups. Thermal stability of the polymers has also been improved, but their thermal depolymerization at 200-250°C. has not yet been overcome.

Several reactions have been developed which allow introduction of new substituent groups in cyclic borophane polymers, and these now open the way to new polymer types.

Significant advances have been made towards the development of both laminating resins and wide liquid range fluids based on cyclic borophane polymers.

Linear borazylene and borazylene oxide polymers have been synthesized and characterized.

New approaches to phosphorus-nitrogen polymers have resulted in the synthesis of arylphosphonyl azides and arylphosponimido-phosphoranes.

I. Introduction

The primary objective of our research program is to develop new candidate materials for application as elastomers, adhesives, resins and/or fluids at elevated temperatures. The borophanes (phosphinoborines), borazines, and phosphorus-nitrogen compounds offer promising fields of study since each of these classes of compounds show good thermal, hydrolytic, and oxidative stabilities.

The early work on borophane compounds led mainly to the cyclic triborophanes which gave the first indication of the inherent stability of the boron-phosphorus bond and indicated further work. The triborophanes have subsequently been used as model compounds to study the effects of substituents on physical and chemical properties. Means of preparing linear borophane polymers were developed but stability of these polymers was low relative to the cyclic compounds. Useful chemical reactions of the borophanes have more recently been developed but are still of limited scope.

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Our research on borazine polymers, consisting of developing suitable syntheses for mono- and di-functionally substituted borazine derivatives and their subsequent polymerization, has all been done since the last Contractors' Conference.

Similarly, research in phosphonyl azide chemistry is of recent origin. The objective of this phase of the work has been to investigate new approaches to thermally stable materials. Most of the effort has been devoted to a study of the reaction of phosphonyl azides with trivalent phosphorus compounds to yield phosphoranes.

II. Borophane Polymers

A. Discussion

1. Linear Borophane Polymers

a. Synthesis

A number of new linear borophane polymers have been prepared during the past three years. Among these are the series of poly-P-methyl-n-alkylborophanes where the n-alkyl group is methyl through n-octyl. Pyrolysis of the methyl-n-alkylphosphine boranes in the presence of 20 mole per cent triethylamine provided the linear polymeric products in increasing yield but with decreasing molecular weight as the chain length of the n-alkyl substituent increased. Presumably an increasing steric requirement of the n-alkyl substituent makes initiation of new chains more favorable than growth of existing chains. Aside from the highly crystalline dimethyl member, these polymers are viscous liquids.

The tentatively characterized poly-P-(3,3-dimethylcyclotrimethylene)borophane was prepared by pyrolysis of 3,3-dimethylcyclotrimethylene-phosphine borane in the absence of excess base to test the hypothesis that a small CPC bond angle would favor linear polymer formation. That the polymeric product was formed without ring opening has not been conclusively established.

A series of experiments using both dimethyl- and methyl-ethylphosphines showed that linear polymers could be prepared when these phosphines were heated with approximately equimolar quantities of triethylamine borane. The yields of polymers were comparable to those obtained from approximately equimolar mixtures of secondary phosphine borane and triethylamine suggesting that rapid equilibration of the system (Eq. 1) precedes thermal dehydrogenation.



Attempts to prepare the fully methylated linear polymer, $[(CH_3)_2PB(CH_3)_2]_n$, by methylation of either $[H(CH_3)PB(CH_3)_2]_n$ or $[(CH_3)_2PBCl_2]_n$ failed. Reaction of $[H(CH_3)PB(CH_3)_2]_n$, prepared by dehydrohalogenation of methylphosphine dimethylbromoborane, gave as the principal product: (1) with methyllithium, trimethylphosphine trimethylborane; and (2) with sodium amide and

methyl bromide, aminodimethylborane trimer. From the reaction of trimethylaluminum with $[(CH_3)_2PBCl_2]_n$, prepared by halogenation of the linear poly-P-dimethylborophane, no identifiable product was obtained.

b. Degradation

Thermal degradation of poly-P-dimethylborophane at 180°C. during 21 hrs. resulted in conversion of approximately half of the polymer to P-hexamethyltriborophane. During the first few hours of heating, 2-3 mole per cent each of hydrogen and a condensable gas (presumably dimethylphosphine and triethylamine) were evolved. The molecular weight of the polymer showed a moderate increase. At the higher temperature of 202°C., $27 \pm 4\%$ of the polymer depolymerized during 1 hr. to P-hexamethyltriborophane containing 2-4 per cent P-octamethyltetra-borophane. Pyrolyses of both a physical equimolar mixture of P-dimethylborophane and P-methylethylborophane and a similar mixture which had been treated with hydrogen chloride to produce some block copolymer, yielded the same nearly statistical mixture of the four possible triborophane derivatives, $[(CH_3)_2PBH_2]_{3-n}[CH_3(C_2H_5)PBH_2]_n$. Based on these and other results the depolymerization appears to proceed by an unzipping of monomer units which recombine to form the observed cyclic products.

Thermal depolymerization of two other linear borophane polymers, P-cyclotetramethyleneborophane and P-(3,3-dimethylcyclo-trimethylene)-borophane, gave in the case of the former, P-tris(cyclotetramethylene)triborophane as the principal product, while the latter polymer gave primarily a nonvolatile material together with some of the expected cyclic degradation product. Whether opening of the tetratomic phosphorus heterocyclic substituent occurred during synthesis or degradation of the polymer cannot be decided from the available data.

c. Stabilization

Treatment of poly-P-dimethylborophane with a variety of acidic and basic reagents was done in an effort to modify the chain ends and inhibit the depolymerization. After treatment with hydrogen chloride, acetic acid-acetic anhydride, sulfuric acid-acetic anhydride, maleic anhydride, nickel carbonyl or butyllithium, the polymer showed a decrease in the amount of depolymerization during 1 hr. at 202°C. from $27 \pm 4\%$ to less than 6% in each case. Polymer treated with triethylenediamine showed no stabilization.

2. Cyclic Borophane Polymers

a. Synthesis

New methods for synthesis of cyclic triborophanes were demonstrated in the preparation of P-hexamethyltriborophane by pyrolysis of the products resulting from the reaction of dimethylphosphonium chloride with lithium borohydride and from the reaction of dimethylphosphine chloroborane with triethylamine.

Pyrolysis of the secondary phosphine borane adducts in the usual manner provided the new triborophanes, P-hexaneopentyl-, P-trineopentyltri-

phenyl-, P-trimethyltriphenyl-, and P-trimethyltris(3-dimethylaminopropyl)triborophane without complication. The stereoisomers of both P-trineopentyltriphenyl- and P-trimethyltriphenyltriborophanes have been isolated. The functionally substituted P-trimethyltris(3-dimethylaminopropyl)triborophane was converted by way of the amine oxide derivative to P-trimethyltriallyltriborophane.

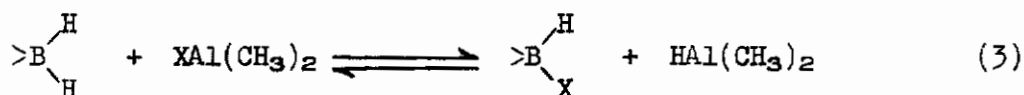
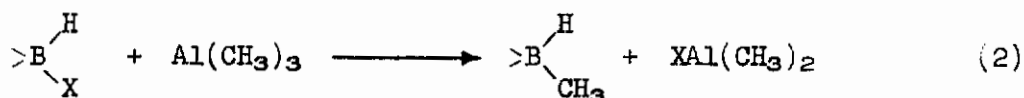
b. Reactions

Halogenation of P-hexamethyltriborophane has been accomplished with cyanogen bromide, mercuric bromide and N-halosuccinimides. With the last reagent and related compounds halogenation was accomplished with sufficient selectivity to prepare the entire series of B-chloro-derivatives of P-hexamethyltriborophane. The stepwise halogenation becomes more difficult as the steric requirement of the halogen increases. With the exception of the B-pentabromo- and B-tetra- and penta-iodo-derivatives, all 18 of the B-substituted chloro-, and iodo-derivatives of P-hexamethyltriborophane have been prepared. Only a few of the stereoisomeric mixtures have been resolved.

