OFFICIAL FILE COPY

ML-TDR-64-181
PART II

AD0470293

PHOSPHORANE POLYMERS

Dr. Roger A. Baldwin and Ming T. Cheng
American Potash & Chemical Corporation

TECHNICAL REPORT ML-TDR-64-181, PART II

June 1965

Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

20040301017

NOTICES

Qualified users may obtain copies of this report from the Defense Documentation Center.

DDC release to CFSTI is not authorized.

Dissemination outside the Department of Defense or to recipients other than Government defense contractors is prohibited.

Copies of this report should not be returned to the Research and Technology Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

PHOSPHORANE POLYMERS

Dr. Roger A. Baldwin and Ming T. Cheng
American Potash & Chemical Corporation

W-6509

FOREWORD

This report was prepared by Dr. Roger A. Baldwin, American Potash & Chemical Corporation, Research Department, Whittier, California, under USAF Contract No. AF 33(657)-11129. This contract was initiated under Project No. 7340 "Nonmetallic and Composite Materials," Task No. 734004, "New Chemicals and Methods." The report was administered under the direction of Polymer Branch, Nonmetallic Materials Division, AF Materials Laboratory, Research and Technology Division, with Dr. W. L. Lehn acting as project engineer.

This report covers work conducted from 1 April 1964 through 31 March 1965. The manuscript was released by the author in May 1965 for publication as an RTD technical report.

The work at American Potash & Chemical Corporation was carried out under the direction of Dr. K. R. Eilar, Manager, Research, and by Dr. Roger A. Baldwin, Head, Organic Section, who acted as project leader, Ming. T. Cheng and, in part, Robert J. Mitchell.

This technical report has been reviewed and is approved.

William E. Gibbs
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

An improved method for the synthesis of phosphonyl azides has resulted in the synthesis of a new class of phosphorane intermediate, the bis-azidophosphorane. Subsequent reaction of these bis-azidophosphoranes with bis-tertiary phosphines has resulted in polyphosphoranes from which, for the first time, fibers and disks (brittle, however) could be formed.

Thermal gravimetric analysis studies continue to indicate that the biphenylene linking unit provides phosphoranes (prototypes as well as polymers) which are more thermally stable than are those with p-phenylene units. An initial thermal evaluation of polyphosphoranes indicated thermal stability to 400° C. and a residue of 40-45 percent which was then stable to 700-800° C.

Additional synthetic effort has resulted in the preparation of two new and useful intermediates, the 3- and 4-bromophenyldiphenylphosphines as well as two bis-phosphonic acids.

A survey of silyl azides and phosphoranes was conducted and the promising results suggest additional studies. An attempt to prepare a triborophane diazide was unsuccessful.

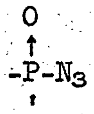
TABLE OF CONTENTS

TABLE OF CONTENTS (CONT)

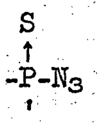
LIST OF TABLES

I. INTRODUCTION

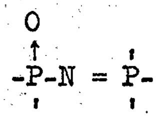
As a result of exploratory research partially supported during 1960 and 1961 by the Air Force under Contracts AF 33(616)-6913 and -7810, several new chemical reactions were discovered. A number of new compounds having the following bond systems were prepared and characterized:



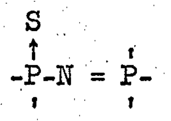
$-\underset{|}{\overset{\overset{O}{\uparrow}}{P}}-N_3$



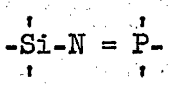
$-\underset{|}{\overset{\overset{S}{\uparrow}}{P}}-N_3$



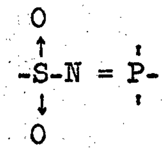
$-\underset{|}{\overset{\overset{O}{\uparrow}}{P}}-N=\underset{|}{\overset{|}{P}}-$



$-\underset{|}{\overset{\overset{S}{\uparrow}}{P}}-N=\underset{|}{\overset{|}{P}}-$



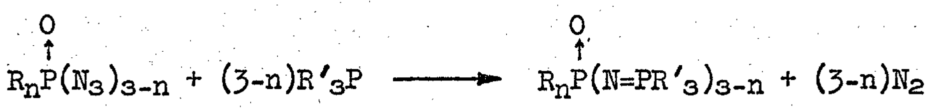
$-\underset{|}{\overset{|}{Si}}-N=\underset{|}{\overset{|}{P}}-$



$-\underset{\underset{O}{\downarrow}}{\overset{\overset{O}{\uparrow}}{S}}-N=\underset{|}{\overset{|}{P}}-$

In general, these compounds showed a high order of thermal and hydrolytic stability. In addition, polymerization reactions based largely on these compounds were discovered. This promising combination of chemical and physical properties suggested that polymers based upon these bonding systems will have hydrolytic, oxidative, and thermal stability.

The chemistry of this research program is then based upon the reactions of metalloid azides with tertiary phosphines to yield phosphoranes and an equivalent of nitrogen gas. This is illustrated in the following equation which demonstrates the reaction of phosphonyl azides and tertiary phosphines.



$$R_n\overset{\overset{O}{\uparrow}}{P}(N_3)_{3-n} + (3-n)R'_3P \longrightarrow R_n\overset{\overset{O}{\uparrow}}{P}(N{=}PR'_3)_{3-n} + (3-n)N_2 \qquad (1)$$

Initial work designed to exploit these basic discoveries demonstrated that polyphosphoranes could indeed be synthesized via the reaction of phenylphosphonyl diazide and various bis-tertiary phosphines although the initial molecular weight values were low.[1] In addition, preliminary thermal studies on a variety of prototypes of and on polyphosphorane polymers indicated thermal stabilities to about 400-450° C.

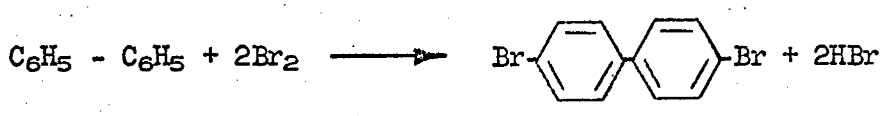
This report describes continuing work to extend and improve the chemistry and properties of a variety of phosphoranes and polyphosphoranes. In addition, the syntheses of various intermediate materials necessary for this program are also presented.

II. PHOSPHORANE POLYMER CHEMISTRY

A. Preparation of Intermediates

1. Bis-Tertiary Phosphines

As a result of the high approximate beginning of decomposition, estimated by DTA to be about 460-475°C.,[2] for the polymer prototype bisphosphorane XLVIII prepared from 4,4′-bis(diphenylphosphino)biphenyl (II) and diphenylphosphonyl azide, considerable effort was devoted to the attempted synthesis and, finally, to the synthesis of II. Since 4,4′-dibromobiphenyl (I) needed in several possible syntheses of II was no longer readily available commercially, the synthesis of a quantity of this dibromide was carried out using a previously described method[3] (Eq. 2). However, on

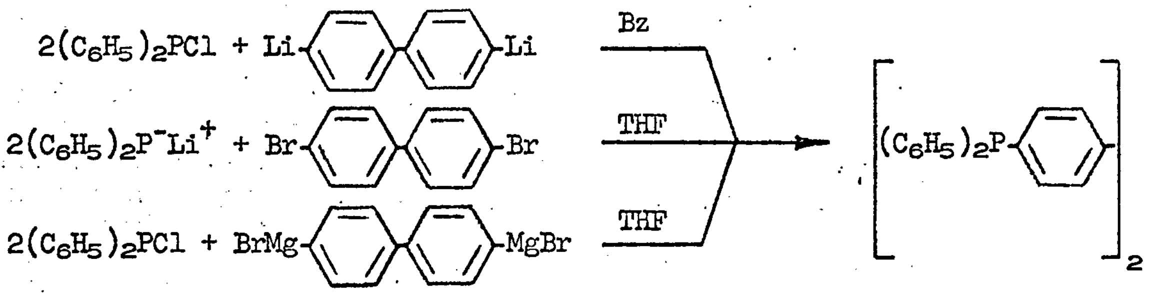


(2)

I

using slightly larger quantities than those described, longer reaction times and lower yields were encountered.

Three methods for the synthesis of II were investigated (Eq. 3a, b, and c). Of these methods, only the reaction of 4,4′-dilithiobiphenyl and



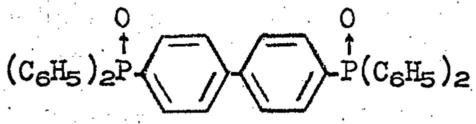
(3a)

(3b)

(3c)

II

diphenylchlorophosphine (Eq. 3a) proved to be useful. Even then the yields were low and varied somewhat as a result of the difficulty encountered in the purification of the crude product as well as the problem of obtaining uniform slurries of the dilithiobiphenyl. In order to remove oxides and other non-basic impurities encountered in some preparations, it was necessary to dissolve the crude yellow-colored bis-tertiary phosphine II in concentrated hydrochloric acid, filter through a glass wool mat on a glass sintered funnel, and then pour the solution into ice-water. The resulting solids were further washed extensively with water, dilute ammonium hydroxide, and ethanol before being vacuum dried. In other experiments, purification of II was readily effected by recrystallization from tetrahydrofuran-methanol or from ethylene glycol dimethyl ether. However, when using the latter solvent, care must be taken to insure that it is peroxide free as the peroxide contaminated solvent will oxidize the bis-tertiary phosphine to the corresponding bis-oxide (IIa).



IIa

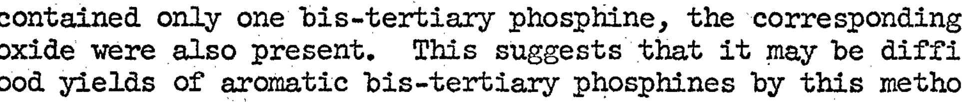
The bis-oxide was further identified by oxidizing the bis-phosphine II with 3% hydrogen peroxide in acetone. The two oxides had identical infrared spectra and similar melting points.

A number of attempts to prepare II by the reaction of lithium diphenylphosphide[4] and 4,4'-dibromobiphenyl (Eq. 3b) gave varying results. In one run, a small amount of crude II was obtained; in a second, starting material 4,4'-dibromobiphenyl was recovered; while in a third preparation, only a variety of impure fractions having wide melting ranges were obtained.

Although this method has been reported[4] to work with p-dibromobenzene, it is difficult to assess the actual yield of 1,4-bis(diphenylphosphino)benzene (IVa) since it was the corresponding bis-oxide which was actually isolated. Furthermore, it was also reported that gas-liquid partition chromatography at 320° C. indicated that while the crude reaction mixture contained only one bis-tertiary phosphine, the corresponding monoxide and bis-oxide were also present. This suggests that it may be difficult to obtain good yields of aromatic bis-tertiary phosphines by this method as a result of considerable oxidation at some as yet undetermined stage before the product is isolated.

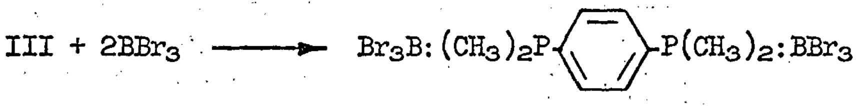
Similar results were obtained in the third method (di-Grignard) shown in Equation 3c. In several preparations, high recoveries of 4,4'-dibromobiphenyl were obtained indicating that the formation of the di-Grignard had not taken place. This was observed with both tetrahydrofuran and p-dioxane as the reaction solvent. These results are to be contrasted with the facile preparation of 1,4-bis(diphenylphosphino)benzene (IVa) by this method (see below).

A small quantity of the new bis-tertiary phosphine, 1,4-bis-(dimethylphosphino)benzene (III) has been prepared and isolated as shown in Equation 4a. The starting compound, 1,4-bis(dichlorophosphino)benzene, for this synthesis was prepared via a high temperature and pressure disproportionation of excess phosphorus trichloride and 1,4-bis(diphenylphosphino)-benzene (IVa).[5] Since the azide functions of the bis-azidophosphoranes



(4a)

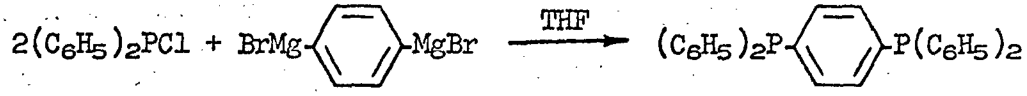
III



(4b)

(see Section II. B.1) have considerably diminished reactivity toward tertiary phosphines, it is expected that III will react more rapidly and completely than do the previously prepared bis-tertiary phosphines containing diphenylphosphino functions, i.e., II and IV. Basis for this hypothesis is the fact that diphenylphosphonyl azide reacts smoothly at 0°C. with phenyldimethylphosphine.[6] This new bis-tertiary phosphine was further characterized by means of the stable bis(tribromoborane) adduct.[7] The synthesis of an additional quantity of III is planned.

Additional quantities of 1,4-bis(diphenylphosphino)benzene (IVa) were prepared as shown in Equation 5. It was found that purification of IVa



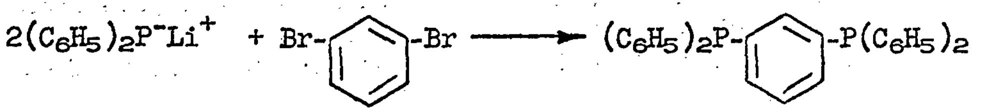
(5)

IVa

to a relatively oxide-free condition could be effected by recrystallization from a benzene-methanol mixture or by means of column absorption chromatography on alumina (see Section I. A.2).

Considerable time and effort were also devoted to the attempted synthesis of 1,3-bis(diphenylphosphino)benzene (IVb) by the method shown in Equations 6a and b. The successful preparation of IVb would hopefully provide a bis-tertiary phosphine for use as a phosphorane polymer intermediate which might be expected to yield somewhat modified polyphosphoranes when compared with the para homologs II and IVa. Unfortunately, neither

$$(C_6H_5)_3P + 2Li \xrightarrow{THF} (C_6H_5)_2P^-Li^+ \qquad (6a)$$



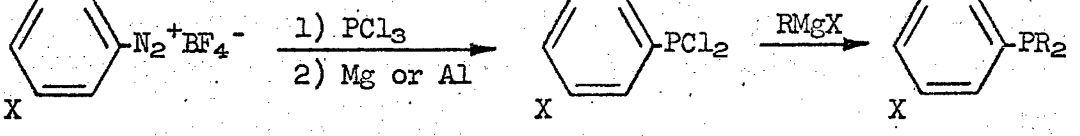
(6b)

IVb

1,3-bis(diphenylphosphino)benzene (IVb) nor its dioxide could be isolated or identified. Analytical data provided surprisingly high phosphorus values (15.8 vs. 12.94% P theory) while molecular weight determinations by either the Neumeyer[8] or Rast camphor method were low. Furthermore, infrared examination of the crude bis-phosphine reaction product indicated a significant P-O and related absorptions at 8.45 and 8.95μ. The infrared spectrum of the crude material oxidized with hydrogen peroxide was very similar to that of the crude bis-phosphine. The apparent oxidation of IVb is difficult to explain at this point since the reaction had been carried out under an argon atmosphere. This difficulty is to be contrasted with the facile preparation of the para homolog, 1,4-bis(diphenylphosphino)benzene (IVa) using this or the diGrignard method.

