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 aryloxophosphinimido-phosphoranes.

1. 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 (phosphinonorovinones), 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 instability 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.
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-alkylphosphorane 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-dimethylcyclotri- methylene)borophane was prepared by pyrolysis of 3,3-dimethylcyclotrimethylene-phosphorane 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.

\[ \text{R}_n\text{PH} + \text{R}_n\text{N}:\text{BH}_3 \longrightarrow \text{R}_n\text{P} + \text{R}_n\text{N}:\text{BH}_3 \]  

Attempts to prepare the fully methylated linear polymer, \([(\text{CH}_3)\text{P} (\text{CH}_3)\text{B}]_n\), by methylation of either \((\text{H}\text{CH}_3)\text{P} (\text{CH}_3)\text{B}]_n\) or \([(\text{CH}_3)\text{P} (\text{H})\text{B}]_n\) failed. Reaction of \[(\text{H}\text{CH}_3)\text{P} (\text{CH}_3)\text{B}]_n\), prepared by dehydrochlorination of methylphosphine dimethylboronborane, gave as the principal product: (1) with methylolithium, trimethylphosphine trimethylborane; and (2) with sodium amide and

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methyl bromide, amidinodimethylborane trimer. From the reaction of trimethylaluminum with [(CH₃)₃P]₃Al, 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 24 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 ± 4% of the polymer depolymerized during 1 hr. to P-hexamethyltriborophane containing 2-4 per cent P-ewamethylderiborophane. Pyrolysis of both a physical equimolar mixture of P-dimethylborophane and P-dimethylethylborophane 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, [(CH₃)₃P]₃Al₃-n[(CH₃)₂Al₂H₃]ₐ[PH₃]ₐ. Based on these and other results the depolymerization appears to proceed by an unzipping of monomer units which react to form the observed cyclic products.

Thermal depolymerization of two other borophane polymers, P-cyclotetramethyleneborophane and P-(3,3-dimethylcyclotrimethylenyl)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 tetramethylenophosphine 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 order 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 ± 4% to less than 5% in each case. Polymer treated with triethylendiamine showed no stabilization.

2. Cyclic Borophane Polymers

a. Synthesis

New methods for synthesis of cyclic triborophanes were demonstrated in the preparation of P-hexamethyldiborophane 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-hexamethyldiborane, P-trimethyldiborane-

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

b. Reactions

Haloamination of P-hexamethylyltriborophane has been accomplished with cyanogen bromide, mercuric bromide and N-bromosuccinimide. With the last reagent and related compounds haloamination was accomplished with sufficient selectivity to prepare the entire series of B-chloro-derivatives of P-hexamethylyltriborophane. The stepwise haloamination becomes more difficult as the steri requirement of the halo increases. With the exception of the B-pentafluoro- and B-tetra- and pentafluoro-derivatives, all B's of the B-substituted chloro-, and iodo-derivatives of P-hexamethylyltriborophane have been prepared. Only a few of the stereoisomeric mixtures have been resolved.

P-Hexamethylyltriborophane 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-bromo-substituted P-hexamethylyltriborophanes have been discovered using in most instances the monochrome-derivative to simplify product characterization. The reactions may be divided into three types: reactions with organometallic reagents, carboxylic acid 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-hexamethylyltriborophane, with the zinc, cadmium and aluminum compounds providing the higher product yields. Analysis of the reaction products showed that the reactions were nespecific and that, in addition to the expected B-alkyl or B-aryl-derivative corresponding to the B-bromo compound used, both more and less highly substituted products were formed in substantial amounts.

\[ \text{H}^+ + \text{Al(C}_2\text{H}_5)_3 \rightarrow \text{B}^+ \text{CH}_3 \times \text{X}^{-} + \text{XAl(C}_2\text{H}_5)_2 \]  

(2)

\[ \text{H}^+ + \text{XAl(C}_2\text{H}_5)_2 \rightarrow \text{B}^+ \text{CH}_3 \times \text{X}^{-} + \text{XAl(C}_2\text{H}_5)_2 \]  