P-Hexamethyltriborophane reacts degradatively at elevated temperatures with silver oxide, sulfur, maleic or acetic anhydrides and formic acid and at ambient temperature with permanganate; reduction of mercuric acetate to mercury in hot methanol was observed but the other products of the reaction were obscure.

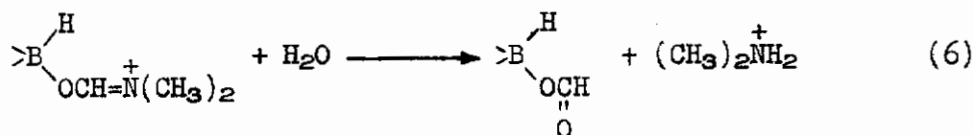
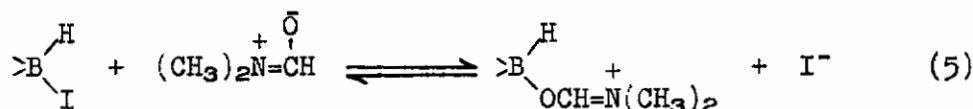
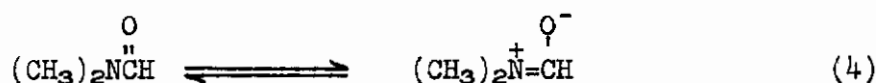
A number of reactions of B-halo-substituted P-hexamethyltriborophanes have been discovered using in most instances the monoiodo-derivative to simplify product characterization. The reactions may be divided into three types: reactions with organometallic reagents, carboxamide derivatives, and metallic salts.

Organic derivatives of lithium, magnesium, zinc, cadmium, mercury, boron and aluminum have been used with varying degrees of success to prepare B-alkyl and B-aryl-derivatives of P-hexamethyltriborophane, with the zinc, cadmium and aluminum compounds providing the higher product yields. Analysis of the reaction products showed that the reactions were nonspecific and that, in addition to the expected B-alkyl or B-aryl-derivative corresponding to the B-halo compound used, both more and less highly substituted products were formed in substantial amounts.



The apparent disproportionation reaction may be rationalized as an initial displacement of a halogen by the organometallic reagent (trimethylaluminum for example) followed by halogenation of the triborophane derivative by the by-product dimethylaluminum halide. Repetition of this process would result in more highly methylated products than expected since trimethylaluminum alone fails to react with P-hexamethyltriborophane. The less highly methylated products must arise of necessity from methylation of a partially reduced B-halo-triborophane derivative since disproportionation of the partially B-halogenated compounds has not been observed under the experimental conditions. Dimethylaluminum hydride, formed when dimethylaluminum halide halogenates the triborophane derivative, presumably is responsible for the observed reduction products. That lesser quantities of apparent disproportionation products are observed as the relative stabilities of the respective metal (Al, Zn, and Cd) hydrides decreases, suggests either suppression of the forward reaction (equation 3) or degradation of the organometal hydride.

Attempts to use dimethylformamide as a reaction solvent for B-halo-derivatives of P-hexamethyltriborophane invariably resulted in the formation of a small amount of a carbonyl-containing product, the yield of which was greater with less carefully dried solvent. A direct study of the reaction of P-hexamethyl-B-iodotriborophane with aqueous dimethylformamide showed that the carbonyl-containing product was P-hexamethyl-B-formoxytriborophane. A proposed mechanism for this reaction is as follows:



Similar reactions were observed with formamide and dimethylacetamide.

The reaction of simple metallic salts with P-hexamethyl-B-iodotriborophane provided a synthetic method for a wide variety of B-substituted derivatives. Reaction of the silver salts of formic, acetic, and benzoic acids in benzene resulted in formation of silver iodide and the corresponding carboxy-compounds, the first two of which were identical with those formed by reaction of the aqueous carboxamides. The reaction of sodium cyanide with P-hexamethyl-B-halotriborophane (chloro-, bromo-, or iodo-) in dimethylformamide or ethanol provided the B-cyano-derivative in high yield; similar reaction of the B-dihalo-derivative yielded P-hexamethyl-B,B'-dicyanotriborophane. Other alkali metal salts were reacted with B-halo-derivatives to obtain the following derivatives of P-hexamethyltriborophane: isocyanato, thiocyno, mercapto and methanethio.

Reaction of P-hexamethyl-B-isocyanatotriborophane with diethylamine converted it to the corresponding diethylureido derivative. Repeated attempts to hydrolyze the cyano group in P-hexamethyl-B-cyanotriborophane to a carboxylic acid failed as did efforts to reduce it to an amine although some reductive cleavage was observed.

c. Evaluation

Relative oxidative stabilities of triborophane derivatives were measured by the spontaneous ignition temperatures of the compounds in air. In the series of 1,3,5-trimethyl-1,3,5-tri-n-alkyltriborophane fluids the spontaneous ignition temperature shows an increasing trend with decreasing volatility as might be expected. Although this series of liquid triborophanes (particularly the higher members) showed a good liquid range, viscosity, and lubricity, the oxidative stability was not sufficient to make them attractive for high temperature applications. P-Neopentyl groups offered no steric inhibition of the oxidation reaction. B-Cyano-derivatives appeared significantly more oxidatively stable than the parent compounds while the reverse was observed with the B-carboxy-derivatives.

The resin, poly-P-methylsesquimethyleneborophane, was used to prepare a glass cloth laminate. The low heat distortion temperature of the resin, presumably due to either thermoplasticity or insufficient cross-linking or both, precluded use of high temperatures. Other resin systems are under investigation.

3. Phosphines

The reaction of an alkyl halide with a metal phosphinide in liquid ammonia was successfully employed to prepare without complication eight new phosphines: methyl-n-alkylphosphine (n-alkyl = C₄-C₈), 3,3-dimethylcyclotrimethylenephosphine, methyl-3-dimethylaminopropylphosphine, and methyl-β-hydroxyethylphosphine (from ethylene oxide).

The reaction of organometallics with aminochlorophosphines has been used to prepare P,P'-bis(methyldimethylamino)-p-phenylenediphosphine, bis-(dimethylamino)methylphosphine, dineopentyldimethylaminophosphine, and neopentylphenyldimethylaminophosphine. The last two compounds were converted through the chloro-derivatives to the corresponding secondary phosphines.

B. Summary and Conclusions

Stabilization toward thermal depolymerization of linear P-dimethylborophane polymer with a variety of acidic and basic reagents has been accomplished, although the improvement observed still is insufficient to permit high temperature applications. Further work directed toward discovery of stable chain terminating groups will be undertaken.

The synthesis and investigation of the chemistry of triborophane derivatives functionally substituted on both boron and phosphorus has markedly accelerated since the discovery of the reactivity of partially B-halogenated triborophanes relative to that of the fully B-halogenated derivatives. Further

work will be directed toward substitution of groups which will either enhance the thermal, oxidative, or hydrolytic stabilities, influence the degree of polymerization, or in themselves be capable of further reaction including polymerization.