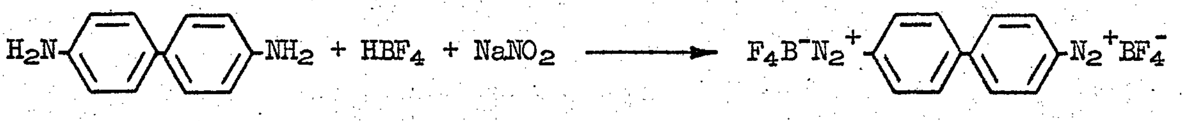
Further workup of the residues remaining from a previous attempted synthesis of IVb via the meta diGrignard resulted in the isolation and identification of diphenylphosphine. The diphenylphosphine apparently resulted from an initial hydrolysis of unreacted diphenylchlorophosphine to diphenylphosphine oxide [$(C_6H_5)_2P(O)H$] which was subsequently thermalized to diphenylphosphine and diphenylphosphonic acid.

The difficulties encountered in the synthesis of 4,4′-bis(diphenylphosphino)biphenyl (II) have been described above. Since it has been reported[9] that substituted phenyl tertiary phosphines could be prepared via diazonium fluoroborates (Eq. 7), it was thought that a modification of this technique might offer an additional route to bis-tertiary phosphines such as II. In this modification, phosphorus trichloride would be replaced with diphenylchlorophosphine (VII) in an effort to circumvent the intermediate phosphorus dichloride V and its subsequent reaction with the Grignard. This procedure is summarized in the following equations:



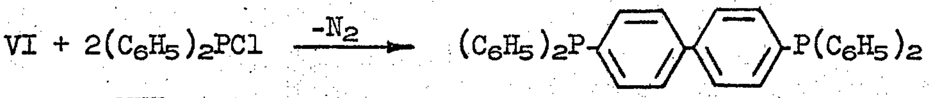
V

(7)



VI

(8)



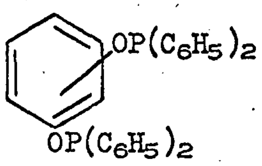
VII

II

(9)

However, nitrogen evolution was only 50% of theory and workup failed to yield any of the desired bis-tertiary phosphine II.

Attempts were also made to react two moles of diphenylchlorophosphine with hydroquinone and with resorcinol, in the presence of pyridine, to obtain the additional new bis-tertiary phosphines VIIIa and b. However,

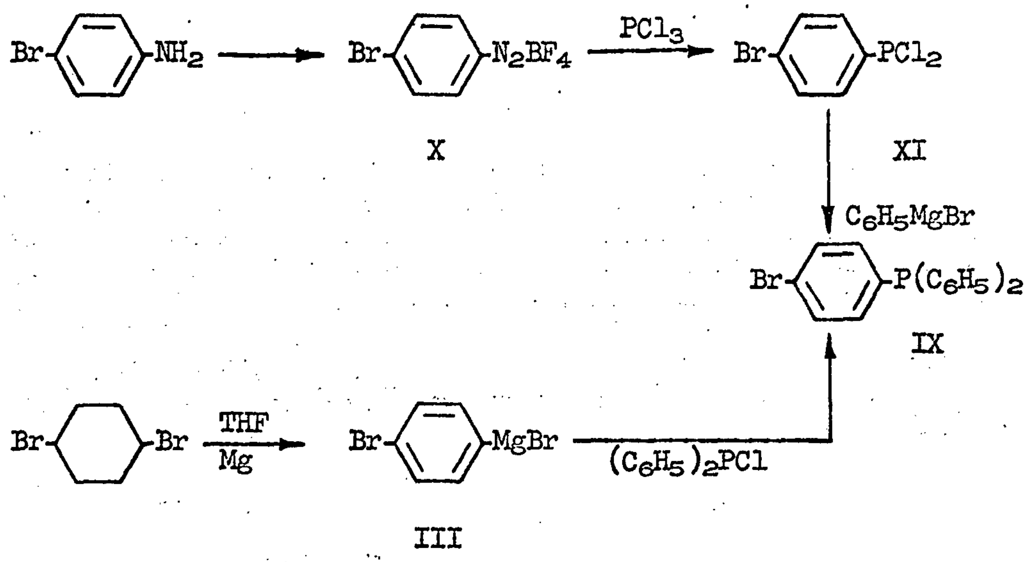


VIII a. para
b. meta

difficulties in readily separating identifiable products and other more pressing areas of investigation resulted in the temporary discontinuation of this work.

2. Mono-Substituted Triphenylphosphines

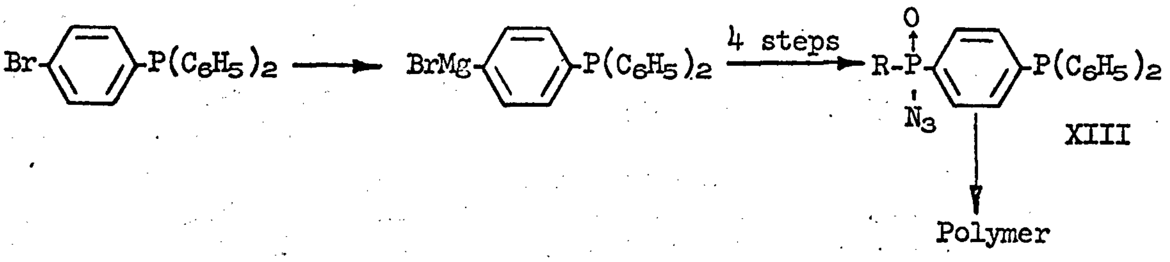
The above diazonium fluoroborate technique was also investigated as part of a two-pronged approach (Eqs. 10 and 11) to p-bromophenyldiphenyl-



(10)

(11)

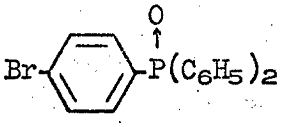
phosphine (IX) which is a necessary intermediate for the synthesis of a mixed tertiary phosphine-phosphonyl azide such as XIII (Eq. 12).



(12)

Examination of some of the recent literature[10] concerned with the preparation of p-bromophenyldichlorophosphine (XI) from the fluoroborate (X) indicated that the phosphorus trichloride had always been added to the diazonium fluoroborate and that the yields of the $ArPCl_2$ compounds were low (33% or less). These low yields are not surprising when one considers that under these reaction conditions any $ArPCl_2$ compound initially formed could react further with the excess diazonium fluoroborate to yield Ar_2PCl and even Ar_3P. Therefore, the reaction illustrated in (Equation 10) was carried out under "inverse" addition conditions; that is, the diazonium fluoroborate was added as a slurry to an excess of the phosphorus trichloride. The yield of XI, while only a disappointing 12.8%, was a slight increase over the 8% yield reported in the literature.[11]

Reaction of p-bromophenyldichlorophosphine (XI) with phenylmagnesium bromide (Eq. 10) which was expected to give the tertiary phosphine IX gave instead a white solid melting at 141-143° C. This material was not soluble in base and had an infrared spectrum which contained absorptions associated with P-O at 8.45 and 8.95μ as well as the 1,4-aromatic substitution at 12.25μ. These results and a molecular weight value of 354 tentatively identified the white solid as the phosphine oxide XIV (M.W., 357) instead of the expected p-bromophenyldiphenylphosphine (IX).



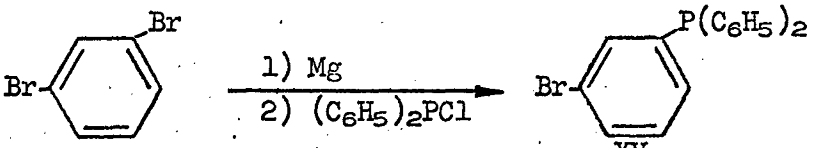
XIV

In the second phase of this two-pronged investigation, as illustrated in Equation 11, a more pronounced effect of the addition sequence for the reactants was observed. If during the preparation of p-bromophenylmagnesium bromide (XII), the usual technique of adding halide to all of the magnesium was followed, a significant amount of di-Grignard was formed, even on addition of excess p-dibromobenzene, and only 1,4-bis(diphenylphosphino)-benzene (IV) was isolated. However, with the inverse addition, magnesium to p-dibromobenzene, a viscous liquid product was obtained. Distillation at 10^{-4} mm. resulted initially in the sublimation of unreacted p-dibromobenzene and then at an oil bath temperature of 165-175°C., a colorless, viscous distillate was obtained. After standing for 24 hrs., the oil solidified to a white, waxy-appearing solid which was identified as the desired p-bromophenyldiphenylphosphine (IX). Relatively pure product was subsequently obtained by dissolving the crude material in ether and filtering to remove insolubles followed by concentration and sublimation to remove p-dibromobenzene. This material solidified to a yellow-colored semi-crystalline mass after standing for several days.

Attempts to further purify the yellow, semi-solid IX by recrystallization as well as by solution in concentrated hydrochloric acid, a technique which had been successfully used to purify tertiary phosphines previously (see Section II. A.1), resulted in the recovery of only oils. However, it was found that adsorption chromatography on alumina resulted in the recovery of a colorless oil which quickly crystallized. The infrared spectrum of this product was sharp and indicated the absence of any absorptions due to P-O. This solid now could be crystallized from methanol.

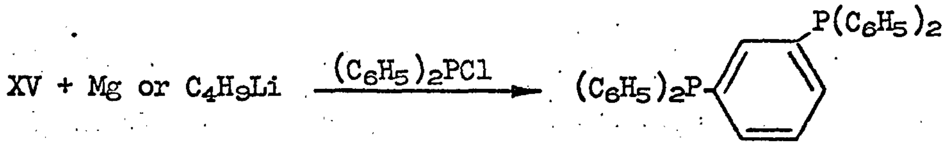
The utility of this purification by adsorption on alumina was further demonstrated during the partial purification of bis-tertiary phosphines and by the separation of triphenylphosphine from its oxide and sulfide. For example, crude, yellow-colored II, melting range 152-172° C., was recovered (84%) as a white powder melting at 186-191° C. after one pass through the column. The further utility of this technique was demonstrated by the fact that the triphenylphosphine can be quantitatively separated from triphenylphosphine sulfide or oxide and from diphenylphosphonimidotriphenylphosphorane. In the runs with the oxide and sulfide, these compounds were subsequently recovered from the column by means of elution with benzene or tetrahydrofuran. Unfortunately, the phosphorane could not be recovered from the column. It was further demonstrated that the alumina could be regenerated by washing it successively with benzene, tetrahydrofuran, and acetone followed by two hours in an oven at 130° C. A preliminary evaluation of silica gel for this purpose indicated that it was not as useful as the alumina. (See Table III for details).

As an extension of the above work, a small amount of the isomeric 3-bromophenyldiphenylphosphine (XV) has been prepared by the same inverse Grignard technique (Eq. 13). Purification and final characterization of XV were hampered by the continued contamination by the starting material, m-dibromobenzene which was not removed on the attempted purification by column chromatography. A more pure fraction of XV was obtained in low yield after distillation at 10^{-2} mm through a short Vigreau column resulted in the removal of m-dibromobenzene. A large distillation residue, as well as the low yield of XV, suggested considerable diGrignard formation with m-dibromobenzene as the starting material. In addition to providing an intermediate for the preparation of the meta isomer of the tertiary phosphine-phosphonyl azide XIII, XV will also be converted to the 1,3-bis(diphenylphosphino)benzene (IVb) which has not previously been available via more



XV

(13)

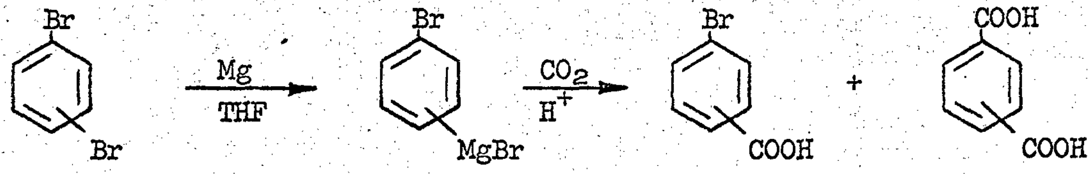


IVb

(14)

direct synthetic methods, i.e., m-phenylene diGrignard or lithium diphenylphosphide (see Section II. A.1 and Equation 3). In view of synthetic problems in the formation of a Grignard reagent from p-bromophenyldiphenylphosphine (IX) (see Section II. A.3), an investigation of the reaction of n-butyl lithium and the bromophenyldiphenylphosphines is planned (Eq. 14).

In an effort to gain some insight into the actual ratio of the mono- and diGrignard reagents resulting from this inverse addition method, two similar preparations were made from meta- and para-dibromobenzene dissolved in tetrahydrofuran. The magnesium additions resulted in exothermic reactions. The resulting Grignard reagents were treated with pieces of Dry-Ice as soon as magnesium was no longer visible (Eq. 15). The crude acids were dissolved in base, treated with charcoal, filtered, and reacidified to yield an obvious mixture of the acids XVI and XVII. The yield of meta-substituted acids was only 50% while a yield of 78% was obtained for the para-substituted acids. Attempted separation of the iso- and terephthalic acids (XVII) from the meta- and para-bromobenzoic acids (XVI) by ether extraction met with only limited success, being more useful in separating the para compounds. Qualitatively these yields are similar to the yields obtained for the bromophenyldiphenylphosphines XI and XV. At this point, this inverse addition method appears to be considerably more practical for use with para-dibromobenzene than with the meta-dibromobenzene. However, the significantly high yield of isophthalic acid obtained from meta-dibromobenzene suggests that a reinvestigation of the direct formation of the meta-diGrignard reagent appears to be worthwhile. Pertinent data for these experiments are given in Tables I and II.



(15)

XVI
a. para
b. meta

XVII
a. para
b. meta

3. Phosphonyl Azides

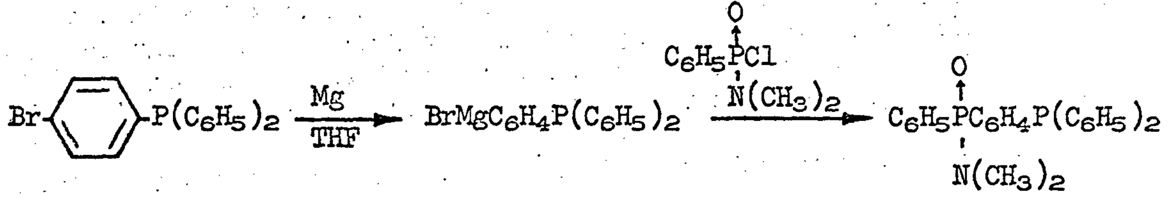
The successful preparation of 3- and 4-bromophenyldiphenylphosphines (IX and XV) has opened the way for the possible synthesis of a mixed phosphonyl azide-tertiary phosphine such as XIII which would then react in a head-to-tail fashion to give the polyphosphorane as shown in Equation 16. In the initial attempt to develop this approach, the attempted synthesis of the intermediate

XIII

(16)

R = C_6H_5- or CH_3-

phosphonamide XVIII was undertaken as illustrated in Equation 17. However,


(17)

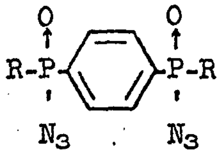
IX XIX XVIII

difficulty was encountered in the formation of the Grignard intermediate XIX and neither the phosphonamide XVIII nor the corresponding phosphonic acid could be isolated and identified after hydrolysis of reaction product of Equation 17. Since the hydrolysis product was largely insoluble in base, it would appear that the formation of the Grignard reagent XIX had not taken place to any significant extent. In view of the potential utility of this approach, this Grignard reaction will be further investigated. In addition, the use of n-butyl lithium to prepare the corresponding lithium aryl XX (Eq. 18) for subsequent conversion to XVIII will also be investigated. An

$$\underset{\text{IX}}{BrC_6H_4P(C_6H_5)_2} + C_4H_9Li \longrightarrow \underset{\text{XX}}{LiC_6H_4P(C_6H_5)_2} \longrightarrow \text{XVIII} \qquad (18)$$

alternative method for the synthesis of XX may be via the direct reaction of IX and lithium metal.[12] However, since aryl-phosphorus bonds can be readily cleaved by lithium[4] in tetrahydrofuran, this alternative method would appear to be of limited potential for this particular application.