(3)
The apparent disproportionation reaction may be rationalized as an initial displacement of a halogen by the organometallic reagent trimethylaluminium for example) followed by halogenation of the triborophane derivative by the by-product dimethylaluminium halide. Repetition of this process would result in more highly methylated products than expected since trimethylaluminium 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. Dimethylaluminium hydride, formed when dimethylaluminium 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 Ga) 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-bromotriborophane with aqueous dimethylformamide showed that the carbonyl-containing product was P-hexamethyl-B-formyloxytriborophane. A proposed mechanism for this reaction is as follows:

\[
\begin{align*}
\text{(CH}_3)_2\text{NCH} & \overset{0}{\longrightarrow} \text{(CH}_3)_2\text{N}^+\text{CL}^- \\
\text{(CH}_3)_2\text{B}^+ & \overset{0}{\longrightarrow} \text{OCB}^- + \text{(CH}_3)_2\text{B} \\
\text{b}\text{(CH}_3)_2\text{B}^+ & \overset{0}{\longrightarrow} \text{OCB}^- \text{H}_2\text{O} \\
\text{b}\text{OCB}^- & \overset{0}{\longrightarrow} \text{OCB}^- + \text{(CH}_3)_2\text{B} \\
\end{align*}
\]

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 iodides and the corresponding carbonyl compounds. The first two of which were identical with those formed by reaction of the aqeous carbonylates. Thus, reaction of sodium cyanide with P-hexamethyl-B-bromotriborophane (chloro-, bromo-, or iodo-) in dimethylformamide or ethanol provided the B-cyano-derivative in high yield; similar reaction of the B-dimale-derivative yielded P-hexamethyl-B,N-dicyanotriborophane. Other alkali metal salts were reacted with B-halo-derivatives to obtain the following derivatives of P-hexamethyliotriborophane: isocyanato, thiocyanato, mercapto and methanethio.
Reaction of P-hexamethyl-8-isocyanatotriborophane with diethylamine converted it to the corresponding diethylureido derivative. Repeated attempts to hydrolyze the cyan group in P-hexamethyl-8-cyanotriborophane to a carboxylic acid failed as did efforts to reduce it to an amine although some reductive cleavage was observed.

3. 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-trinitro-1-alkyltriborane 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-Nepentyl groups offered no sterol 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-methylacrylamidemethyleborophane, 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-α-alkylphosphine (α-alkyl = C₆H₅, C₇H₈), 1,3,5-dimethyl pentamethylenephosphine, α-methyl-3,5-diethylbenzophosphine, and methyl-β-hydroxyethylphosphine (from ethylene oxide).

The reaction of organostannalum with chlorostannostannanes has been used to prepare P₃SnS₃ (bis[3,3'-diethylamino]·p-phenylenediphosphine, bisdimethylaminometa-ethylphosphine, disepentylamidemethyldiphosphine, and nepentylbenzoyldimethyldiphosphine. 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 dust 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 affect unsymmetrical substitution on the nitrogen atoms 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 methylthiium.

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 2-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 N-N bonding between borazine rings.

Pyrolysis of an equimolar mixture of isomeric pentamethylborazines gave only a trace of decahydro-3,6-biborazyl (I) indicating a remarkable resistance of these substituted derivatives toward elimination of hydrogen.

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_2 & \quad \text{B} & \quad \text{N} & \quad \text{B} & \quad \text{CH}_3 \\
+ & \quad \text{HBr} & \quad \text{BCH}_3 \\
\text{CH}_2 & \quad \text{B} & \quad \text{N} & \quad \text{B} & \quad \text{CH}_3 \\
& \quad \text{CH}_3 & \quad \text{BCH}_3 & \quad \text{H}_2 \\
\xrightarrow{400^\circ} & \quad \text{CH}_3 & \quad \text{B} & \quad \text{N} & \quad \text{B} & \quad \text{CH}_3 \\
& \quad \text{BCH}_3 & \quad \text{BCH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

In each of the independent pyrolyses of the pentamethylborazine isomers the major portion (ca. 85%) 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 \( \text{N}-\text{liithiopentamethylborazine} \) and \( \text{pentamethyl-B-chloroborazine} \) 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 diborosphane polymer (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 25.
IV. Phosphorus-Nitrogen Chemistry

A. Introduction

Aside from the phosphoritrilic 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).
2. Properties

The diarylphosphanyl 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 diphenylphosphanyl azide was stable for 8 months in a sealed ampoule under ambient conditions, and a sample of crude material exhibited no decomposition in the presence of 316 stainless steel during several weeks. Diphenylphosphanyl azide was distilled at 157-160°C, at 0.09 mm.; bis-(p-tolyl)phosphanyl azide distilled at 190-195°C, at 0.5 mm. with slow decomposition; bis-(p-chlorophenyl)phosphanyl azide distilled at 100°C, without apparent decomposition; diphenylthiophosphanyl azide turned red and could be distilled only with difficulty at 10-4 mm. The infrared spectra of crude (yellow) and distilled Diarylphosphanyl 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 Diarylphosphanyl azides:

\[
\text{O} > (\text{Cl-} \text{C}_6\text{H}_4)\text{SPH}_3 > (\text{CH}_3- \text{C}_6\text{H}_4)\text{SPH}_3 > (\text{C}_6\text{H}_5)\text{SPH}_3 > (\text{C}_6\text{H}_5)_2\text{SPH}_3
\]