III. Borazine Polymers

1. Synthesis of Starting Materials

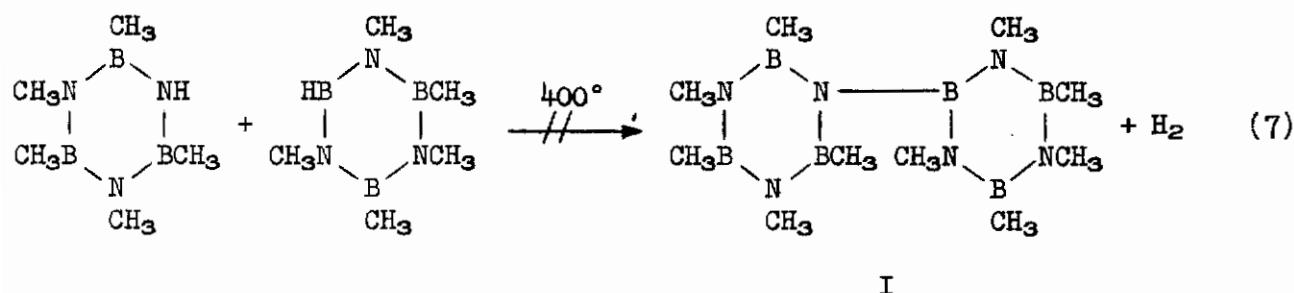
Only a few borazine derivatives which are unsymmetrically substituted with respect to one or both of the skeletal atoms have been reported. During the course of an investigation directed toward preparation of linked-ring borazine polymers a new type of borazine derivative was prepared which can be used to effect unsymmetrical substitution on the nitrogen atom of the borazine ring, i.e., N-lithio-derivatives. The N-lithioborazine compounds were prepared by reaction of the stoichiometric quantities of the borazine and methyllithium.

B-Mono- and -dihalo-substituted borazines were conveniently prepared in high yield and purity by reaction of a borazine suitably blocked with one or two B-methyl substituents with a hydrogen halide at such a temperature that only the B-H bonds and not the B-CH₃ bonds were cleaved. The same compounds, prepared by partial methylation of a B-trichloroborazine derivative with an organometallic reagent, were obtained as mixtures which were only partially resolved after tedious attempted purification.

2. Polymerization of Borazine Rings

Three means of effecting direct condensation polymerization of borazines were investigated: pyrolytic dehydrogenation, dehydrohalogenation, and lithium chloride elimination. Only the last reaction was successful in effecting direct B-N bonding between borazine rings.

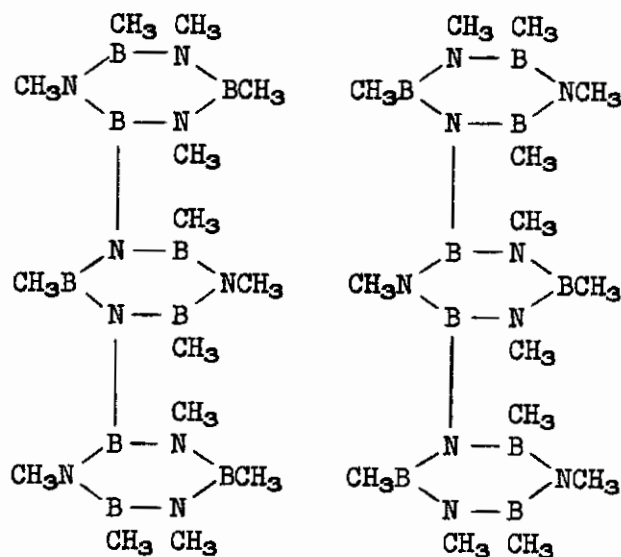
Pyrolysis of an equimolar mixture of isomeric pentamethylborazines gave only a trace of decamethyl-N,B'-biborazyl (I) indicating a remarkable resistance of these substituted derivatives toward elimination of hydrogen.



In each of the independent pyrolyses of the pentamethylborazine isomers the major portion (ca. 89%) of the starting material was recovered and all but a trace of the remainder was accounted for as disproportionation products (tri-, tetra-, and hexamethylborazines). Exchange of methyl groups and hydrogen atoms

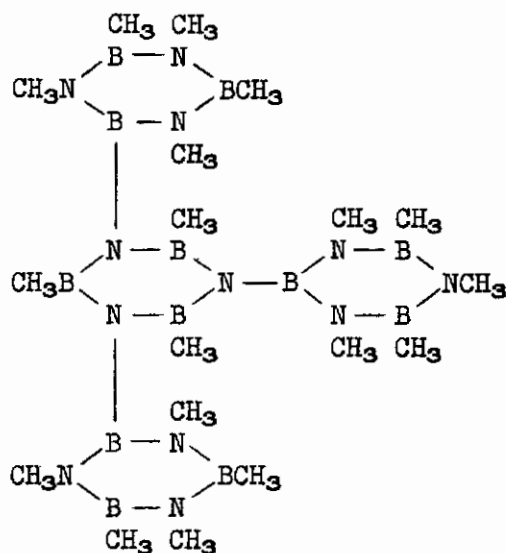
occurred only between like skeletal atoms.

Elimination of lithium chloride between N-lithiopentamethylborazine and pentamethyl-B-chloroborazine gave (I) in good yield. Extension of this type of reaction to polyfunctional borazine derivatives led to the preparation of two isomeric diborazylborazines (II), one of the isomeric triborazylborazines (IIIb), and finally a biborazylene polymer (IV).