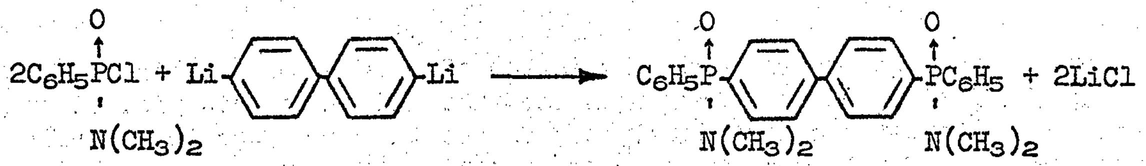
A previous[13] comparison of the thermal stabilities of a variety of phosphoranes indicated that phosphoranes based upon the $(C_6H_5)_2P(O)$- unit are somewhat more stable than those based upon the $C_6H_5P(O)=$ unit. These results then suggested that phosphorane polymers and polymer prototypes synthesized from bis-phosphonyl azides such as XXI would have increased



XXI

thermal stabilities.

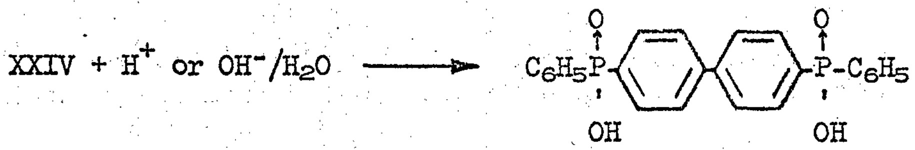
In the first step toward the preparation of such a bis-phosphonyl azide, phenyl-N,N-dimethylaminophosphonyl chloride (XXII) was reacted with 4,4'-dilithiobiphenyl (XXIII) (Eq. 19) to yield the bis-phosphonamide XXIV.



(19)

XXII XXIII XXIV

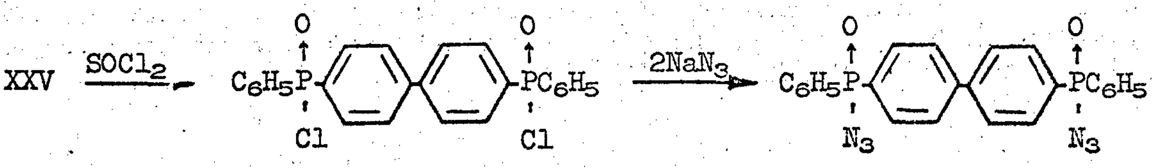
Although infrared examination of the crude product showed all of the expected absorptions, attempted isolation of pure XXIV resulted in only tacky materials which resisted crystallization. Therefore, the crude bis-phosphonamide was hydrolyzed under both basic and acidic conditions (Eq. 20) in an effort to



(20)

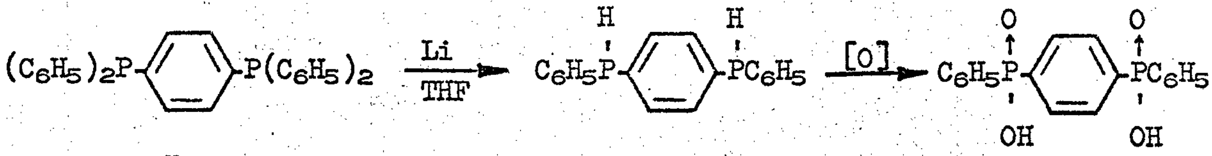
XXV

determine the best method for this conversion. At present, it appears that the acidic hydrolysis is more rapid and gives a solid product which is more easily purified. During the various workups of both XXIV and XXV, viscous, yellow-colored products were encountered which would not crystallize. However, after hydrolysis and subsequent repeated purification of the acid by treating it in basic solution with activated charcoal, a relatively pure sample of XXV was isolated. The preparation and isolation of an additional quantity of the bis-phosphonic acid XXV will be made and this will be used for studying the conversion to the bis-phosphonyl chloride and then to the corresponding bis-phosphonyl azide as illustrated in Equation 21.



(21)

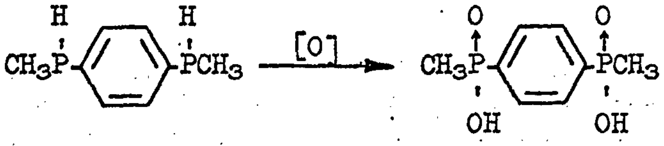
In addition to the synthetic routes outlined above, the oxidation of appropriate bis(secondary phosphines) to the necessary bis(phosphonic acids) was also investigated. Previous work[14] had shown that it was possible to partially cleave 1,4-bis(diphenylphosphino)benzene (IVa) with lithium metal in tetrahydrofuran so as to yield 1,4-bis(phenylphosphino)benzene (XXVI) (Eq. 22). Oxidation of the crude bis(secondary phosphine) with iodic acid



(22)

IV XXVI XXVII

gave only a tacky brown residue. Oxidation of 1,4-bis(methylphosphino)-benzene (XXVIII) by means of hydrogen peroxide and iodic acid yielded only a small quantity of the bis(methylphosphonic acid) which was tentatively identified by infrared comparison with authentic acid.[15] Since an improved



(23)

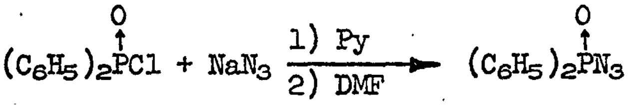
XXVIII

XXIX

method for the synthesis of the 1,4-bis(methylphosphino)benzene (XXVIII) is now available,[16] additional experiments in this area are planned.

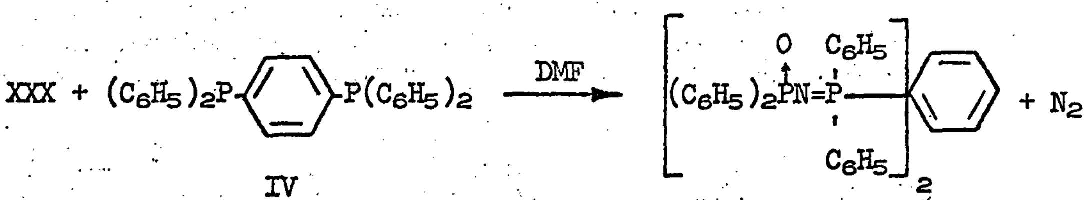
The investigation of the potential usefulness of other solvents, such as dimethylformamide (DMF) and hexamethylphosphoric triamide (HPT), $[(CH_3)_2N]_3PO$, for the preparation of phosphonyl azides and phosphoranes was continued. This work was initiated in part, since certain of the phosphorane prototypes such as XXXI have limited solubilities in the usual reaction solvent pyridine. It was hoped that any new solvents would then lead to polyphosphoranes of increased molecular weights. Since it had been previously[17] observed that DMF was not suitable for use in the initial preparation of diphenylphosphonyl azide, it and phenylphosphonyl diazide were then first prepared in pyridine. Then DMF or HPT was added and the pyridine was removed at reduced pressure.

In the resulting study of diphenylphosphonyl azide (XXX) in DMF, no difficulty was encountered in the synthesis of the azide (Eq. 24) in pyridine and then adding DMF before removal of the pyridine. Reaction with 1,4-bis(diphenylphosphino)benzene (IV) resulted in an 83% yield of nitrogen (Eq. 25). The yield of XXXI was 97.9%.



$$(C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}Cl + NaN_3 \xrightarrow[2)\ DMF]{1)\ Py} (C_6H_5)_2\overset{O}{\overset{\uparrow}{P}}N_3 \qquad (24)$$

XXX



(25)

IV

XXXI

However, when the DMF was added to the pyridine and phenylphosphonyl diazide, which is needed to prepare a polyphosphorane, it appeared that a gas (nitrogen) was being evolved during the removal of the pyridine. Infrared examination of the resulting mixture subsequently indicated a complete loss of the azide absorption at 4.65μ. At present there is no explanation for these different characteristics of diphenylphosphonyl azide (XXX) and of phenylphosphonyl diazide in the solvent DMF. However, this unexpected decomposition appears to rule out the possible use of DMF in polyphosphorane preparations involving phenylphosphonyl diazide.

The use of hexamethylphosphoric triamide (HPT) as the reaction solvent for use with both phosphonyl azides and the phosphoranes was also investigated. While no nitrogen was evolved during the formation of diphenylphosphonyl azide, the rate of formation (via infrared spectroscopy) was slower than had been observed previously in pyridine.[18] Subsequent reaction of the diphenylphosphonyl azide formed in HPT with triphenylphosphine resulted in only a 41.5% evolution of nitrogen and a 23% recovery of very impure phosphorane. These results do not indicate much promise for HPT as an improved solvent for these reactions.

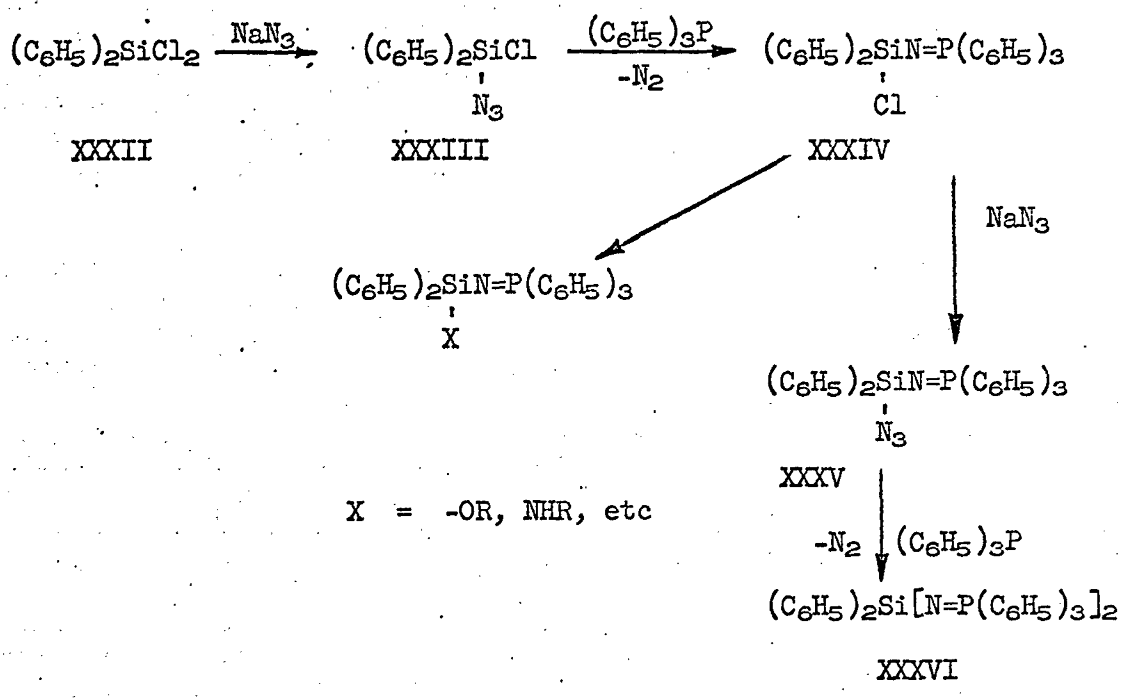
In the continuing evaluation of potential new and better reaction solvents, several pyridine derivatives, α- and γ-picoline and 3,4- and 2,6-lutidine, were also investigated. If these pyridine derivatives would maintain the same rate of formation of the phosphonyl azides as was found in pyridine, then the higher reaction temperatures possible with these new solvents would be expected to speed up and/or force the polyphosphorane formation to completion. In similar experiments, diphenylphosphonyl chloride and sodium azide were allowed to stir at ambient temperature and the progress of azide formation was followed by monitoring the increase of the azide absorption at 4.65μ. The infrared data for this study are shown in Table IV.

Azide formation in α- and γ-picoline was found to be rapid, with no increase in the azide absorption after six hours which is similar to the rate in pyridine. An 89.6% yield of brown-colored diphenylphosphonimidotriphenylphosphorane was obtained from the azide prepared in α-picoline. These results suggested then that the picolines appear to be potential reaction solvents for polyphosphorane preparations. The apparent rates of formation of diphenylphosphonyl azide (XXX) in the lutidines were very slow and the yield of phosphorane from 2,6-lutidine was only 64.6%. These results would, on the other hand, appear to rule out the use of the lutidines in these reactions.

Although there was no evidence for the formation of phosphonyl azides in benzene, an additional solvent study using varying ratios of pyridine to diphenylphosphonyl chloride in an excess of benzene was undertaken. Molar ratios of pyridine to diphenylphosphonyl chloride of 1:1, 2:1, 3:1, and 4:1 were studied, as described above, by infrared spectroscopy. In order to further define this system, the resulting phosphonyl azide was then directly reacted with triphenylphosphine to yield nitrogen and diphenylphosphonimidotriphenylphosphorane. The results shown in Table V show that the 2:1 ratio gave results which were approximately equal to those obtained previously in pyridine alone and further suggest possible utility in phosphonyl azide-phosphorane preparations. In addition, workup of the reaction mixtures was found to be more facile than in pyridine alone. This has, indeed, been shown to be the case for the syntheses of bis-azidophosphoranes, see Section II. B.1.

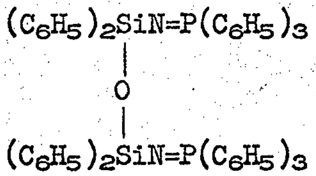
4. Silyl Azides

In a survey to further define the chemistry of silyl azides and silylimidophosphoranes, the following sequence of reactions was briefly investigated (Eq. 26). This investigation was readily followed by infrared



(26)

spectroscopy and by nitrogen evolution where appropriate. After stirring overnight at ambient temperature, the conversion of diphenylsilyl dichloride (XXXII) to the chloroazide XXXIII had been accomplished as was confirmed by a strong azide asymmetric stretching at 4.64μ and a medium azide symmetric stretching absorption at 7.57μ. Reaction of the silyl chloroazide with one equivalent of triphenylphosphine to yield the chlorophosphorane XXXIV was followed by both nitrogen evolution and infrared. In addition to the nitrogen evolution of 921 cc (102.6% of theory), there was an almost complete loss of the azide absorptions and the development of the broad, medium P=N due to phosphorane formation at 7.38 and 7.70μ. An aliquot was removed at this point for use in studying the chemistry of the chlorophosphorane XXXIV and of its derivatives XXXVII. An initial hydrolysis of XXXIV resulted in the formation of an oily gum from which white crystals grew. These crystals were subsequently identified as triphenylphosphine oxide. This preliminary result implies a complete hydrolysis of XXXIV as opposed to the more desired hydrolysis of only the chloro function. It is hoped that controlled hydrolysis may lead to a siloxy compound such as XXXVIII. Such a Si-O-Si



$$\begin{array}{c}(C_6H_5)_2SiN{=}P(C_6H_5)_3\\ |\\ O\\ |\\ (C_6H_5)_2SiN{=}P(C_6H_5)_3\end{array}$$

XXXVIII

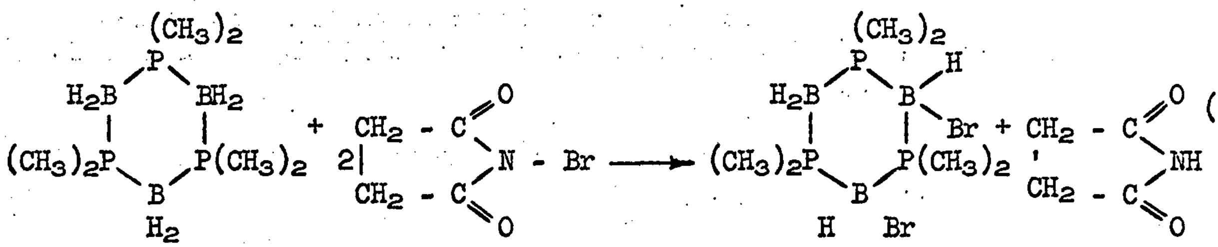
compound would then support the possibility of cross-linking linear phosphorane chains by means of the Si-O-Si linkage to yield an even more stable system.