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

\[
\text{O} > (\text{C}_6\text{H}_5)\text{SPH}_3 > (\text{Cl-} \text{C}_6\text{H}_4)\text{SPH}_3 > (\text{CH}_3- \text{C}_6\text{H}_4)\text{SPH}_3 > (\text{C}_6\text{H}_5)_2\text{SPH}_3
\]

1. Reactions of Diarylphosphanyl Azides

Diphenylphosphanyl azide undergoes solvolytic reactions such as hydrolysis (Eq. 10a), alcoholyysis (Eq. 10b), and aminolyysis (Eq. 10c).
The alcoholysis reaction (Eq. 10a) 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 diphenylphosphinoyl 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 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 diphenylphosphinoyl chloride and sodium azide reacted in dimethylformamide to give an immediate evolution of nitrogen. However, when diphenylphosphinoyl azide was added to dimethylformamide (dried over anhydrous sodium sulfate), no nitrogen evolution was observed. When the dimethylformamide was dried by distillation

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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.

Aromasulfonfyl azides have been reported to undergo reaction with aromatic compounds to yield arnesulfonamides. 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).

\[
\text{(C}_6\text{H}_5\text{H})_2\text{P(O)}\text{N}_3 + \text{ArH} \rightarrow \text{(C}_6\text{H}_5\text{H})_2\text{P(O)NAr} + \text{N}_2
\]  (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 6.65 μ 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, aminesulfonfyl azides have been shown to react with pyridine.\(2,3\). Diphenylphosphonyl azide reacts with triethylendiamine 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 6.65 μ, but exhibited a broad, strong absorption characteristic of a phosphorus-ammonium salt. The material melted at 172-175°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 summarised 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).

1. T. Curtius and J. Risom, J. Prakt. Chem. 129, 303 (1930)

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Figure 1. Reactions of Diphenylphosphonyl Azide
Diphenylphosphonyl azide reacts slowly with triphenylphosphine in ether to yield diphenylphosphinomidotriphenylphosphorane 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 phenyltrimethylphosphine 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 diphenylphosphinomidotrimethylphosphorane (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:

\[ \text{PhPPh}_3 \text{P(Ph)}_3 > (\text{Ph}_2 \text{P})_3 \text{P} > (\text{Ph}_2 \text{P})_3 \text{P} > (p-\text{ClC}_6 \text{H}_4 \text{P})_3 \text{P} > (p-\text{ClC}_6 \text{H}_4 \text{P})_3 \text{P} > \]

\[ p-(\text{Ph}_2 \text{P})_3 \text{P}-\text{C}_6 \text{H}_4 \text{P}(\text{Ph}_2 \text{P})_3 \text{P} > (\text{Ph}_2 \text{P})_3 \text{Sb} \]

2. **In Situ Procedure**

An in situ procedure for the preparation of triarylphosphinomidotriphenylphosphoranes 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 diphenyl phosphonyl 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 diphenyl phosphonyl chloride was added to a hot solution of sodium azide and triphenylphosphine in dimethylformamide a good yield of diphenylphosphonomidotriphosphine 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 diphenylphosphonomidotriphosphine, 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. 16).

\[
\begin{align*}
\text{S} & \quad \xrightarrow{\text{S}} \quad \text{(C}_6\text{H}_5\text{)}_2\text{P}=\text{P}(\text{C}_6\text{H}_5)_3 + \text{NaCl} + \text{N}_2 \\
\text{(C}_6\text{H}_5\text{)}_2\text{PCl} + \text{NaCl} + \text{(C}_6\text{H}_5\text{)}_3\text{P} & \quad \xrightarrow{\text{S}} \quad \text{(C}_6\text{H}_5\text{)}_2\text{PS} + \text{[(C}_6\text{H}_5\text{)}_2\text{PN}]_x + \text{NaCl} + \text{N}_2
\end{align*}
\]

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 trimmer (XII) by a comparison of its melting points and infrared spectra with an