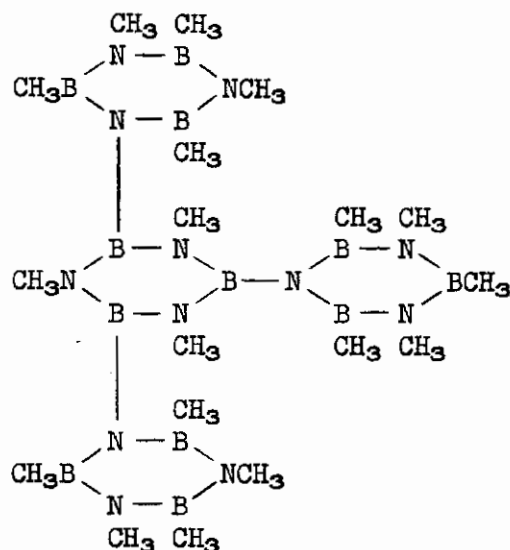


IIa

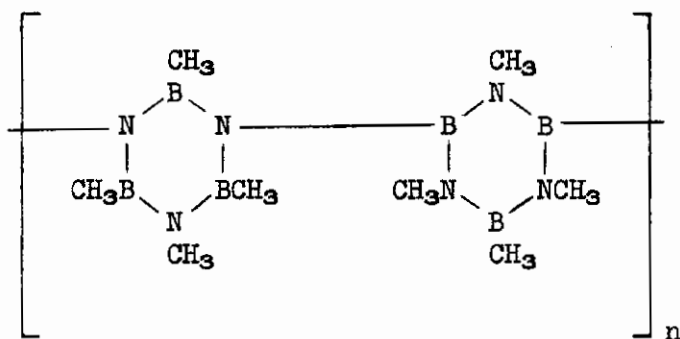
IIb



IIIa

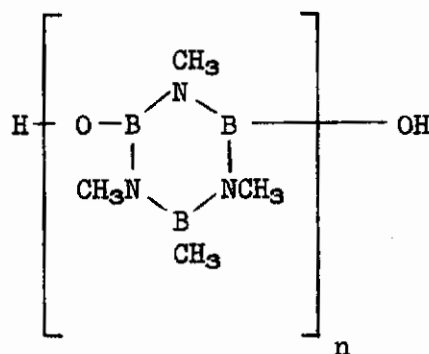
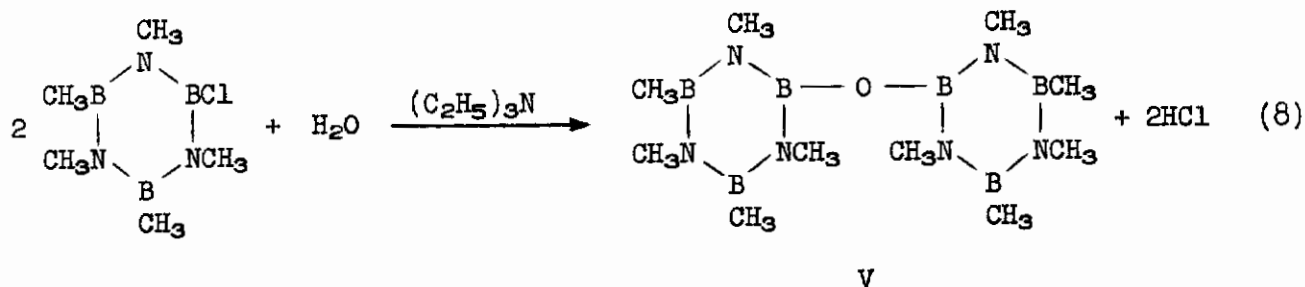


IIIb



IV

Attempts to prepare (I) (and related compounds) by dehydrohalogenation of mixtures of borazines carrying N-H and B-Cl substituents gave instead a compound (V) which was identical to that obtained by hydrolysis of the chloro-substituted derivative alone. Hydrolysis of tetramethyl-B-dichloroborazine with the stoichiometric quantity of water produced, as a glassy product, a polymeric chain of rings (VI) with a degree of polymerization of approximately 23.



IV. Phosphorus-Nitrogen Chemistry

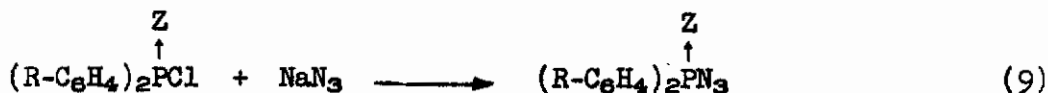
A. Introduction

Aside from the phosphonitrilic halides, phosphorus-nitrogen bonded compounds have not been systematically investigated as possible thermally stable polymer systems or precursors. We wished to explore routes to such compounds by means of reactions in which either no by-product is formed, or only volatile by-products are formed. As a starting point we have investigated the preparation and reactions of organophosphorus azides.

B. Azides

1. Preparation

It was found that equal molar quantities of diarylphosphonyl chlorides (VII) and sodium azide undergo reaction in anhydrous pyridine or acetonitrile to provide the corresponding diarylphosphonyl azides (VIII) in essentially quantitative yields (Eq. 9).



VII

VIII a, R = H, Z = O

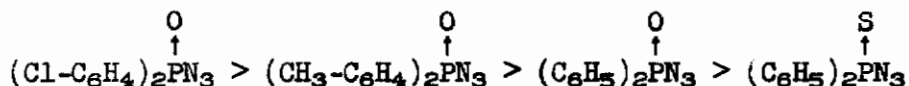
b, R = p-CH₃-, Z = O

c, R = p-Cl-, Z = O

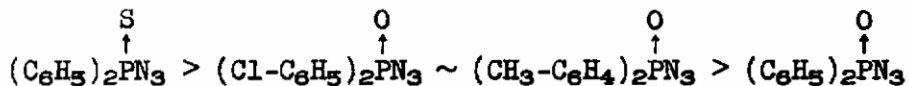
d, R = H, Z = S

2. Properties

The diarylphosphonyl azides were found to be unexpectedly stable; they were distilled, burned, and hit with a hammer without any evidence of violent decomposition. Also, a sample of distilled diphenylphosphonyl azide was stable for 8 months in a sealed ampule under ambient conditions, and a sample of crude material exhibited no decomposition in the presence of 316 stainless steel during several weeks. Diphenylphosphonyl azide was distilled at 137-140°C. at 0.05 mm.; bis-(p-tolyl)phosphonyl azide distilled at 190-195°C. at 0.5 mm. with slow decomposition; bis-(p-chlorophenyl)phosphonyl azide distilled at 10⁻⁵ mm. without apparent decomposition; diphenylthiophosphonyl azide turned red and could be distilled only with difficulty at 10⁻⁴ mm. The infrared spectra of crude (yellow) and distilled diphenylthiophosphonyl azide were identical. The red color changed to yellow on standing; there was no apparent evolution of nitrogen accompanying the color changes from yellow-to-red and red-to-yellow. These observations suggest the following qualitative order of thermal stability for the diarylphosphonyl azides:

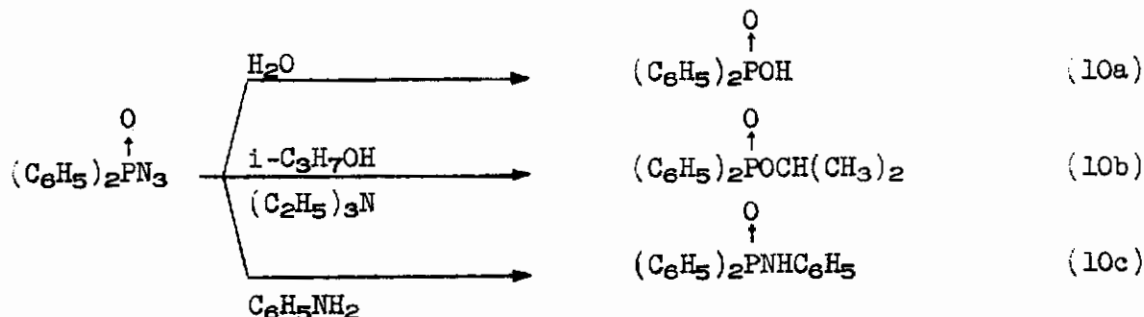


The hydrolytic stability of the diarylphosphonyl azides varies markedly; diphenylphosphonyl azide appears to hydrolyze in a matter of minutes whereas under the same conditions diphenylthiophosphonyl azide is not completely hydrolyzed after several hours. Qualitatively, the relative order of hydrolytic stability appears to be:



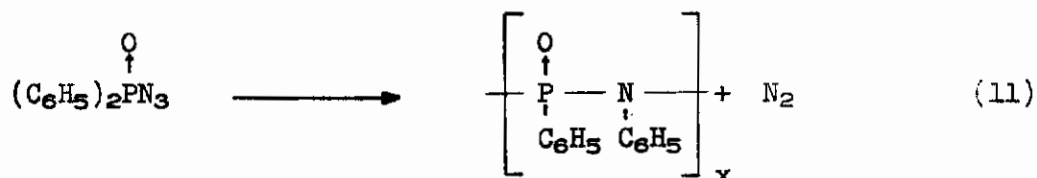
3. Reactions of Diarylphosphonyl Azides

Diphenylphosphonyl azide undergoes solvolytic reactions such as hydrolysis (Eq. 10a), alcoholysis (Eq. 10b), and aminolysis (Eq. 10c).