The reaction of sodium azide with the chlorophosphorane XXXIV was also followed by infrared examination. This technique showed that there was no significant increase in the azide absorption at 4.68μ after only four hours. This facile displacement resembles similar results obtained previously with phosphorane chlorides.[19] The phosphorane absorptions were unchanged after this displacement reaction. Another aliquot was removed to allow comparison of the chemistry of the azidophosphorane XXXV with that of the chlorophosphorane XXXIV.

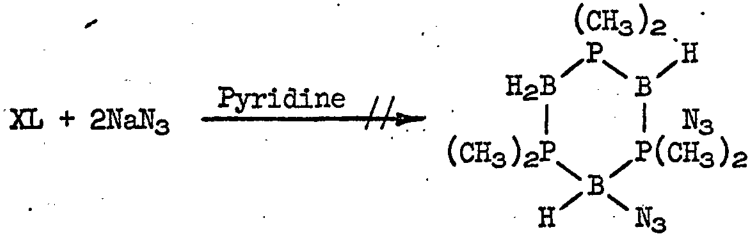
The remaining azidophosphorane was reacted with a second equivalent amount of triphenylphosphine to yield the known silyl bisphosphorane XXXVI.[20] The nitrogen evolution of 456 cc. corresponded to a yield of 101.8% for this last step. Again, infrared examination showed the loss of the azide absorption at 4.68μ (2137 cm^{-1}). In view of these preliminary but encouraging results further studies on the silyl azides are planned.

5. Triborophane Azides

A brief investigation of the possibility of preparing azides from the cyclic triborophane XXXIX was also carried out. A quantity of the dibromotriborophane XL prepared as shown in Equation 27 and obtained in 99% purity by repeated recrystallization from methanol was treated with two equivalents of sodium azide in pyridine, first at ambient temperature and later at reflux. Unfortunately, frequent infrared observations indicated that no azide was being formed as expected in Equation 28.



XXXIX XL (27)



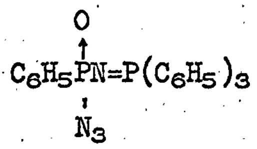
XLI (28)

Furthermore, evolution of a gas and formation of an orange-colored solid were observed during the reflux period. In view of these negative results, this investigation was discontinued and no attempt was made to identify the products of the reaction of XL and sodium azide.

B. Preparation of Phosphorane Prototypes

1. Bis-Azidophosphoranes

Since arylphosphonyl diazides have been shown to be extremely heat and shock sensitive,[21] the purification of larger quantities of these vital polyphosphorane intermediates has not been possible. The chemical and thermal stability[22] of the azidophosphorane XLII, however, suggested that the synthesis and purification of similar bis-azidophosphoranes would be

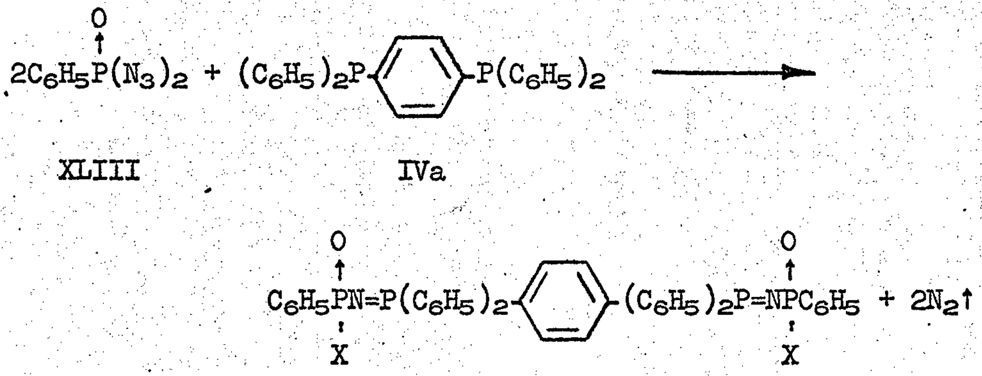


$$\mathrm{C_6H_5}\overset{\mathrm{O}}{\overset{\uparrow}{\underset{\underset{\mathrm{N_3}}{|}}{\mathrm{P}}}}\mathrm{N{=}P(C_6H_5)_3}$$

XLII

feasible. Separation and purification of such bis-azidophosphoranes would then result in the better control of the stoichiometry in polymer preparations and hopefully in polymers of higher molecular weight. The successful preparation of such an intermediate depends upon the greatly decreased reactivity of the remaining two azide functions of the azidophosphorane toward tertiary phosphines which suppresses potential polymer formation.

Reaction of two equivalents of phenylphosphonyl diazide (XLIII) and 1,4-bis(diphenylphosphino)benzene (IVa) in pyridine at ambient temperature

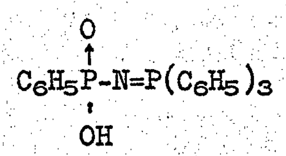

XLIII IVa

(29)

XLIV

a. $X = -N_3$
b. $X = -OH$

resulted in quantitative evolutions of nitrogen and the isolation of white and yellow powders which appeared to be the desired bis-azidophosphorane XLIVa. One fraction having a melting point of 136-138° C. was found to have a molecular weight of 821 (806 theory). The infrared spectrum of this material contained a strong azide absorption at 4.72µ as well as the typical phosphorane absorptions in the region 7-9µ. Isolation of XLIVa by simply pouring the pyridine reaction mixture into water, as had been possible with XLII,[22] resulted in the separation of mostly tacky materials. Like the azidophosphorane XLII, the crude bis(azidophosphorane) XLIVa is relatively stable toward hydrolysis as only small absorptions associated with hydrolysis products were observed in various fractions isolated. Comparison with the infrared spectrum of the previously prepared[23] acid phosphorane XLV confirmed



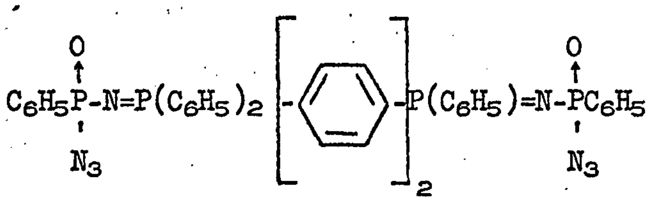
$$C_6H_5\underset{\underset{OH}{\vdots}}{\overset{\overset{O}{\uparrow}}{P}}-N=P(C_6H_5)_3$$

XLV

the presence of some hydrolysis product.

Purification of the crude, yellow-colored XLIVa was initially accomplished by means of a complex, tedious, and prolonged crystallization from a pyridine-water-ethanol system. However, the yields of the crystallized product were only approximately 30%. From the residues remaining after this purification, a considerable quantity of the corresponding acid XLIVb was recovered. Since the product was obviously not this impure before recrystallization, it will be necessary to develop a better, nonprotonic if at all possible, purification technique for future use.

Similar results were encountered in the initial synthesis of the homologus bis-azidophosphorane XLVI in pyridine. Again, the crude reaction product had a tendency to gum and contained absorptions due to hydrolysis products. Concurrent with the synthesis of XLVI in pyridine was an additional preparation using the new benzene and 2:1 ratio of pyridine to phosphonyl chloride method (see Section II.A. 3.). In view of the promising results obtained via this method (see below), the above pyridine investigation was terminated.

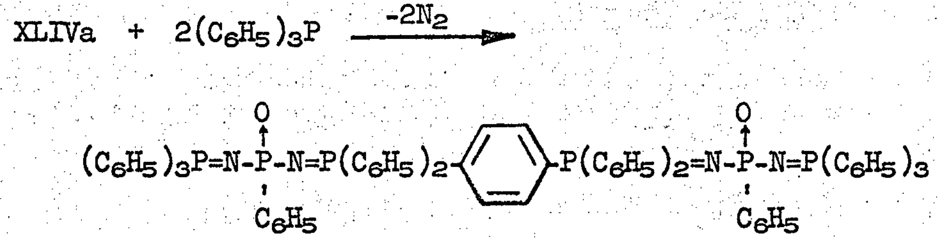


XLVI

Since previous studies had shown that a 2:1 ratio of pyridine to phosphonyl chloride in benzene resulted in a rapid and high conversion to phosphonyl azide and subsequently to phosphorane, the use of this technique for the syntheses of the bis-azidophosphoranes XLIVa and XLVI was studied. Initial preparations have resulted in almost quantitative yields of considerably more pure products in both cases. Particularly encouraging have been the increased rates of reaction in this mixed solvent system of phenylphosphonyl diazide and the appropriate bis-tertiary phosphines. The product bis-azidophosphoranes XLIVa and XLVI are now off-white to white powders instead of yellow, gummy residues. Infrared examination of both XLIVa and XLVI obtained via this new method showed that hydrolysis products were no longer present as had been the case in the previous preparations and purifications carried out in pyridine. These bis-azidophosphoranes were subsequently used in further polyphosphorane studies (see Section II. C.1).

However, in order to fully characterize and to take advantage of these new bis-azidophosphoranes, it will be necessary to develop an analytical technique which will distinguish between the azide nitrogen and the imido nitrogen. The use of the standard Kjeldahl method at present results in nitrogen analyses which do not readily relate to the total nitrogen content or to any proportion of it (i.e., one of four nitrogen atoms present, etc.). As a result, it is not clear then whether the difficulty is due to impurities in the sample or to incomplete analyses.

To further characterize and to gain insight of the reactivity of the remaining azide functions, a quantity of the XLIVa was reacted in



(30)

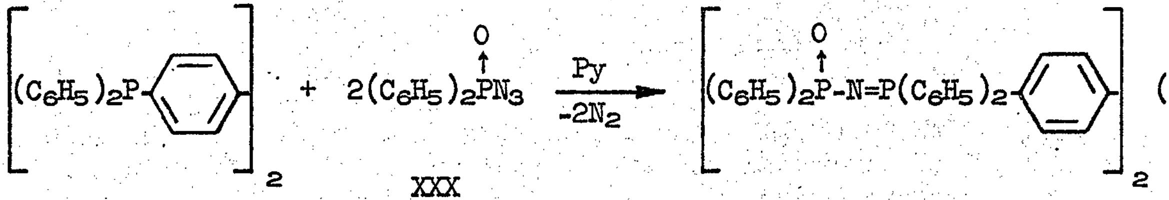
XLVII

toluene with two equivalents of triphenylphosphine. Although the azide absorption disappeared and 84% of nitrogen was collected, the reaction product appeared to be grossly impure as evidenced by an extremely wide melting range and poor analytical values. The infrared spectrum contained a strong absorption at 10.8-10.95μ due to hydrolysis product.

A second preparation in pyridine using XLIVa obtained from the new mixed solvent method resulted in a 90.8% yield of XLVII. The nitrogen evolution required more than six hours for completion. This result again points out the diminished reactivity toward tertiary phosphines of the azide functions remaining in the azidophosphoranes. As a result it will be necessary to insure that polyphosphorane preparations are carried out long enough to complete the nitrogen evolution. In addition, this decreased reactivity emphasizes the need for more reactive bis-tertiary phosphines such as 1,4-bis(dimethylphosphino)benzene (III) which is now available for study (see Section II. A.1).

2. Arylene-Linked Bis-phosphoranes

An additional quantity of the bis-phosphorane XLVIII was prepared as shown in Equation 31. Thermogravimetric analysis of this compound



(31)

II XXX XLVIII

indicated no weight loss to about 410° C. and only 10% loss at 460° C. Furthermore, the black residue, about 26% of the original weight, did not show any additional weight loss over the temperature range of approximately 525-750° C. The initial decomposition temperature (~ 410° C.) by TGA is somewhat lower than that previously[2] estimated by differential thermal analysis (~ 460-475° C.).

However, the results are very encouraging and additional work is planned using 4,4′-bis(diphenylphosphino)biphenyl (II) as the linking unit.

3. Silylimidophosphoranes

An additional quantity of the silylbis-phosphorane XXXVI was also prepared via the in situ reaction[24] illustrated in Equation 32. This method

$$2(C_6H_5)_3P + 2NaN_3 \xrightarrow[\text{Pyridine}]{(C_6H_5)_2SiCl_2} \underset{\text{XXXVI}}{(C_6H_5)_2Si[N{=}P(C_6H_5)_3]_2} + 2N_2 \qquad (32)$$

involves the addition of the silyl dichloride XXXII to a mixture of sodium azide and triphenylphosphine in refluxing pyridine. Although the evolution of nitrogen was 92.5% of theory, the yield of recrystallized XXXVI, m.p. 191.5-193° C., was only 50%. This additional quantity of the silylbis-phosphorane was desired for the reinvestigation of the thermal and hydrolytic properties of this material. These new tests showed good hydrolytic stability and indicated good thermal properties. The differential thermal analysis curve for XXXVI did not reveal any definite decomposition point to approximately 512° C. It appeared that the compound was simply refluxing in the sample tube. This increased thermal stability is in marked contrast to a previous DTA observation which showed decomposition to occur at only 292° C.[25] This value will be rechecked on a third sample.

It will also be necessary to improve the yield of XXXVI in order to fully demonstrate any potential utility for preparing polysilylimidophosphoranes (see also Section II. A.4 for a stepwise synthesis leading to XXXVI).

C. Preparation of Phosphorane Polymers

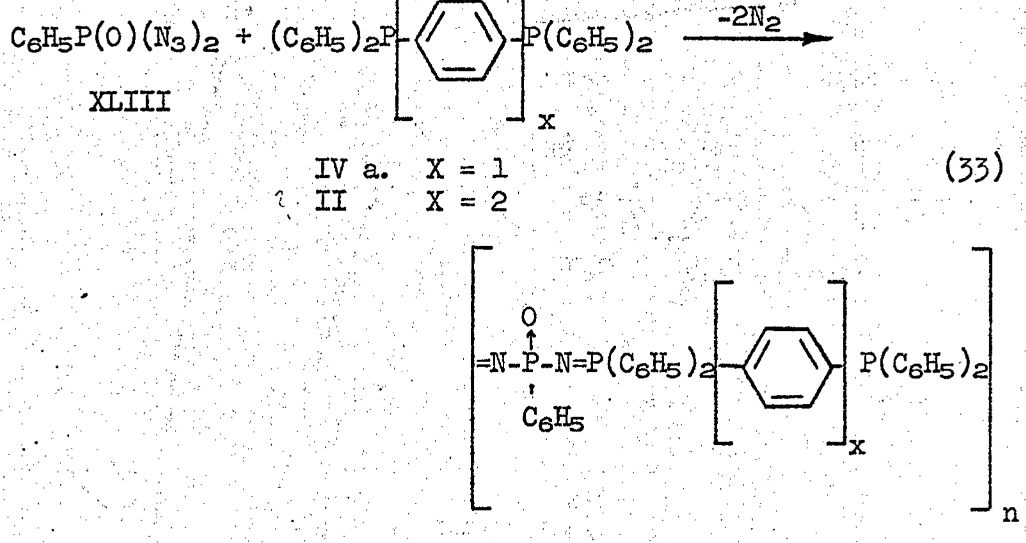
1. Polyphosphonimidophosphoranes

a. In Situ Preparations

Additional preparations of polyphosphoranes from phenylphosphonyl diazide (XLIII) and both 1,4-bis(diphenylphosphino)benzene (IVa) and biphenyl (II) were carried out in pyridine as illustrated in Equation 33. An initial preparation of biphenylene linked polymer XLIXb provided a crude

$$C_6H_5P(O)Cl_2 + 2NaN_3 \xrightarrow{\text{Pyridine}} C_6H_5P(O)(N_3)_2 + 2NaCl$$

XLIII



XLIII

IV a. X = 1
II X = 2

(33)

XLIX
a. X = 1
b. X = 2

sample of this new phosphorane polymer which still contained an azide absorption at 4.65µ. Differential thermal analysis, however, implied thermal stability to approximately 490° C.