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authentic sample

\[
\begin{align*}
(C_{6}H_{5})_{3}PPCl + NaCl & \xrightarrow{165^\circ} [(C_{6}H_{5})_{2}P]_{x} + NaCl + \text{Ne} \\
(C_{6}H_{5})_{3}PPCl + NaCl + (C_{6}H_{5})_{2}P & \xrightarrow{115^\circ} \text{N.R.}
\end{align*}
\]

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

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

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


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

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\[
\begin{align*}
\text{S} \quad (\text{C}_6\text{H}_5)_2\text{PCl} + (\text{C}_6\text{H}_5)_3\text{P} & \xrightarrow{\text{115°C}.} \quad (\text{C}_6\text{H}_5)_2\text{PS} + (\text{C}_6\text{H}_5)_2\text{PCl} \\
\text{S} \quad (\text{C}_6\text{H}_5)_2\text{P} = (\text{C}_6\text{H}_5)_3\text{P} & \quad \text{N.R.}
\end{align*}
\]

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

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

\[
\begin{align*}
\text{S} \quad (\text{C}_6\text{H}_5)_2\text{PP} = (\text{C}_6\text{H}_5)_3\text{P} & \quad \text{Cl}^- \\
\quad \text{XIII}
\end{align*}
\]

This possibility remains to be proven.

E. Properties of Phosphoranes

In preparing a large quantity of diphenylphosphonioimidodiphenylphosphorane by the in situ procedure (Eq. 15) the product obtained had a higher melting point (170-172°C.) than the product first obtained (169-169.5°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, 177-187°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 diphenyl-phosphonioimidodiphenylphosphorane exhibits two crystal forms (see below).

When diphenylphosphonioimidodiphenylphosphorane was heated in an

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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 diphenylphosphinimidotriphenyl phosphorane 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 described. Diphenylphosphon-, bis-[p-chloropheny]phosphon-, bis-[p-toly]phosphon-, and diphenylphosphinimidotriphenylphosphorane, and diphenylphosphinimidophenylisopropylphosphorane did not auto-ignite up to the temperature limit of the apparatus which was approximately 450°C. Furthermore, diphenylphosphinimidotriphenylphosphorane 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 water, dilute ammonium hydroxide and dilute hydrochloric acid. In addition, the hydrolytic stability of diphenylphosphinimidotriphenylphosphorane was tested under more vigorous conditions. It was found to be stable toward 6 N sulfuric acid at 100°C. for 16 hrs. and to be stable toward boiling alcoholic sodium hydroxide for 15 hrs. The combination of excellent hydrolytic, oxidative and thermal stabilities of the diarylphosphinimidophosphoranes 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 benzimidotriphenylphosphorane has been reported to undergo a thermal redistribution at 150°C.

\[
\text{Ar}_2\text{P} + (\text{RO})_3\text{P} \rightarrow \text{Ar}_2\text{P} + (\text{RO})_3\text{P} + \text{H}_2 \quad (21)
\]

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

\[
\text{C}_6\text{H}_5\text{N} = \text{P} + \text{HCl} \rightarrow \text{C}_6\text{H}_5\text{N} + \text{HCl} \quad (22)
\]

\[
\text{C}_6\text{H}_5\text{N} + (\text{C}_6\text{H}_5\text{P})_3 \rightarrow \text{C}_6\text{H}_5\text{N} + (\text{C}_6\text{H}_5\text{P})_3 \quad (23)
\]

F. Structure and Spectra

The unusual properties of the diarylphosphinyl azides and diarylphosphinimidophosphoranes can be rationalized by considering the resonance forms.


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

\[
\begin{align*}
\text{(XIV a)} & \quad (\text{C}_6\text{H}_5\text{P})_2^+ - \text{N} - \text{N} = \text{N} \\
\text{(XIV b)} & \quad (\text{C}_6\text{H}_5\text{P})_2^+ - \text{N} = \text{N} = \text{N} \\
\text{(XIV c)} & \quad (\text{C}_6\text{H}_5\text{P})_2^+ = \text{N} = \text{N} = \text{N}
\end{align*}
\]

Infrared absorptions at 1665 cm\(^{-1}\) (P=O) and at 1250 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).

\[
\begin{align*}
\text{(XV a)} & \quad (\text{C}_6\text{H}_5\text{P})_2^+ = \text{N} = \text{N} + (\text{C}_6\text{H}_5\text{P})_2^+ \\
\text{(XV b)} & \quad (\text{C}_6\text{H}_5\text{P})_2^+ = \text{P}(\text{C}_6\text{H}_5\text{P})_2
\end{align*}
\]