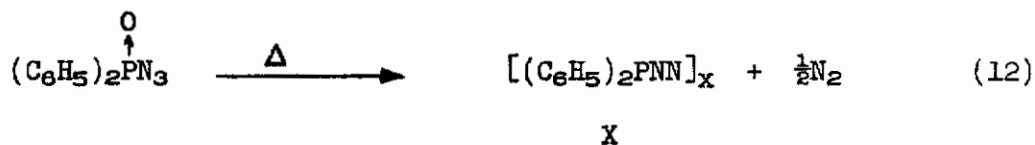


The alcoholysis reaction (Eq. 10b) must be performed under anhydrous conditions to prevent the preferential formation of diphenylphosphonic acid. Furthermore, the alcoholysis reaction did not occur readily except in the presence of a tertiary amine.

The attempted conversion of diphenylphosphonyl azide to a linear P-N polymer (IX) was unsuccessful under a variety of conditions (Eq. 11).



The use of sulfuric acid in an attempted acid catalyzed reaction was unsuccessful; the azide hydrolyzed and the only product isolated was diphenylphosphonic acid. In a further attempt to cause the rearrangement shown in Equation (11) using boron trifluoride in ether at reflux for 48 hrs. there was no nitrogen evolution or other evidence of reaction; infrared examination of the reaction mixture indicated that little or no reaction had occurred. Attempted thermal rearrangement according to Equation (11) did not yield the expected one mole of nitrogen but, instead, one-half mole of nitrogen was obtained (Eq. 12).



The product, X, has the empirical composition shown; the structure of X has not been determined.

In a preliminary experiment it was observed that diphenylphosphonyl chloride and sodium azide reacted in dimethylformamide to give an immediate evolution of nitrogen. However, when diphenylphosphonyl azide was added to dimethylformamide (dried over anhydrous sodium sulfate), no nitrogen evolution was observed. When the dimethylformamide was dried by distillation

from calcium hydride it was found to contain some free amine, and the impure dimethylformamide appeared to cause gas evolution (see below). It has also been found that diphenylphosphonyl azide reacts with dimethylsulfoxide with the liberation of nitrogen. The nature of the products obtained in the dimethylformamide and dimethylsulfoxide reactions has not been determined.

Arenesulfonyl azides have been reported to undergo reaction with aromatic compounds to yield arenesulfonanilides¹. It appeared possible that a similar reaction between diarylphosphonyl azides and aromatic compounds might occur. Such a reaction would extend the chemistry of the phosphonyl azides and would provide a convenient route to a variety of phosphonanilides (Eq. 13).



Such reactions were attempted in refluxing benzene and in p-xylene using azo-bis-isobutyronitrile as a radical source. In both cases, no phosphonanilide was obtained and no nitrogen evolution was observed; infrared examination of the residual liquids indicated that the strong azide absorption at 4.65μ was unchanged. In this same connection, pyridine appears to be an excellent solvent for the preparation of diarylphosphonyl azide with no apparent reaction occurring with the solvent. However, arenesulfonyl azides have been shown to react with pyridine^{2,3}. Diphenylphosphonyl azide reacts with triethylenediamine with the immediate formation of a white, water-soluble salt without the evolution of nitrogen. Infrared examination of this material did not show a distinct azide band at 4.65μ , but exhibited a broad, strong absorption characteristic of a phosphorus-ammonium salt. The material melted at $172-180^\circ\text{C}$. and was soluble in ethanol. When a water solution of the material was acidified, diphenylphosphonic acid precipitated.

Diarylphosphonyl azides react with trivalent phosphorus compounds to yield phosphoranes (Eq. 14). This reaction is discussed separately, below. The reactions of diphenylphosphonyl azide are summarized in Fig. 1.

C. Phosphoranes

1. From Phosphonyl Azides

Equal molar quantities of diarylphosphonyl azides and trivalent phosphorus compounds (Eq. 14) react to provide excellent yields of diarylphosphonimidophosphoranes (XI a-g).

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1. T. Curtius and J. Rissom, J. Prakt. Chem. 125, 303 (1930)
 2. T. Curtius and K. Vorbach, J. prakt. Chem. 125, 303 (1930).
 3. R. M. Levine and G. L. Buchanan, J. Chem. Soc., 2248 (1950).

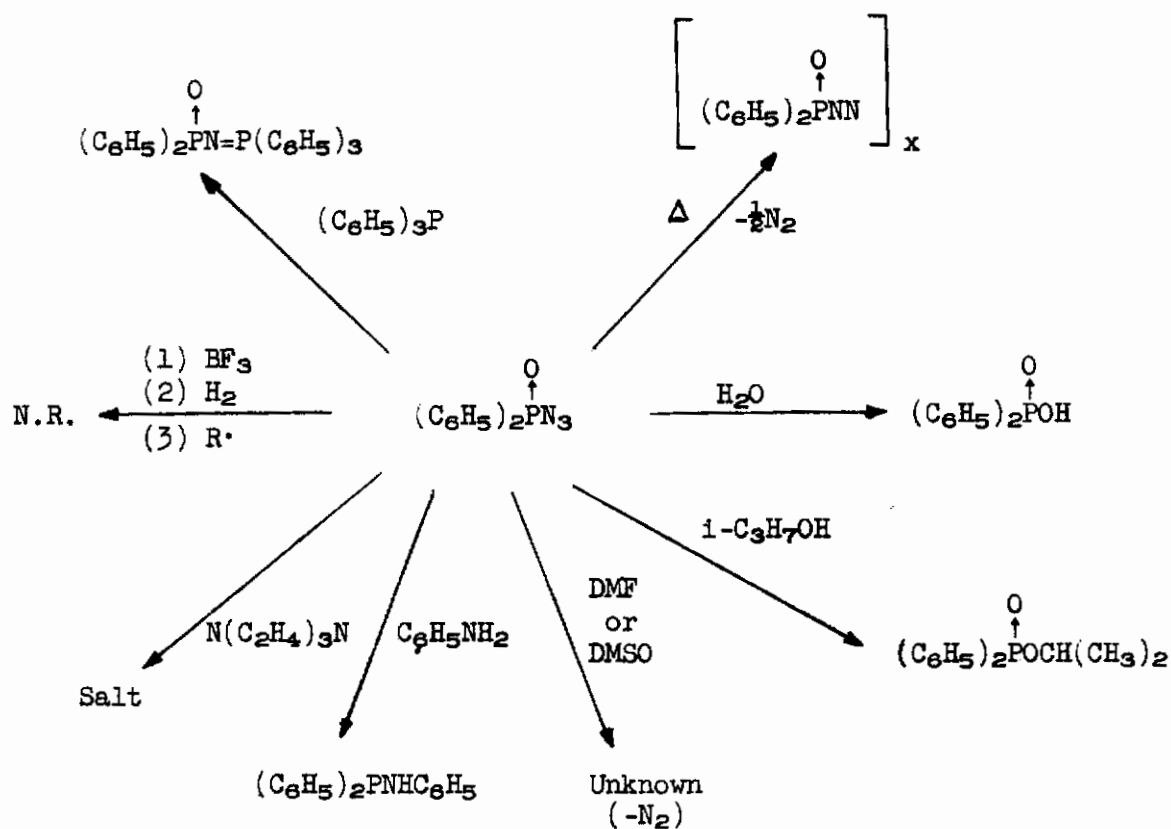
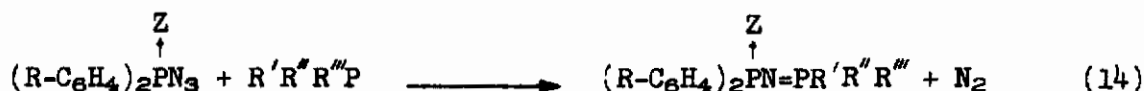