Additional preparations were also made to provide samples for thermal gravimetric analysis. The resulting curves are shown in Figure 1. The initial, small (~ 10%) weight losses may suggest entrained solvent loss. The temperatures at which the major weight losses began are similar to those obtained for the previously prepared phosphorane prototype compounds.[26] However, the percentage of stable residue has approximately doubled when compared with the residues left by the prototype compounds. Also, the biphenylene based polymer XLIXb appears to be somewhat more stable than XLIXa with the p-phenylene linking unit. This stability relationship has also been demonstrated recently by Parts and coworkers during the syntheses of several cyclic polyphosphonamides which contained these same linking groups.[27]

A preparation of XLIXa in γ-picoline, suggested as a result of azide formation studies in Section II. A.3, resulted in recovery of the same tan-colored powder as had been obtained from preparations in pyridine. Attempts to form fibers or effect adhesion to glass were unsuccessful (however, see below). During heating experiments, approximately 10% weight losses were observed. These values are similar to the initial weight losses observed by means of thermogravimetric analysis and further suggested that the pyridine solvents are held tenaciously by the polyphosphoranes.

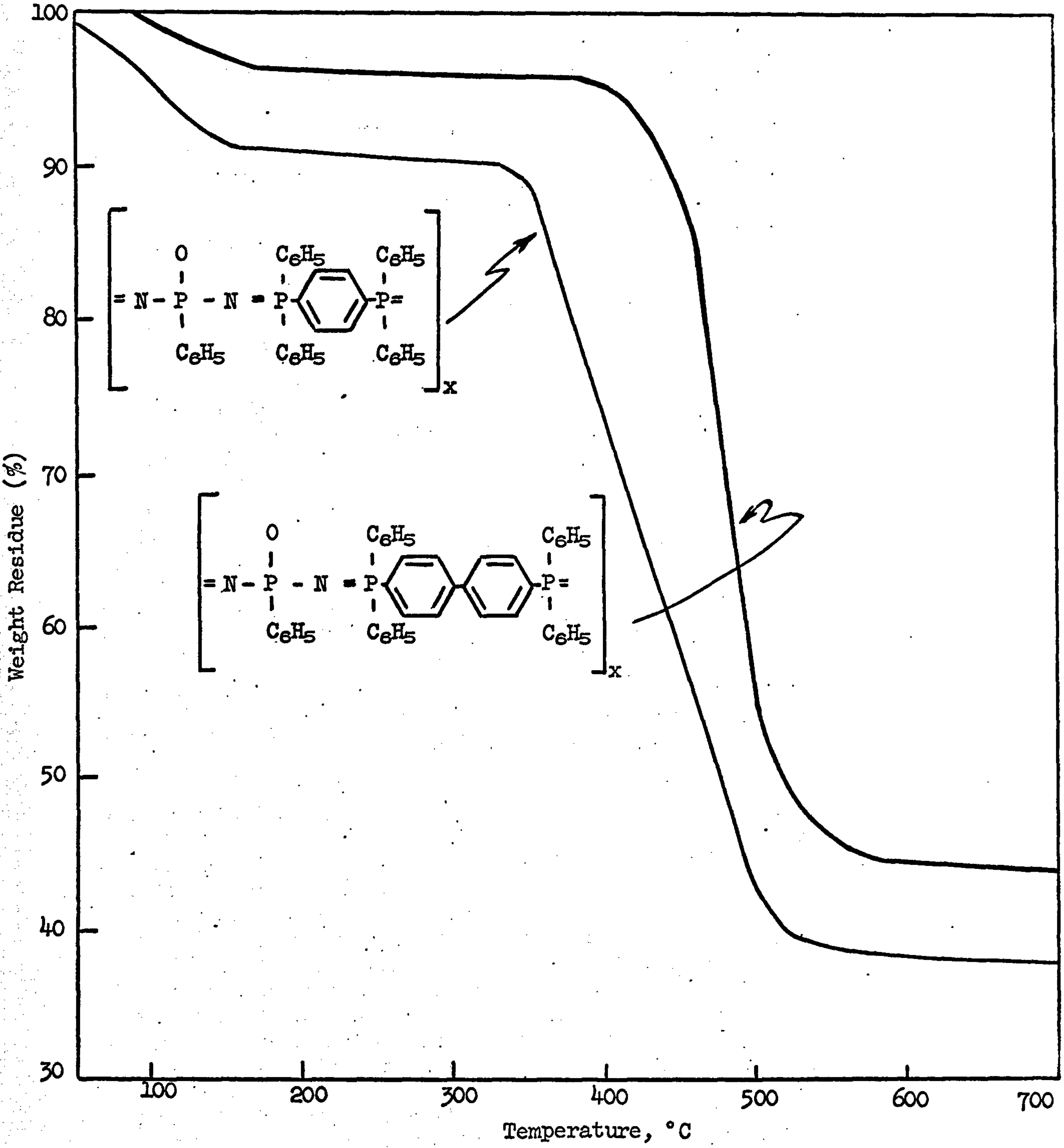


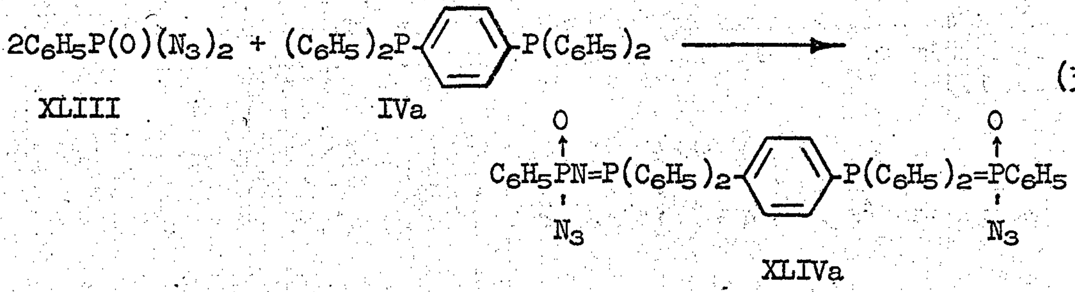
Figure 1

Comparison of TGA Curves for Phosphorane Polymers

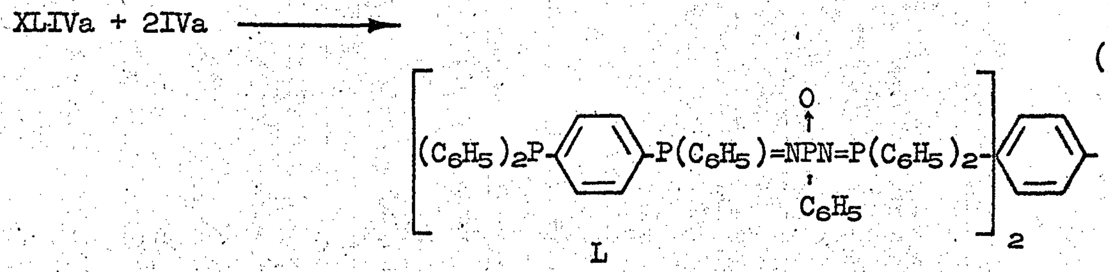
A polymerization of phenylphosphonyl diazide (XLIII) and 1,4-bis(diphenylphosphino)benzene (IVa) was also carried out using both pyridine and dimethylformamide in an effort to effect changes in the properties of the resulting polymer. The bis-tertiary phosphine IVa was dissolved in warm dimethylformamide before XLIII in pyridine was introduced. While the yield of nitrogen was only 68%, the reaction mixture was found to not have an infrared absorption due to azide. These results appear to be similar to those obtained from the attempted preparation of the phenylphosphonyl diazide in dimethylformamide in which there was a decomposition of the diazide. Furthermore, it was not possible to draw fibers from this material.

b. Sequential Preparation

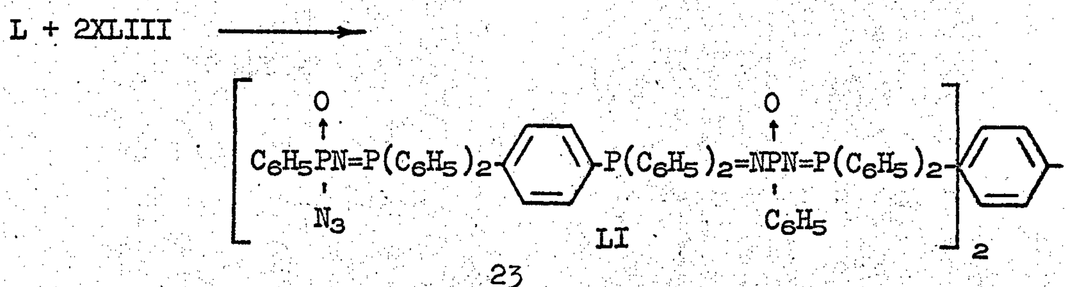
As a result of the ready preparation and isolation of the new polymer intermediates, the bis-azidophosphoranes, XLIVa and XLVI, (see Section II. B.1), two new approaches to the problem of synthesizing polyphosphoranes are now available. The first of these is a stepwise, sequential build-up of polymer intermediates or prepolymers as illustrated in Equations 34-36. Reaction of the bis-azidophosphorane with two moles of a bis-tertiary



(34)



(35)

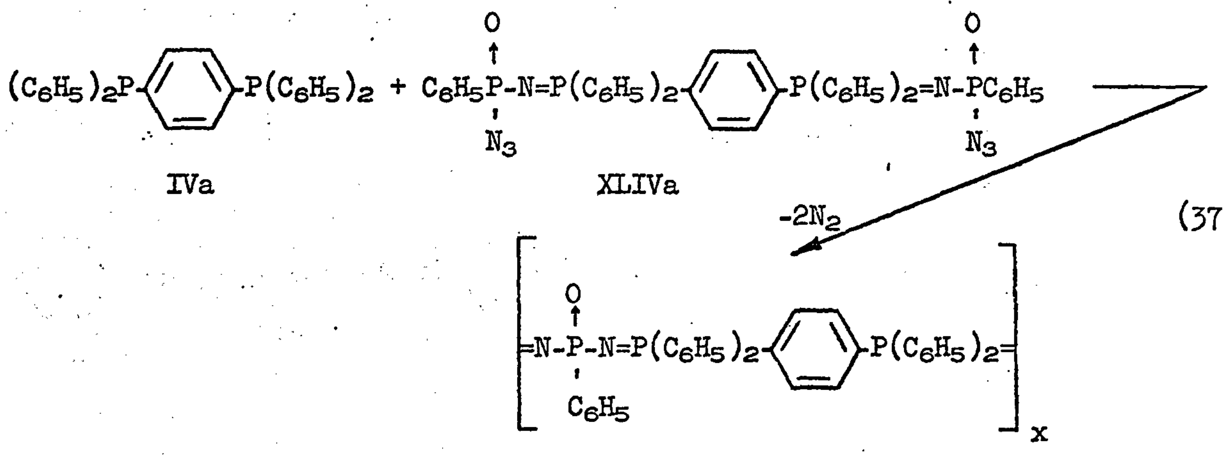


(36)

phosphine such as IVa could then yield a tertiary phosphine terminated intermediate such as L. Further reaction of L with two moles of phenylphosphonyl diazide would yield a new azide terminated intermediate LI. Isolation and purification of this series of intermediates, XLIVa, L, and Li would allow greater control of stoichiometry and reaction conditions in subsequent polymer preparations. In addition, various copolymer compositions could be readily prepared by reacting, for example, the bis-azidophosphorane XLIVa with 4,4′-bis(diphenylphosphino)biphenyl (II) instead of 1,4-bis-(diphenylphosphino)benzene (IVa) as illustrated in Equation 35. However, on the negative side, a most critical step in this sequential method would be in the preparation of the bis-tertiary phosphine terminated compounds such as L where polyphosphorane formation must be avoided (Eq. 35). Nonetheless, this approach appears to offer a multitude of possible variations and will be thoroughly investigated.

In a preliminary investigation of this approach, the steps outlined in Equations 34-36 as well as two subsequent steps were surveyed in pyridine without isolation of any of the intermediates L, LI, etc. While azide absorptions appeared and disappeared as expected, the nitrogen evolutions were erratic and better measuring techniques will be needed. The material isolated as a brown powder from this procedure had an infrared spectrum which was similar to those obtained from previous <u>in situ</u> preparations in pyridine. To properly evaluate this method, it will now be necessary to isolate and characterize the various intermediates such as L and LI.

The second utilization of the bis-phosphoranes XLIVa and XLVI is by means of their stoichiometric reaction with bis-tertiary phosphines (Eq. 37). This reaction has been evaluated in several solvents



IVa

XLIVa

XLIXa

(37)

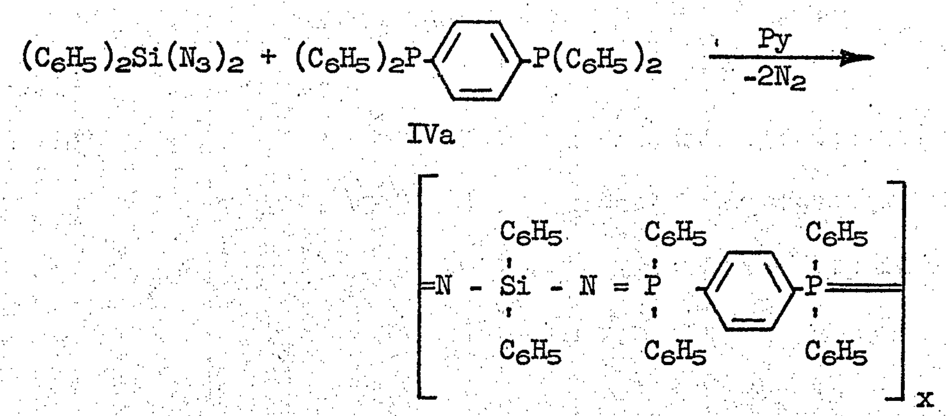
(dimethylformamide, dimethylsulfoxide, hexamethylphosphoric triamide) and the initial results are most encouraging.

At the same time, solvent compatibility studies were also carried out with 1,4-bis(diphenylphosphino)benzene (IVa) and these solvents at 100° C. or above. The bis-tertiary phosphine IVa was recovered unchanged from dimethylformamide and dimethylsulfoxide but was considerably oxidized by hot hexamethylphosphoric triamide. This oxidation was shown by a very broad melting range and by new absorptions due to P-O and PO-phenyl in the infrared spectrum of the recovered material. At 85° C., no oxidation was observed and, as a result, the run in hexamethylphosphoric at reflux was discontinued. However, a run in this solvent at 85° C. was subsequently carried out without any evidence for the oxidation of the bis-tertiary phosphine.