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 157°C, as evidenced by the lack of reactivity of diphenylphosphonyl azide with benzene and xylene. Under similar conditions, sulfonyl azides react to form sulfonamides. 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

\[
\begin{align*}
\text{(XVI a)} & \quad (\text{C}_6\text{H}_5\text{P})_2^+ = \text{N} \\
\text{(XVI b)} & \quad (\text{C}_6\text{H}_5\text{P})_2^+ \text{N}
\end{align*}
\]


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appears that diphenylphosphinyl azide is considerably more stable thermally than benzene-sulfonyl azide. The two forms of diphenylphosphinimidotriphenyl phosphorane show an energetically equivalent (Xa and b) actually could be expected to have different potential energies. It is possible that Xa being a less stable form is capable of existence provided that the potential energy barrier necessary for conversion to the thermodynamically more stable Xb is not exceeded as slight melting for the low melting forms (170-171°C.) of diphenylphosphinimidotriphenylphosphorane referred to above. It is also possible that diphenylphosphinimidotriphenylphosphorane 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 diacrylphosphinyl azides and the diacylphosphinimidophosphoranes shows two absorptions of interest which are common to both classes of compounds. The absorption at about 1150 cm\(^{-1}\) in the phosphoranes and at about 1250 cm\(^{-1}\) in the phosphinyl azides has been assigned to the P = O absorption. For comparison, triphenylphosphine oxide absorbs at 1190 cm\(^{-1}\). The second absorption of even more interest is that at 1316-1312 cm\(^{-1}\) in the phosphoranes and at about 1290 cm\(^{-1}\) in the azides. These absorptions have been assigned to a P = N absorption, in accord with similarly assigned absorptions in phosphonitrile chloride trimer and tetramer\(^{10}\), in diphenylphosphinic nitride trimer and tetramer, and in the recently reported sulfoniimidophosphoranes\(^8\). The P = O and P = N absorptions for the compounds studied are given in Table I.

The ultraviolet spectra of the phosphinyl 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 μ (log ε 3.2, 3.5) and at about 224-5 μ (log ε 4.5). Diphenylphosphinimidotriphenylphosphorane exhibits enhanced aromatic absorptions (log ε 3.7, 3.05) at the same wavelengths as the oxygen analog and triphenylphosphine sulfide also exhibits a similar enhancement of the aromatic absorptions compared to triphenylphosphine oxide. Diphenylphosphinyl azide has an ultraviolet spectrum similar to that of the phosphoranes.

3. Applications

Two interesting applications for the phosphinyl azides and phosphoranes have been briefly investigated. Firstly, the addition of diphenylphosphinimidotriphenylphosphorane 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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## TABLE I

**Infrared Assignments (cm⁻¹)**

<table>
<thead>
<tr>
<th>Compound</th>
<th>P - O</th>
<th>P - N</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅₃PO</td>
<td>1190</td>
<td>--</td>
</tr>
<tr>
<td>C₆H₅₃P - N-P(C₆H₅)₃</td>
<td>1167</td>
<td>1316, 1302</td>
</tr>
<tr>
<td>(p-CH₃C₆H₅)₃P - N-P(C₆H₅)₃</td>
<td>1170</td>
<td>1227</td>
</tr>
<tr>
<td>(p-ClC₆H₄₃)₃P - N-P(C₆H₅)₃</td>
<td>1176</td>
<td>1239</td>
</tr>
<tr>
<td>C₆H₅₃P - N-P(C₆H₅)₃</td>
<td>--</td>
<td>1230</td>
</tr>
<tr>
<td>(C₆H₅₃)₃P - N-P(C₆H₅₄-p-Cl)₃</td>
<td>1170</td>
<td>1245</td>
</tr>
<tr>
<td>(C₆H₅₃)₃P - N-P(C₆H₅₄-p-CH₃)₃</td>
<td>1176</td>
<td>1266</td>
</tr>
<tr>
<td>(C₆H₅₃)₃P - N-P(CH₃)₃C₆H₅</td>
<td>1170</td>
<td>1250</td>
</tr>
<tr>
<td>C₆H₅₃P(CH₃)₃</td>
<td>1229</td>
<td>1265</td>
</tr>
<tr>
<td>C₆H₅₃P(CH₃)₃</td>
<td>--</td>
<td>1255</td>
</tr>
<tr>
<td>(p-ClC₆H₄)₃P(CH₃)₃</td>
<td>1227</td>
<td>1258</td>
</tr>
</tbody>
</table>