Figure 1. Reactions of Diphenylphosphonyl Azide

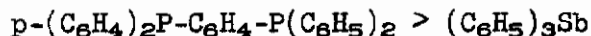
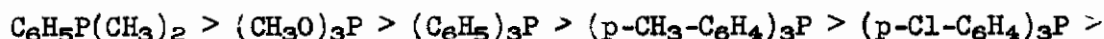


- XI. a. $R=H$; $R'=R''=R'''=C_6H_5$; $Z=O$
 b. $R=p-Cl$; $R'=R''=R'''=C_6H_5$; $Z=O$
 c. $R=p-CH_3$; $R'=R''=R'''=C_6H_5$; $Z=O$
 d. $R=H$; $R'=R''=R'''=C_6H_5$; $Z=S$
 e. $R=H$; $R'=R''=R'''=p-Cl-C_6H_4$; $Z=O$
 f. $R=H$; $R'=R''=R'''=p-CH_3-C_6H_4$; $Z=O$
 g. $R=H$; $R'=R''=CH_3$; $R'''=C_6H_5$; $Z=O$

Diphenylphosphonyl azide reacts slowly with triphenylphosphine in ether to yield diphenylphosphonimidotriphenylphosphorane with the concurrent liberation of equal molar quantities of nitrogen. However, pyridine appears to be a more generally useful solvent for this reaction. Whereas diphenylphosphonyl azide reacts only slowly in ether at reflux, the reaction is essentially quantitative in pyridine at reflux within about one-tenth the time required for ether.

The reaction of phenyldimethylphosphine and diphenylphosphonyl azide in cold ether is so vigorous that it cannot be simply controlled. However, the same reaction occurs in pyridine solution at 0°C. to give a vigorous but controllable evolution of nitrogen and a good yield of diphenylphosphonimido-phenyldimethylphosphorane (XI g).

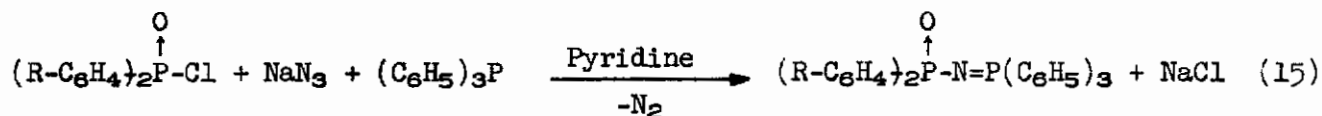
In a survey of the scope of phosphorane formation, diphenylphosphonyl azide was allowed to react with a variety of Lewis bases in different solvents. Qualitatively, it appears that the rate of reaction of various Lewis bases with diphenylphosphonyl azide is in the order;



2. In Situ Procedure

An in situ procedure for the preparation of diarylphosphonimidotriphenylphosphoranes and other metalloid phosphoranes has been developed

which does not require isolation of the phosphonyl azide or other metalloid azide. In the in situ procedure, a mixture of sodium azide and triphenylphosphine in pyridine solvent is warmed to gentle reflux under an argon atmosphere and then the phosphonyl chloride in pyridine is slowly added at such a rate that an easily controlled evolution of nitrogen is obtained (Eq. 15). The pyridine is removed at reduced pressure and the solid residue washed with ether and ammonium hydroxide. The in situ procedure offers some advantages in



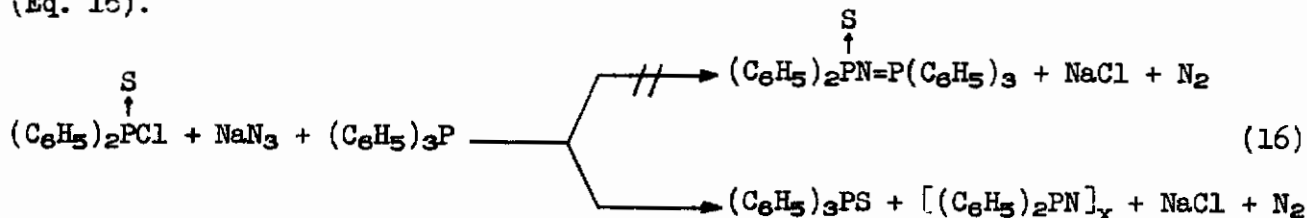
choice of solvent. For example, when diphenylphosphonyl chloride and sodium azide were allowed to react in dimethylformamide there was an immediate evolution of nitrogen indicating decomposition of the azide (see above). However, when the diphenylphosphonyl chloride was added to a hot solution of sodium azide and triphenylphosphine in dimethylformamide a good yield of diphenylphosphonimidotriphenylphosphorane was obtained.

A useful modification of the in situ procedure just described involves the addition of the phosphonyl chloride to sodium azide in pyridine followed by removal of the precipitated sodium chloride by filtration. This leaves a pyridine solution of the phosphonyl azide which can then be allowed to react with a phosphine to yield a phosphorane.

Using the in situ procedure most of the phosphorane preparations can be completed within 10-15 minutes in a small run (10 g.), and the yields of phosphorane are generally about 95%.

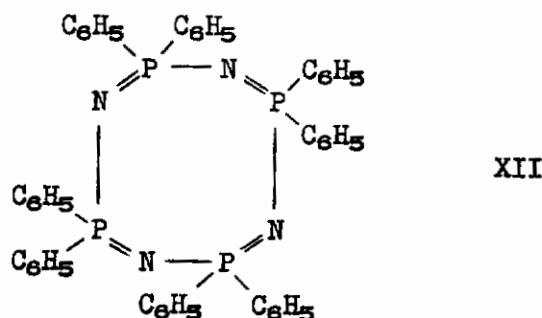
D. Anomalous In Situ Reaction:
Formation of Diphenylphosphinic Nitride

When an attempt was made to use the in situ procedure for the preparation of diphenylthiophosphonimidotriphenylphosphorane, none of the desired material was obtained. Instead, an 87% yield of triphenylphosphine sulfide and a yellow, gummy material which was insoluble in benzene was obtained (Eq. 15).

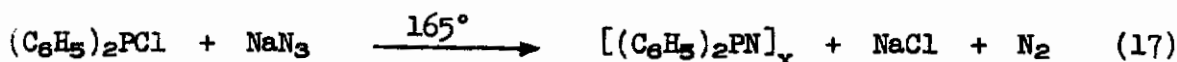


After heating a portion of the yellow material at 275-280°C. for 3 hrs. in a high vacuum, it was extracted with benzene. A white solid was obtained from the benzene extract which was identified as diphenylphosphinic nitride tetramer (XII) by a comparison of the melting points and infrared spectra with an

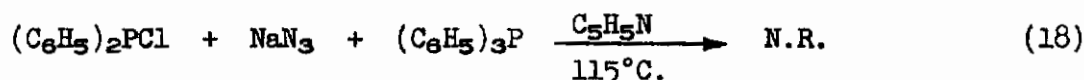
authentic sample*.



Herring⁴ found that the reaction of diphenylchlorophosphine and sodium azide at 165°C. yielded a mixture of diphenylphosphinic nitride polymers (Eq. 17).



However, when we attempted to prepare diphenylphosphinimidotriphenylphosphorane by the in situ reaction of diphenylchlorophosphine, sodium azide, and triphenylphosphine in pyridine at 115°C., there was no evidence of reaction (Eq. 18).