The polyphosphorane XLIXa recovered from dimethylformamide, from dimethylsulfoxide, and from hexamethylphosphoric triamide at 85° C. was a pale yellow-colored, powdery material with properties not observed from any previous preparations. When placed in hot water at about 65° C., a very tacky ball of phosphorane formed from which long, brittle fibers could be drawn. In addition, clear, but again brittle, disks were pressed from the powder isolated after removal of the reaction solvent. These results imply that longer chain lengths are now being obtained by the introduction and use of the bis-azidophosphoranes in place of phenylphosphonyl diazide in the polymerization studies. Further preparations and evaluations of this method and the resulting polyphosphoranes are underway.

2. Polysilylimidophosphoranes

In a second area of phosphorane polymers, the first synthesis of a silicon containing polyphosphorane has been carried out (Eq. 38) in both pyridine and tetrahydrofuran. The product silylphosphorane obtained from



IVa

LII

pyridine had a differential thermal analysis curve which suggested that this material was stable to about 450-500° C. Molecular weight determinations on LII fractions suggested a low value of x, only approximately 3. Further evaluation of the silylphosphoranes will continue as time permits.

D. Experimental

Caution! Certain of the phosphonyl azides of this study have extreme sensitivity to heat and shock and should be handled with care![1] All azide reactions were carried out under an inert atmosphere and in anhydrous solvents.

The infrared spectra were determined on a Perkin-Elmer Model 21 spectrophotometer. Molecular weights were determined using the Neumayer thermistor method.[8] Volumes of nitrogen are always corrected unless otherwise noted. Boiling and melting points are not corrected.

1. Preparation of Intermediates

a. Commerical Intermediates

Several commercial phosphorus-chlorine compounds and other intermediates were purified by distillation or by recrystallization as was appropriate. Oxygen and water sensitive compounds were sealed in glass vials in varying quantities to provide uniform samples as needed. Pertinent data for compounds purified are listed below:

	m.p.	
Triphenylphosphine	80.5-82 °C	Recrystallized from isopropyl alcohol

	b.p.	n_D^{20}
Diphenylchlorophosphine	87-89° C/0.3 mm	1.6362
Phenylphosphonyl dichloride	140-142° C/20 mm	1.5580-1.5590
Diphenylphosphonyl chloride	128-132° C/0.1 mm	1.6100
Diphenylsilyl dichloride	102-104° C/0.5 mm	-

b. Phenyl-N,N-dimethylaminophosphonyl Chloride (XXII) (1935-15,18)

A 90 g. (2 mole, ~ 132 ml.) quantity of dimethylamine was allowed to distill with rapid stirring into a reaction mixture consisting of 195 g. (1 mole, 162 ml.) of phenylphosphonyl dichloride and 300 ml. of toluene which was cooled by means of an ice bath. The precipitate of dimethylamine hydrochloride, which made complete agitation of the mixture difficult, was removed by pressure filtration under nitrogen through a fine glass sintered funnel. The solvent was removed at reduced pressure and the yellow-colored liquid residue was distilled through a spinning band column. A 48.2 g. (0.25 mole) forerun of unreacted phenylphosphonyl dichloride, b.p. to 65° C. at 0.2 mm., n_D^{20} 1.5602, was collected before 132.2 g. (0.65 mole, 86.7% based on consumed dichloride) of phenyl-N,N-dimethylaminophosphonyl chloride; b.p. 86° C. at 0.2 mm. was obtained. *Anal.* calcd. for $C_8H_{11}ClNOP$: Cl, 17.41; N, 6.88; P, 15.21; Cl:P, 1.00. Found: Cl, 17.2; N, 6.53; P, 15.3; Cl:P, 0.98.

In a second preparation, 195 g. (1.0 mole) of phenylphosphonyl dichloride dissolved in 400 ml. of toluene was reacted with a slight excess of dimethylamine, 102 g. (2.27 mole), over a 6-hour period. Following the preceding work-up and distillation, 142.6 g. (0.70 mole) of the aminochloride, b.p. 90° C/0.25 mm., n_D^{20} 1.5469 was obtained. The yield, based on consumed phenylphosphonyl dichloride was 88.6%.

c. 4,4'-Dibromobiphenyl (I) (1935-2 and 3)

Following a previously described procedure,[3] 30.8 g. (0.2 mole) of biphenyl and 78 g. (24 ml., 0.48 mole) of bromine in separate dishes were allowed to react at room temperature, with occasional stirring of the biphenyl, in a vented desiccator. After 24 hrs. the bromine had been consumed and the crude product was allowed to degas. As a result of a wide melting point range, 135-155° C., the crude product was treated with an additional 12 ml. (0.24 mole) of bromine. Crystallization from benzene and Norite A provided 43.8 g. (0.14 mole, 69.5% yield) of white crystals, m.p. 163-166, reported[3] m.p. 166° C.

A second preparation was carried out as above to yield only 27 g. (0.0865 mole, 50.9% yield) of recrystallized 4,4'-dibromobiphenyl, m.p. 163-166° C.

d. Preparation of 4,4'-Biphenylbis(phenylphosphinic Acid) (XXV) (1887-191)

A 168.3 g. quantity of a benzene slurry of 4,4'-dilithiobiphenyl (Lithium Corporation of America) thought to contain approximately 0.0805 mole of the dilithio compound was siphoned under argon into a 500 ml. round-bottom flask fitted with a thermometer, a condenser and an addition funnel. The system was filled with argon and protected from the atmosphere by means of a mercury bubbler. To this slurry, held at 10° C. or less by means of an external ice-water bath, was slowly added 10 ml. of a solution of 25 ml. of benzene and 32.8 g. (0.161 mole) of phenyl-N,N-dimethylaminophosphonyl chloride. Only a slight exotherm was noted and no color change occurred. No increase in temperature was noted on addition of all the chlorophosphine. After an additional 10 ml. of excess chloro-compound had been added, the reaction was allowed to warm up. At 15° C. an exotherm was noted and the temperature increased to 36-38° C. where it was held by means of the ice-water bath. As the temperature began to drop, the bath was replaced with warm water so as to maintain the temperature at 36-38° C. for 30 minutes. The color of the mixture now changed to a light-tan color.

The solids were separated by filtration and washed with ether to yield 59.5 g. of a tan-colored powder. The combined ether-benzene fractions were concentrated to give a brown goo which resisted solidification. The infrared spectrum of the tan powder contained the expected absorptions associated with P-O at 8.45 and 8.88μ as well as $P-N(CH_3)_2$ at 10.25μ[15] and 1,4-aromatic at 12.22μ. Attempts to recrystallize this solid resulted in only the recovery of brown-yellow gums. Hydrolysis of the tan solids under both basic and acidic conditions in ethanol yielded various base soluble fractions which frequently precipitated white, tacky substances on acidification with concentrated hydrochloric acid.

A 15.3 g. quantity of the tan solids was refluxed with 5 g. of sodium hydroxide dissolved in 85 ml. of ethanol and 50 ml. of water for 64 hrs. The mixture was treated with activated charcoal, filtered, and the filtrate was acidified with concentrated hydrochloric acid to give 5.2 g. of a bulky, white precipitate. Anal. calcd. for $C_{24}H_{20}O_4P_2$: P, 14.26; M.W., 434.4. Found: P, 14.1; M.W., 470. Further investigation of the synthesis of this material is to be undertaken.

e. p-Phenylene-Bis-Phosphonic Acids

Preliminary experiments were carried out in an effort to gain some insight into possible alternate methods of syntheses of these acids.

(1) 1,4-Phenylene-Bis(methylphosphonic Acid) (XXIX) (1945-49)

A chlorobenzene solution containing an unknown quantity of 1,4-bis(methylphosphino)benzene-bis(borane) (XXVIII) was first treated with cold concentrated hydrochloric acid. After 1 hr. on a steam bath, the mixture was concentrated at reduced pressure nearly to dryness before 75 ml. of methanol was added. After distillation to remove methyl borate-methanol azeotrope, the excess methanol was removed to give a tacky, pale greenish-white residue. Attempted crystallization from isopropyl alcohol resulted in the isolation of a white solid melting over the range 180-192° C. (reported[15] for XXIX, m.p. 231-236° C. after four recrystallizations from ethanol). The infrared spectrum of this crude acid was, however, similar to that for the previously prepared material.[15]

(2) Attempted Synthesis of 1,4-Phenylene-bis(phenylphosphonic Acid) (XXVII) (1945-49)

The distillates obtained from the lithium cleavage of 1,4-bis(diphenylphosphino)benzene (IVa)[14] were combined, slurried in water, and treated with iodic acid solution. The resulting by-product iodine was removed by means of sublimation on a steam bath. The oil slowly darkened on successive treatments with the iodic acid solution. Addition of hydroiodic acid, after it appeared that no further iodine was being formed, caused additional iodine formation. However, only a brown, tacky residue was obtained. Initial attempts to recover XXVII were not successful; however, the residues were retained for further study at a later date.

f. P-Hexamethyl-B,B'-dibromotriborophane (XL) (1935-30)

To 11.08 g. (0.05 mole) P-hexamethyltriborophane (XXXIX) in 100 ml. of stirred benzene was added 18.69 g. (0.105 mole) of N-bromosuccinimide in powder form. The reaction was maintained at room temperature in a water bath for 5 hrs. The solvent was evaporated under a stream of nitrogen and the residue was triturated with water to remove the succinimide. The remaining solids were filtered and vacuum dried, yielding 18.5 g. of white, crystalline powder which contained 90% dibromo and 8.4% monobromotriborophane by VPC analysis. A recrystallization from isohexane, and several subsequent recrystallizations from methanol yielded 7.2 g. of white crystals, m.p. 127-129° C., (lit.[28] m.p. 126.5-128.5° C.) representing 38% of theory. M.W.: 379 (calcd); 356 (Neumayer). This material was indicated to be 99% dibromotriborophane by vapor phase chromatography.

g. Attempted Preparation N,N-Dimethyl-4-(diphenylphosphino)diphenylphosphonamide (XVIII) (1945-18)

To 2.25 g. (0.0926 g-atom) of magnesium turnings and 60 ml. of tetrahydrofuran was added 100 ml. of a solution of tetrahydrofuran and 31.6 g. (0.026 mole) of 4-bromophenyldiphenylphosphine (IX). As there was no evidence of reaction after 2 hrs. at reflux, a small crystal of iodine was added to the reaction mixture. The resulting black-colored mixture was refluxed for 20 hrs. and cooled to room temperature before the addition of 18.8 g. (0.0926 mole) of phenyl-N,N-dimethylaminophosphonyl chloride dissolved in 30 ml. of tetrahydrofuran was begun. However, it appeared that there was an excessive amount of unreacted magnesium still present after this prolonged reflux period. The addition of the phosphonyl chloride was not exothermic and did not cause the black color to dissipate. After 2 hrs. at reflux and 64 hrs. at ambient temperature the color had become brown. Approximately 20 ml. of saturated ammonium chloride solution was added (only slight exotherm) to the mixture. The resulting white solids were removed by filtration, washed with ether, and dried before an infrared examination showed that they were only salts.

Concentration of the organic phase at reduced pressure gave a brown-colored, tacky residue which foamed badly during the concentration. Further drying at 10^{-3} mm. gave a friable, pale-yellow colored solid which melted incompletely over the range 54-300° C. Infrared examination revealed only the expected absorptions - P-O at 8.5μ, ArP-O at 8.9μ, $P-N(CH_3)_2$ at 10.45-10.5μ, and 1,4-disubstituted aromatic at 12.1-12.15μ. Attempted crystallization of this friable material from a variety of organic solvents only resulted in the formation of gums.

Hydrolysis in aqueous base and acid resulted in the liberation of dimethylamine but the resulting material was only very slightly soluble in sodium hydroxide solution. Since these combined results obtained suggested strongly that the Grignard formation was poor or did not proceed at all, this experiment was terminated.

2. Preparation of Bis-Tertiary Phosphines

a. 1,4-Bis(diphenylphosphino)benzene (IVa)

(1) Runs 1935-17,23

To the di-Grignard prepared from 118 g. (0.5 mole) of p-dibromobenzene and 24.3 g. (1 g-atom) of magnesium in 1500 ml. of tetrahydrofuran (12 hrs. at reflux) was slowly added 243 g. (1.1 mole) of diphenylchlorophosphine and 500 ml. of tetrahydrofuran. During the addition (about 1 hr.) the reaction temperature was held at 15-20° C. by means of an ice-water bath. The clear, yellow-colored mixture was refluxed for 1 hr. and then cooled to room temperature before 200 ml. of saturated ammonium chloride solution was added. The tetrahydrofuran phase was decanted from the white solids and concentrated on a Rinco evaporator to give a yellow, tacky residue. After digestion with isopropyl alcohol, the white, crude product weighed 125 g. (0.28 mole, 56% yield) and melted over the range 156-170° C. Approximately one-half of the crude product was recrystallized from benzene-methanol to give 49 g. of white, crystalline 1,4-bis(diphenylphosphino)benzene, m.p. 165.5-167° C. Work-up of the mother liquors yielded 11 g. of very impure material, m.p. 170-190° C. Infrared examination of the pure product indicated as a result the disappearance of the absorption at 8.5μ that the majority of any oxide contaminate had been removed. The second, wide melting range material contained a considerable amount of oxide as evidenced by the P-O absorption at 8.5μ.

Additional quantities of previously prepared 1,4-bis-(diphenylphosphino)benzene were recrystallized in a similar manner which resulted in an 82% recovery of the bis-tertiary phosphine, m.p. 166-169° C. Again the residues showed a strong P-O absorption in the infrared.

(2) Run 1935-61

Following the inverse Grignard procedure successfully used for the preparation of bromophenyldiphenylphosphines from p-dibromobenzene (see below), 24.3 g. (1.0 g-atom) of magnesium turnings were added, in small portions over a two-hour addition period, to 118 g. (0.5 mole) of p-dibromobenzene dissolved in 800 ml. of tetrahydrofuran. The initial reaction was exothermic and caused spontaneous reflux for the first hour of the addition, after which external heating was needed to maintain reflux. After 5 hrs. at reflux, the mixture was cooled and subsequent addition of 220.6 g. (1 mole) of diphenylchlorophosphine dissolved in 300 ml. of tetrahydrofuran was carried out at 20° C. with external cooling. The reaction mixture was refluxed for $1\frac{1}{2}$ hrs. to complete the reaction.

Addition of 180 ml. of saturated ammonium chloride solution caused the precipitation of a granular solid which was then removed by filtration. From the organic phase were isolated 44.0 g. of bis-tertiary phosphine, melting at 164-166° C. and a second crop of greenish-white colored solids melting at 165-167° C. The combined yield was only 26.6% which is considerably below the average 50-60% yields obtained previously.

b. <u>4,4'-Bis(diphenylphosphino)biphenyl (II)</u>

(1) From 4,4'-Dilithiobiphenyl

(a) Run 1887-172

A 234.3 g. quantity of a benzene slurry of 4,4'-dilithiobiphenyl assumed to contain 0.105 mole of the dilithiobiphenyl, was siphoned into a 500 ml. Morton flask fitted with a mechanical stirrer, condenser, thermometer, and dropping funnel. Diphenylchlorophosphine, 54.8 g. (0.249 mole, 18% excess) dissolved in 75 ml. of benzene was added over 20 minutes to the slurry. A reaction temperature of approximately 40° C. was maintained by means of an external ice-water bath. The reaction was then allowed to stir at room temperature briefly before it was refluxed for 2 hours.

The reaction mixture was concentrated using a Rinco evaporator at water aspirator pressure to yield a yellow-brown, tacky residue. Trituration with methanol, filtration, and washing with dilute ammonium hydroxide resulted in the recovery of 47.0 g. (0.0076 mole, 85.6% yield) of crude, pale-yellow colored 4,4'-bis(diphenylphosphino)biphenyl, m.p. 175-185° C.

Recrystallization from benzene-ethanol gave a white precipitate which softened at 186° C. and melted at 191-192° C. while a second recrystallization resulted in a melting point of 190-192° C. A molecular weight value of 518 (theory, 522) was obtained for material from the first crystallization.

(b) Run 1887-175

In a second preparation, 263.6 g. of the benzene slurry of 4,4'-dilithiobiphenyl, assumed to contain 0.17 mole of the biphenyl derivative, reacted as above with 75 g. (61.5 ml., 0.34 mole) of diphenylchlorophosphine dissolved in 50 ml. of benzene. In this run, however, the reaction was held at 25-28° C. during the addition of the chlorophosphine (25 min.).

After stirring for 64 hrs. under argon, the solvent was removed at reduced pressure to give a brown, tacky residue. After digestion with methanol and with ethyl acetate, 70.7 g. (0.135 mole, 79.4% yield) of pale-yellow colored bis-tertiary phosphine was isolated. Crystallization of an analytical sample from ethylene glycol dimethyl ether resulted in white, crystalline 4,4'-bis(diphenylphosphino)biphenyl (II), m.p. 191-193° C. Anal. calcd. for $C_{36}H_{28}P_2$: C, 82.74; H, 5.40; P, 11.85. Found: C, 82.51; H, 5.92; P, 11.4.

When the purification of a larger quantity of the crude product was attempted using a different quantity of ethylene glycol dimethyl ether and Norite A, a white powder which was no longer soluble in hot ethylene glycol dimethyl ether, m.p. ~ 290° C., was isolated. Infrared examination of this material indicated that it was more than likely the bis-oxide as evidenced by a strong, sharp infrared absorption at 8.5μ. The recrystallization solvent was then tested for peroxide and found to be highly contaminated (starch-iodide method).

Identification of the suspected bis-oxide was carried out by oxidizing a small quantity of pure 4,4'-bis(diphenylphosphino)-biphenyl (II) with 3% hydrogen peroxide in acetone. The white crystalline bis-oxide IIa was recrystallized from ethanol and melted at 299-301.5° C. Anal. calcd. for $C_{36}H_{28}P_2O_2$: C, 77.97; H, 5.09; P, 11.17. Found: C, 77.6; H, 5.08; P, 10.9. The infrared spectrum of this material was identical to that obtained from the previous, inadvertent oxidation of the bis-phosphine.

(c) Run 1887-171

In yet another run, approximately 224.6 g. (0.1 mole) of the same slurry was reacted with 44.1 g. (0.2 mole) of diphenylchlorophosphine dissolved in 60 ml. of benzene. The addition, without external cooling, was initially exothermic with the reaction temperature raising to 60° C. However, after only about 20 ml. of the chlorophosphine solution had been added, the reaction temperature began to drop. After two hrs. at reflux and removal of the solvent, attempted recrystallization of the residual yellow-colored liquid from ethylene glycol dimethyl ether resulted in the recovery of only 6.6 g. of diphenylphosphonic acid, m.p. 193-195° C., mixture melting point with diphenylphosphonic acid, 192-194° C. The infrared spectra were identical.

(d) Run 1945-26

Following the previously described procedure, a slurry of 4,4'-dilithiobiphenyl in benzene thought to contain 0.415 mole of dilithio compound was reacted at 20-26° C. with 183 g. (0.83 mole) of diphenylchlorophosphine. After removal of the solvent and digestion with methanol and with dilute ammonium hydroxide solution, approximately 122.2 g. (0.234 mole, 56.4% yield) of pale-yellow colored 4,4'-bis(diphenylphosphino)biphenyl, m.p. 188-193° C., was isolated. This material was further purified as needed.

(e) Purification of 4,4'-Bis-(diphenylphosphino)biphenyl (II) (1887-183)

In order to obtain colorless bis-tertiary phosphine from the crude, yellow-colored products, it was sometimes necessary to carry out the following typical purification. A 17.3 g. quantity of the crude material was partially dissolved in 250 ml. of concentrated hydrochloric acid and filtered through glass-wool on a medium porosity glass-sintered funnel. The filtrate was poured onto ice-water to precipitate a white solid. After filtration and washing with water and ethanol, 13.5 g. of white powder, m.p. 185-190° C., was recovered. A mixture melting point with diphenylphosphonic acid was 178-190° C. showing that this material was not impure diphenylphosphonic acid. The infrared spectra were different as expected.

Further crystallization from a mixture of tetrahydrofuran and methanol resulted in the recovery of crystalline 4,4'-bis-(diphenylphosphino)biphenyl, m.p. 190.5-193.5° C. In view of the difficulties of keeping the ethylene glycol dimethyl ether peroxide free, this methanol-tetrahydrofuran method is probably the more useful. A second recrystallization of the above white bis-phosphine from ethylene glycol dimethyl ether (distilled from calcium hydride) gave an analytical sample, m.p. 192.5-194° C. Anal. Found: C, 82.27; H, 5.58; P, 11.4.

A second method which was also available for the purification of this bis-tertiary phosphine involved the use of column adsorption chromatography developed for use with the bromophenyldiphenylphosphines.

A 12.5 g. quantity of crude, yellow-colored bis-tertiary phosphine, melting range 152-172° C., dissolved in 200 ml. of benzene was passed through a 600 x 15 mm. column of activated alumina. The recovered white-colored powder, melting point 186-191° C., weighed 10.5 g. (84.0% recovery). A second pass through the column of 6.0 g. of the white powder resulted in only recovery of 4.4 g. (73.3% recovery) of product, m.p. 186-191° C.

(2) Attempted Preparation Via 4,4'-Biphenylene di-Grignard

(a) Run 1887-152

A solution of 93.6 g. (0.3 mole) of practical grade 4,4'-dibromobiphenyl (I) in 450 ml. of tetrahydrofuran (orange-colored solution) was added (1.5 hrs.) to 14.6 g. (0.6 g-atom) of magnesium in 300 ml. of refluxing tetrahydrofuran. The reaction mixture turned black during six hours' reflux. Diphenylchlorophosphine, 132 g. (0.6 mole) dissolved in 375 ml. of tetrahydrofuran was added over 1.25 hrs. to the refluxing di-Grignard mixture with the reaction color changing to an orange-brown color.

After 2.5 hrs. additional reflux, the reaction was cooled to room temperature before 90 ml. of saturated ammonium chloride solution was added. The yellow tetrahydrofuran layer was decanted from the granular white precipitate and concentrated on a Rinco evaporator using water aspirator pressure. The resulting yellow, tacky residue was digested with methanol to yield a yellow powder, m.p. 165-170° C. but not clear to above 200° C. Solution of the yellow powder in concentrated hydrochloric acid was only partially successful as a yellow, insoluble oil separated which could not be readily separated by filtration through glass-wool on a fine porosity glass filter. Dilution with ice-water precipitated a white solid intermixed with yellow solids which softened at 162-170° C. and melted at 175-180° C. to a clear yellow liquid. Infrared spectra of both the yellow and white-yellow solids were similar with the yellow solids having somewhat more P-O absorption at 8.48μ.

Recrystallization of the white-yellow solids from ethylene glycol dimethyl ether and activated charcoal resulted in the isolation of a white powder, m.p. 183-191° C. Recrystallization of another sample from tetrahydrofuran and methanol gave pale-yellow crystals, m.p. 180-185° C. As a result of the grossly impure nature of the reaction solids, work on this preparation was discontinued.

(b) Runs 1887-158 and 160

In a repetition of the previous experiment, recrystallized 4,4'-dibromobiphenyl (I) was used instead of the practical grade material for use in the preparation of the di-Grignard. After 15 hrs. at reflux and stirring for an additional 64 hrs., it appeared that little reaction had occurred. The solvent was decanted from the magnesium and concentrated to yield 76.3 g. (0.244 mole) of 4,4'-dibromobiphenyl (I), m.p. 164-166° C. and 8.4 g. (0.027 mole) of impure dibromide for a 90.5% recovery of the starting material.

In a similar attempted preparation, a 50 ml. portion of the tetrahydrofuran solution of the dibromide and the magnesium were strongly refluxed in the presence of several crystals of iodine until the purple color had dissipated. The remaining dibromide solution and 300 ml. of solvent were added and the mixture was refluxed for three 8-hr. periods.

Again no reaction had taken place as evidenced by the clear nature of the reaction solvent and the presence of the magnesium turnings. Approximately 80.7 g. (0.259 mole, 86.3% recovery) of 4,4'-dibromobiphenyl (I), m.p. 163-166° C. was recovered.

(c) Runs 1935-5,9 and 13

A 15.6 g. (0.05 mole) quantity of the 4,4'-dibromobiphenyl (I) was reacted at reflux with 2.4 g. (0.1 g-atom) of magnesium turnings in 165 ml. of tetrahydrofuran for 10 hrs. Diphenylchlorophosphine, 22 g. (0.1 mole, 18.3 ml.) was added and the mixture refluxed for only 1 hr. After the addition of saturated ammonium chloride solution, separation and concentration of the solvent, attempted solidification of the yellow, semi-solid residue with various solvents was unsuccessful. Attempted solution in concentrated hydrochloric acid and dilution in ice-water precipitated only a small quantity of a tacky, white solid. This experiment was discontinued.

A second similar run was initiated, differing only in that 40 mesh magnesium powder was used and the mixture was refluxed 20 hrs. instead of 10 hrs. Work-up gave 7.5 g. of a yellow powder, m.p. 170-180° C. Solution in concentrated hydrochloric acid and filtration followed by dilution of the filtrate with ice-water precipitated a white solid which was further washed with water, dilute ammonium hydroxide and ethanol. Recrystallization from tetrahydrofuran and methanol yielded 4 g. of slightly yellow powder, m.p. 188-190° C.

A third run again using magnesium turnings and the same quantities of reactants except that 500 ml. of solvent was used. After 20 hrs. of reflux and the usual work-up, the yellow solids were found to be mostly insoluble in concentrated hydrochloric acid. While soluble in tetrahydrofuran and ethylene glycol dimethyl ether, it was difficult to reprecipitate them once in solution. The melting point range was 240-320° C. which implied the presence of oxide. Infrared examination showed a strong P-O absorption at 8.5μ.

(d) Run 1887-161

In this attempted preparation, 18.7 g. (0.06 mole) of 4,4'-dibromobiphenyl (I) and 2.9 g. (0.12 g-atom) of magnesium turnings were refluxed in 180 ml. of p-dioxane for 20 hrs. Several crystals of iodine were added at the beginning to help initiate the reaction. However, no evidence of reaction was observed and 16.9 g. (0.0542 mole, 90.4%) of the starting dibromide I, m.p. 163-166° C., was recovered.

(3) Attempted Preparation via Lithium Diphenylphosphide

(a) Run 1887-163

Following the previously described method,[4] 26.2 g. (0.1 mole) of triphenylphosphine was cleaved by 1.4 g. (0.2 g-atom) of lithium in 125 ml. of tetrahydrofuran and 9.3 g. (0.1 mole) of t-butyl chloride was used to destroy the resulting phenyl lithium.

A solution of 15.5 g. (0.05 mole) of 4,4'-dibromobiphenyl (I) dissolved in 90 ml. of tetrahydrofuran was added to the gently refluxing, red-colored lithium diphenylphosphide solution. After only about 30 ml. of the dibromide solution had been added, the reaction mixture became dirty-brown colored and at the completion of the addition, the mixture was black in color.

After 2.5 hrs. at reflux, 5 ml. of water and 5 ml. of methanol were added which caused a slight exotherm and a small amount of precipitate to form. The solid was removed and the yellow-brown tetrahydrofuran phase was concentrated at reduced pressure. The resulting brown gum dissolved in concentrated hydrochloric acid but when poured into ice, only an oil separated. In retrospect, this oil may have been p-bromophenyldiphenylphosphine (IX).

(b) Run 1887-167

In a similar manner, a second cleavage run was carried out except that an excess of the lithium diphenylphosphide was provided for by using only 0.06 mole (18.7 g.) of 4,4'-dibromobiphenyl (I) for 0.125 mole of triphenylphosphine.

The reaction mixture was concentrated at reduced pressure to yield a yellow oil from which only a small quantity of 4,4'-dibromobiphenyl (I) (2.6 g.) m.p. 163-166° C., was recovered on digestion with methanol and water.

(c) Run 1887-169

In the third attempt, 47.2 g. (0.18 mole) of triphenylphosphine was cleaved by means of 2.5 g. (0.36 g-atom) of lithium metal in 125 ml. of tetrahydrofuran. The phenyl lithium was destroyed with 16.7 g. (0.18 mole) of tertiary butyl chloride before 18.7 g. (0.06 mole) of solid 4,4'-dibromobiphenyl (I) was added in three portions to the reaction mixture at ambient temperature. These additions resulted in a reaction temperature increase to 50° C. and the formation of a brown color.

One hundred ml. of methanol was added to the reaction after 2 hrs. at reflux. One portion (~ 90 ml.) of the clear, yellow-colored reaction mixture was concentrated to give an off-white solid residue. The residue was dissolved in concentrated hydrochloric acid, filtered and poured into 225 ml. of water. The resulting yellow oil was digested with methanol and acetone to yield 1.5 g. of a white solid, m.p. 152-172° C. An additional 5.4 g., m.p. 140-150° C., was recovered from the methanol-acetone mother liquors.

Water was added to the remaining reaction mixture to precipitate a yellow oil. Digestion of the oil separated 1.9 g. of a waxy solid, m.p. 125-155° C.

(4) Attempted Preparation via 4,4'-Bis-(diazonium fluoroborate)biphenyl (VI) (1943-37 and 39)

A mixture of 28.5 g. (0.154 mole) of commercial benzidine and 90 ml. of concentrated hydrochloric acid was placed in a 300 ml. round-bottom flask and warmed on a hot water bath for one hour with stirring. The flask was then equipped with an addition funnel and cooled with stirring to -5° C. in an ice-salt bath. When this temperature had been reached, 25.4 g.

(0.368 mole) of sodium nitrite in 100 ml. of water was added. The temperature was kept below -5°C. during the addition. To this cold diazonium chloride mixture was added 150 ml. 50% cold hydrofluoroboric acid and the temperature was held at about 10°C. The pale-yellow solids were filtered through a Buchner funnel with suction. The filter cake was washed with 50 ml. cold water, 50 ml. cold methanol, and 50 ml. cold ethyl ether; the cake was sucked as dry as possible between washings. The washed solids were then dried in a vacuum dessicator over concentrated sulfuric acid overnight. The yield was 50.0 g. (0.131 mole) or 85% based on benzidine.[29]

In a 500 ml. three-necked flask equipped with an addition funnel, condenser, and magnesium powder delivery device, 25.0 g. (0.065 mole) of 4,4'-bis(diazonium fluoroborate)biphenyl and 0.9 g. of cuprous chloride were suspended in 180 ml. of anhydrous ethyl acetate. The suspension was stirred vigorously under nitrogen for 5 minutes. The gas was shut off and a tube was connected from the condenser to a gas collection apparatus to measure the volume of nitrogen gas evolved. To this mixture, 28.8 g. (0.131 mole) diphenylchlorophosphine which was already in the addition funnel was added slowly. No significant volume of nitrogen gas was evolved until the bath temperature had been increased to 77°C., the refluxed temperature of ethyl acetate. After the evaluation reached 50% in 4½ hrs., the rate began to level off. After 13 hrs. a total of 2315.5 ml. of nitrogen gas at standard condition was collected which is equivalent to 78.9% conversion.