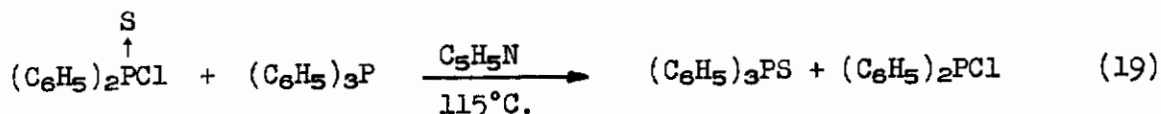
On the other hand, while the in situ reaction of diphenylthiophosphonyl chloride, sodium azide, and triphenylphosphine underwent reaction in pyridine to yield Herring's polymer mixture (Eq. 16), diphenylthiophosphonyl azide reacted readily with triphenylphosphine in pyridine solution (Eq. 14) to give an 87% yield of diphenylthiophosphonimidotriphenylphosphorane. In contrast, diphenylphosphonimidotriphenylphosphorane was obtained in 85% yield from diphenylphosphonyl azide (Eq. 14) and in 97% yield by the in situ reaction of diphenylphosphonyl chloride, sodium azide and triphenylphosphine (Eq. 15).

In an attempt to better understand this anomalous in situ reaction of diphenylthiophosphonyl chloride, sodium azide, and triphenylphosphine (Eq. 16), it was found that diphenylthiophosphonyl chloride and triphenylphosphine react in pyridine at 115°C. to form triphenylphosphine sulfide in about 95% yield (Eq. 19).

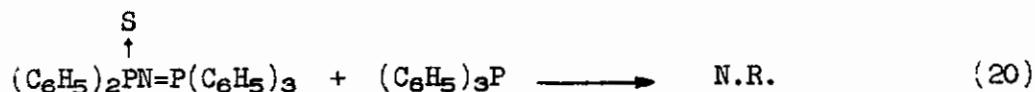
4. D. L. Herring, Chemistry and Industry, 717, 1960.

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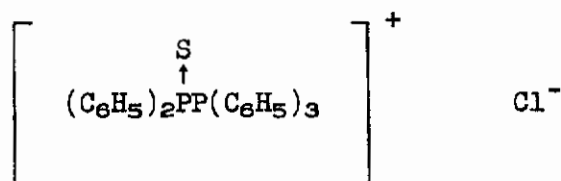
We wish to thank Mr. D. L. Herring, U. S. Naval Ordnance Laboratory, Corona, California, for a sample of diphenylphosphine nitride tetramer and its infrared spectrum.



It seems unlikely, however, that Equation (19) represents the first step in the formation of diphenylphosphinic nitride polymer, since diphenylchlorophosphine was not observed to react under the same conditions (Eq. 18). It was also determined that diphenylthiophosphonimidotriphenylphosphorane does not react with triphenylphosphine under the same conditions (Eq. 20).



The above information and the facts that phosphonyl chlorides and diphenylphosphonyl azide form salts with amines, suggest that the intermediate step in the formation of triphenylphosphine sulfide and diphenylphosphinic nitride polymer might be a displacement or rearrangement reaction of a phosphonium salt, such as XIII.



XIII

This possibility remains to be proven.

E. Properties of Phosphoranes

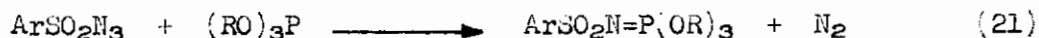
In preparing a large quantity of diphenylphosphonimidotriphenylphosphorane by the *in situ* procedure (Eq. 15) the product obtained had a higher melting point (170-171°C.) than the product first obtained (149-150°C.) by the reaction of diphenylphosphonyl azide with triphenylphosphine (Eq. 14). Subsequent reactions of diphenylphosphonyl azide and triphenylphosphine gave the higher melting product. Elemental analyses and molecular weights were virtually the same for both products. Solution infrared and ultraviolet spectra of both materials were identical but shifts in several absorption bands were observed on comparison of the infrared spectra of the solids in potassium bromide pellets. A sample of the lower melting material which had been standing for several months had a wide melting range, 147-167°C., which suggests a slow conversion of low-melting to high-melting material. The low-melting material was readily converted to the high-melting material by recrystallization from isopropyl alcohol-water mixture. Although it is conceivable that the observed differences in physical properties are due to a difference in purity, the data suggest that diphenylphosphonimidotriphenylphosphorane exhibits two crystal forms (see below).

When diphenylphosphonimidotriphenylphosphorane was heated in an

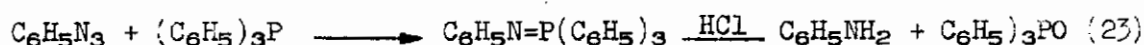
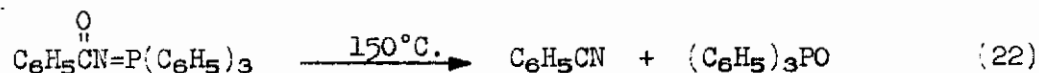
evacuated tube at 216-244°C. for 20 hrs. a glass was obtained whose infrared spectral absorptions were in between those of the high and low-melting forms discussed above. However, recrystallization of the glass from isopropyl alcohol-water mixture gave an essentially quantitative recovery of diphenylphosphonimidotriphenylphosphorane melting at 170-171°C.

The general thermal and oxidative stability of the phosphoranes was demonstrated by dropping samples of the materials onto a heated copper block as previously described⁵. Diphenylphosphon-, bis-(p-chlorophenyl)phosphon-, bis-(p-tolyl)phosphon-, and diphenylthiophosphonimidotriphenylphosphorane, and diphenylphosphonimidophenyldimethylphosphorane did not auto-ignite up to the temperature limit of the apparatus which was approximately 450°C. Furthermore, diphenylphosphonimidotriphenylphosphorane would not support combustion; it burned only when in direct contact with a Bunsen flame.

All of the phosphoranes isolated and characterized were found to be hydrolytically stable toward warm, dilute ammonium hydroxide and dilute hydrochloric acid. In addition, the hydrolytic stability of diphenylphosphonimidotriphenylphosphorane was tested under more vigorous conditions. It was found to be stable toward 6N sulfuric acid at 100°C. for 18 hrs. and to be stable toward boiling alcoholic sodium hydroxide for 18 hrs. The combination of excellent hydrolytic, oxidative and thermal stabilities of the diarylphosphonimidophosphoranes appears to be much better than the most closely related materials containing phosphorus-nitrogen bonds. For example, the preparation of a series of sulfonimidophosphoranes having relatively good thermal stability but having poor hydrolytic stability was reported recently (Eq. 21)⁶. Also benzoimidotriphenylphosphorane has been reported to undergo a thermal redistribution at 150°C.



(Eq. 22) and phenyliminotriphenylphosphorane is cleaved by hydrochloric acid (Eq. 23)⁷.

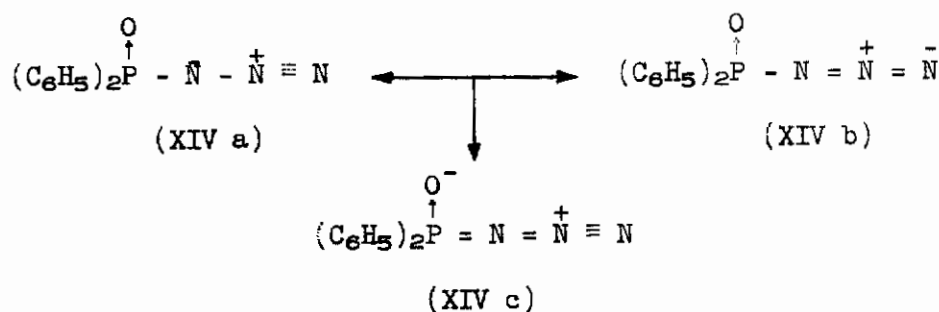


F. Structure and Spectra

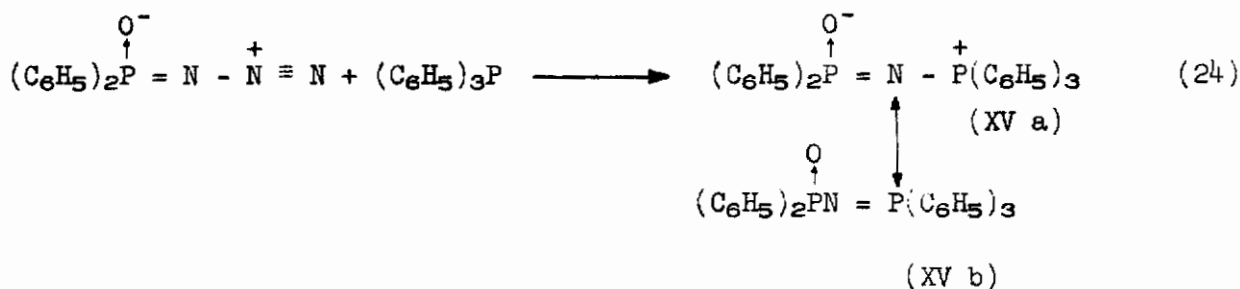
The unusual properties of the diarylphosphonyl azides and diarylphosphonimidophosphoranes can be rationalized by considering the resonance forms

5. R. I. Wagner, et al., WADC Technical Report, 57-126, Part I, March 1957, p. 31.
6. J. Goerdler and H. Ullmann, Ber. 94, 1067 (1961).
7. N. Staudinger and E. Hauser, Helv. Chim. Acta 4, 861, (1921).

which contribute to the total structure (XIV, a-b).



Infrared absorptions at 1265 cm^{-1} (P=N) and at 1230 cm^{-1} (P → O) suggest that the phosphonyl azides exist primarily as the charge-separated structure, XIV c. Structure XIV c is also suggested by the reaction of the azides with trivalent phosphorus compounds to yield phosphoranes (Eq. 24).



There are insufficient data available to draw definite conclusions concerning the nature of the intermediate in the reaction of phosphonyl azides with trivalent phosphorus compounds. By analogy with the sulfonyl azides, it might be argued that a highly reactive triplet state nitrogen would obtain; however, this does not appear to be the case up to temperatures of about 137°C . as evidenced by the lack of reactivity of diphenylphosphonyl azide with benzene and xylene. Under similar conditions, sulfonyl azides react to form sulfon-anilides^{1,8}. This difference in apparent reactivity may involve stabilization of the intermediate by electron delocalization as shown for XVIa and b so that a higher activation energy would be necessary for reaction. In this connection it



8. O. C. Dermer and M. T. Edmison, J. Am. Chem. Soc. 77, 70 (1955).

appears that diphenylphosphonyl azide is considerably more stable thermally than benzenesulfonyl azide. The two forms of diphenylphosphonimidotriphenyl phosphorane shown as energetically equivalent (XVa and b) actually would be expected to have different potential energies. It is possible that XVa being a higher energy form is capable of existence provided that the potential energy barrier necessary for conversion to the thermodynamically more stable XVb is not exceeded. This might account for the low melting (150°C.) and high melting forms (170-171°C.) of diphenylphosphonimidotriphenylphosphorane referred to above. It is also possible that diphenylphosphonimidotriphenylphosphorane can exist in two energetically different geometric isomers; models show that there is possible restricted rotation about the phosphorus-nitrogen single bond due to the phenyl groups.

Examination of the infrared spectra of the diarylphosphonyl azides and the diarylphosphonimidophosphoranes shows two absorptions of interest which are common to both classes of compounds. The absorption at about 1180 cm^{-1} in the phosphoranes and at about 1250 cm^{-1} in the phosphonyl azides has been assigned to the $\text{P} \rightarrow \text{O}$ absorption. For comparison, triphenylphosphine oxide absorbs at 1190 cm^{-1} .⁹ The second absorption of even more interest is that at 1316-1212 cm^{-1} in the phosphoranes and at about 1258 cm^{-1} in the azides. These absorptions have been assigned to a $\text{P}=\text{N}$ absorption, in accord with similarly assigned absorptions in phosphonitrilic chloride trimer and tetramer¹⁰, in diphenylphosphinic nitride trimer and tetramer, and in the recently reported sulfonimidophosphoranes⁶. The $\text{P} \rightarrow \text{O}$ and $\text{P}=\text{N}$ absorptions for the compounds studied are given in Table I.

The ultraviolet spectra of the phosphonyl azides and phosphoranes have been determined using ethanol or acetonitrile as the solvent. The phosphoranes show greatly enhanced aromatic absorptions at 264-5 and 266-7 $\text{m}\mu$ ($\log \epsilon$ 3.2, 3.5) and at about 224-5 $\text{m}\mu$ ($\log \epsilon > 4.5$). Diphenylthiophosphonimidotriphenylphosphorane exhibits enhanced aromatic absorptions ($\log \epsilon$ 3.7, 3.85) at the same wavelengths as the oxygen analog and triphenylphosphine sulfide also exhibits a similar enhancement of the aromatic absorptions compared to triphenylphosphine oxide. Diphenylphosphonyl azide has an ultraviolet spectrum similar to that of the phosphoranes.

G. Applications

Two interesting applications for the phosphonyl azides and phosphoranes have been briefly investigated. Firstly, the addition of diphenylphosphonimidotriphenylphosphorane to epoxy resins appears to impart useful fire retardant properties and, secondly, if the phosphorane is prepared in situ the nitrogen gas liberated effectively acts as a blowing agent for the preparation of epoxy foams.

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9. L. W. Daasch and D. C. Smith, *Anal. Chem.* 23, 853 (1951).
 10. L. W. Daasch, *J. Am. Chem. Soc.* 76, 3403 (1954).

TABLE I

Infrared Assignments (cm⁻¹)

Compound	P → O	P = N
$(C_6H_5)_3PO$	1190	--
$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}-N=P(C_6H_5)_3$	1167	1316, 1302
$(p-CH_3C_6H_4)_2\overset{\overset{O}{\uparrow}}{P}-N=P(C_6H_5)_3$	1170	1227
$(p-ClC_6H_4)_2\overset{\overset{O}{\uparrow}}{P}-N=P(C_6H_5)_3$	1176	1239
$(C_6H_5)_2\overset{\overset{S}{\uparrow}}{P}-N=P(C_6H_5)_3$	--	1230
$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}-N=P(C_6H_4-p-Cl)_3$	1170	1212
$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}-N=P(C_6H_4-p-CH_3)_3$	1176	1266
$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}-N=P(CH_3)_2C_6H_5$	1170	1250
$(C_6H_5)_2\overset{\overset{O}{\uparrow}}{P}N_3$	1229	1263
$(C_6H_5)_2\overset{\overset{S}{\uparrow}}{P}N_3$	--	1255
$(p-Cl-C_6H_4)_2\overset{\overset{O}{\uparrow}}{P}N_3$	1227	1258