The flask was then cooled to room temperature before magnesium powder, 3.18 g. (0.131 mole), was added slowly through the addition device. Since there was no evidence of an exothermic reaction, the reaction temperature was again brought up to 77°C. for 1½ hrs. Excess solvent was then removed at reduced pressure to yield a dark-brown colored residue. To this residue, 200 ml. tetrahydrofuran was added before the mixture was heated on a steam bath for 30 mins. The mixture was cooled and filtered before 150 ml. of cold saturated ammonium chloride solution was added. The tetrahydrofuran phase was separated and methanol was added to it in an attempt to precipitate the product bis-tertiary phosphine. Only about 1 g. of a tan powder which had a decomposition point of approximately 205°C. was isolated. It could not be recrystallized to allow identification.

c. Attempted Synthesis of 1,3-Bis-(diphenylphosphine)benzene (IVb) (1943-5)

In a thoroughly dry system filled with argon were placed 26.2 g. (0.1 mole) of triphenylphosphine and 1.4 g. (0.2 g-atom) of lithium pieces. Approximately 150 ml. of tetrahydrofuran was slowly added causing the cleavage to take place and a red color to form. The reaction temperature increased to 40-45°C. and was held at this temperature for 8 hrs. or until all the lithium had reacted. By-product phenyl lithium was destroyed by the addition, at 20°C., of 9.3 g. (0.1 mole) of t-butyl chloride after which the reaction was held at reflux for 0.5 hr.

The reaction mixture was then cooled to 20°C. before the addition of 12.0 g. (0.05 mole) 1,3-dibromobenzene was carried out. After

2 hrs. at reflux, the mixture was concentrated at reduced pressure to yield a yellow-green viscous residue. After trituration with cold methanol, 12.0 g. of a white powder, melting over the range 125-130° C. was isolated. Sublimation at 135° C. and 10^{-3} mm. yielded a white solid melting at 116-118° C. Anal. calcd. for $C_{30}H_{24}P_2$: P, 13.82. Found: P, 16.50. Both fractions were found by infrared spectroscopy to contain considerable P-O materials as evidenced by the presence of strong absorptions at 8.45μ and 8.95μ. An additional 1.2 g. of solids melting at 160-170° C. were recovered by diluting the acetone with water.

Two additional runs gave similar yellow oils which yielded a variety of solids having varied melting point ranges. Work was discontinued on this approach as a result.

From the residues remaining from the attempted preparation of IVb via the meta-diGrignard[30] was recovered at 100° C. and 0.1 mm. a quantity of diphenylphosphine (n_D^{22} 1.6263). The infrared spectrum and index of refraction were identical to those of authentic diphenylphosphine.

d. Attempted Synthesis of Bis-Tertiary Phosphites

(1) From Hydroquinone (1935-68)

Into a thoroughly dry flask and under an inert atmosphere, were introduced 61.3 ml. of diphenylchlorophosphine (0.30 moles), 26.9 ml. of pyridine (0.30 moles), and 400 ml. of toluene. The flask was cooled by an ice bath to ~ 10° C. before one-quarter of the slurry of 16.5 g. (0.15 moles) of hydroquinone in 125 ml. of toluene was added. After stirring for 1.5 hrs. no visual or physical evidence of a reaction was noticed. The remaining slurry was added and the mixture brought to reflux for 3.5 hrs., at which time a light-yellow color was noted in both the liquid and solid portions of the reaction. Reflux was continued for an additional 3.5 hrs.

An aliquot of the organic phase was washed with dilute NH_4OH and rinsed with H_2O, causing the formation of a white precipitate. Concentration of the organic phase at reduced pressure left an off-white powder of m.p. 118-130° C. Recrystallization from toluene/ether yielded white needles, m.p. 134.5-137° C. The remainder of the organic phase was concentrated at reduced pressure to yield 66.2 g. crude material. Infrared examination of the solids revealed an extremely complex spectrum containing absorptions due to P-O, POAr, and also apparently hydrolytic products.

When these crude solids were slurried in methanol, and then heated, the solids went into solution, which then turned bright yellow. Concentration at reduced pressure, addition of toluene, removal of excess water on a Dean-Stark trap, and reconcentration at reduced pressure yielded an oily, yellow, sticky mass which refused to solidify. A portion washed with acetone yielded a white powder, m.p. 185.5-190.5° C., with an infrared spectrum identical to that of diphenylphosphonic acid which melts at 192-194° C.

Upon prolonged exposure to air, the crude solids, m.p. 118-130° C., were discovered to have altered to m.p. 100-110° C. Attempted recrystallizations yielded only products with wide melting ranges and complex infrared spectra.

(2) From Resorcinol

An experiment stoichiometrically identical to the above, except using resorcinol instead of the hydroquinone was attempted. Concentration of the organic phase at reduced pressure again yielded a yellow, oily mass similar to the hydroquinone reaction. Both lines of investigation were temporarily abandoned.

e. 1,4-Bis(dimethylphosphino)benzene (III) (1943-140)

To the Grignard solution of methyl magnesium bromide, prepared from 11.2 g. (0.46 mole) of magnesium turnings and 43.6 g. (0.46 mole) of methyl bromide in 250 ml. of tetrahydrofuran at 30° C., was slowly added 25 g. (0.13 mole) of 1,4-bis(dichlorophosphino)benzene[5] dissolved in 82 ml. of tetrahydrofuran. The reaction temperature was held at or below 5° C. during the addition. After warming to room temperature, the mixture was filtered before the solvent was removed at reduced pressure. The hydrolysis of the magnesium halide-phosphine complex by means of a saturated solution of ammonium chloride was inadvertently omitted and partially explains the extremely low yield of product.

Distillation of the dark-colored residue at 10^{-3} mm. of pressure was accomplished at a bath temperature of 80° C. to give about 5 g. of colorless III. The liquid III had an infrared spectrum with absorptions due to P-aryl at 6.99 and 9.98μ, possibly P-CH_3 at 7.75μ, and para-substitution at 12.45μ.

<u>Anal</u>: calcd. for $C_{10}H_{16}P_2$: C, 60.60; H, 8.14; P, 31.26; M.W., 198.2. Found: P, 29.2; M.W., 193.1; n_D^{20} 1.6021.

A bis-boron tribromide adduct[7] was prepared by adding an excess quantity of boron tribromide to a petroleum ether solution of 1,4-bis-(dimethylphosphino)benzene at -78° C. The isolated bis-tribromoborane, a white powder, melted at about 305 to 315° C. (dec.).

<u>Anal.</u> calcd. for $C_{10}H_{16}B_2Br_6P_2$: B, 3.09; Br, 68.6; P, 8.86; B/P/Br ratio = 1:1:3. Found: B, 3.11; Br, 67.9; P, 9.26; B/P/Br ratio = 1:1.04:2.96.

3. Preparation of Monosubstituted Triphenylphosphines

a. 4-Bromophenyldichlorophosphine (XI) (1943-58)

Into a two-necked 500 ml. flask equipped with addition funnel and condenser were placed excess phosphorus trichloride (62.9 g. or 0.457 mole), 0.70 g. of cuprous chloride and 100 ml. of ethyl acetate. In the addition funnel 34.0 g. (0.125 mole) of p-bromophenyl diazonium fluoroborate and 200 ml. ethyl acetate were placed. The solution under a nitrogen atmosphere was then brought to reflux temperature by means of a hot water bath. The purge nitrogen was shut off and a tube was connected between the condenser and a gas collection apparatus. Into this hot solution was slowly added with stirring the diazonium fluoroborate suspended in ethyl acetate which resulted in the rapid evolution of nitrogen. The total volume of nitrogen evolved, calculated at standard condition, was 2368 ml. as compared to the theoretical volume of 2800 ml. which was an 84.5% conversion. The reaction mixture was cooled to room temperature before 3.04 g. of magnesium turnings (0.125 mole) were added in four portions with vigorous stirring. Upon addition of the magnesium turnings, solids settled out from the wine-colored liquid. The condenser and dropping funnel were disconnected and the flask was connected through a Dry Ice trap to a water aspirator to remove solvent and the ethyl acetate-boron trifluoride complex. To this residue were added 38.0 g. of freshly distilled phosphorus oxychloride and 250 ml. of benzene. The mixture was transferred under nitrogen gas pressure to a 500 ml. flask where it was continuously extracted with benzene for 8 hrs. The benzene was filtered and then concentrated at reduced pressure to yield a dark-brown colored viscous liquid. This residue was vacuum distilled to yield 4.16 g. of pale-yellow liquid boiling at 55-60° C./0.7 mm. Hg. The yield was 12.8%; n_D^{22} 1.5382; M.W. (determined by Neumeyer method) 228; M.W. (calculated) 257.9.

b. Preparation of p-Bromophenyl Diazonium Fluoroborate (1943-54) (X)

In a 300 ml. 3-necked, round-bottom flask 50.0 g. (0.29 mole) of p-bromoaniline and 145 cc. (50%) of fluoroboric acid were mixed. The mixture, a cream-colored paste, was cooled to -5° C. in an ice-salt bath with stirring. To this mixture 22.62 g. (0.328 mole) of sodium nitrite in 45 ml. of water was slowly introduced through an addition funnel while the reaction temperature was held below 0° C. with vigorous stirring. After the addition was completed, the ice-salt bath was removed and the mixture was warmed to room temperature with stirring for 30 mins. The solid formed was collected by filtering through a Buchner funnel with suction. The cake was washed first with 50 ml. of 50% cold fluoroboric acid, then three times with 50 ml. of cold ethanol and, finally, four times with cold 50 ml. portions of ethyl ether. The cake was sucked as dry as possible between washings. It was dried in a vacuum dessicator over concentrated sulfuric acid overnight. The yield of X was 68.0 g. (0.25 mole) or 86% based on p-bromoaniline.[31]

c. p-Bromophenyldiphenylphosphine (XI) (1935-35,37,39)

(1) Normal Grignard Procedure

A solution of 118 g. (0.5 mole) of p-dibromobenzene in 500 ml. of tetrahydrofuran was added to 12.1 g. (0.5 g-atom) of magnesium with the reaction beginning immediately. Since after several hours at reflux, excess magnesium turnings were still present, an additional 12 g. (0.05 mole, 10% excess) of p-dibromobenzene was added to the reaction mixture. Yellow-green solids were noted in the reaction mixture after 8 hrs. at reflux.

To the above Grignard mixture was slowly added 104 g. (0.47 mole) of distilled diphenylchlorophosphine so that the reaction temperature could be held at about 20° C. by means of an ice bath. The reaction was refluxed for 2 hrs., cooled to room temperature, and sufficient saturated ammonium chloride solution was added to form a granular precipitate. The yellow tetrahydrofuran was decanted and concentrated on a Rinco evaporator using aspirator pressure to yield a light-brown colored liquid residue. Attempts to solidify this residue were not successful. The residue was, however, partially dissolved in concentrated hydrochloric acid which on dilution with ice-water precipitated a tacky, white material. Digestion and extraction with ethanol resulted in the isolation of a white solid melting at 162-164° C. which was suspected to be 1,4-bis(diphenylphosphino)benzene. A mixture melting point with authentic 1,4-bis(diphenylphosphino)benzene was 164-167° C. and a molecular weight determination gave a value of 427 (theory, 446.5). Concentration of the ethanol extracts yielded a yellow-green liquid which solidified on standing overnight to semi-crystalline mass. This was retained for study at a later date [see below 3.c.(2)].

(2) Inverse Grignard Procedure

To 118 g. (0.5 mole) of p-dibromobenzene dissolved in 500 ml. of tetrahydrofuran at ambient temperature was added over 4 hrs. small increments of the magnesium turnings (12.1 g., 0.5 g-atom). Although the mixture turned dark-green in color, no solids or magnesium turnings were observed.

Addition of 102.9 g. (0.465 mole) of diphenylchlorophosphine and workup as described above yielded a yellow syrup, n_D^{20} 1.6666. During the distillation of a small sample (3 ml.) of this liquid at 10^{-4} mm., an initial sublimate was observed at about 90-100° C. (oil bath temperature) and was assumed to be excess p-dibromobenzene. It was sublimed from the distillation apparatus before continuing the distillation. A colorless, viscous distillate was then obtained at an oil bath temperature of 165-175° C. at approximately 10^{-3} mm. of pressure. Anal. calcd. for $C_{18}H_{14}BrP$: Br, 23.42; P, 9.08; M.W., 341.2. Found: Br, 22.9; P, 9.04; M.W., 329; n_D^{20} 1.6741. After standing for 36 hrs., the distillate solidified to a white, waxy solid. Infrared comparison of the distillate with the crude, yellow oil showed essentially the same spectra but with less P-O and a sharper spectrum for the distilled p-bromophenyldiphenylphosphine.

The remaining oil was dissolved in ether, filtered to separate a tan powder which was moisture sensitive, and then the ether was concentrated on a Rinco evaporator at reduced pressure. The oily residue was attached to a vacuum system at about 0.5 mm. pressure and heated in boiling water to remove excess p-dibromobenzene. Infrared inspection of the residual oil showed it to contain less P-O absorption and to have a generally sharper spectrum. A molecular value of 313 was obtained for this liquid residue. After standing for 24 hrs., the yellow oil, 125.5 g. (0.368 mole, 79.1%), solidified to a yellow-white crystalline mass.

In a similar manner, 11.4 g. (0.47 g-atom) of magnesium was added in portions to 130 g. (0.55 mole) of p-dibromobenzene in 600 ml. of tetrahydrofuran. The addition of 101.9 g. (0.462 mole) of diphenylchlorophosphine to the Grignard solution was carried out at -10° C. After work-up, extraction of the residual oil with ether precipitated 40.9 g. of the tan, moisture sensitive solids. After removal of the ether and excess p-dibromobenzene as described above, the yellow oil weighed 103.3 g. and slowly solidified over a week to a yellow, semi-crystalline mass. Anal. Found: Br, 22.2; P, 8.74; M.W., 330; n_D^{20} 1.6724. Infrared examination indicated a considerable amount of P-O material as evidenced by the increased absorption at 8.30μ.

Further purification of the crude yellow solid was made by adsorption chromatography on activated alumina. A large burette (215 ml. capacity) was filled to the 200 ml. mark with 190 g. of alumina which had been dried in an oven at 130° C. for 1.5 hrs. Hexane was used to fill the column before 12 g. of the crude material dissolved in 10 ml. of benzene was added. A 1:1 benzene-hexane mixture was then used to elute the column and the course of elution was followed by the index of refraction of the elutrate. Fractions containing: (a) 1.8 g., (b) 6.3 g. ($n_D^{21.8}$ 1.6680), (c) 0.5 g., and (d) 0.2 g. were isolated which is a 73.3% recovery. Fractions 1,2, and 3 solidified on standing to white solids. Infrared examination of fraction 2 indicated the absence of absorptions due to any P-O containing compounds. Anal. Found: Br, 24.4; P, 7.05; M.W., 338. Fraction 2 melted over the range 63-67° C. An additional 44.5 g. quantity of the crude product was then dissolved in benzene and placed on the column and the column then was eluted with 1:2 benzene-hexane. Fractions containing: (e) 15.8 g. ($n_D^{21.8}$ 1.6655), (f) 10.3 g., and (g) 1.5 g. of pale-yellow oil were obtained. This corresponds to only 62% recovery. Fractions e and b solidified to pale-yellow-white crystalline masses. These solids could then be crystallized from ethanol-water to yield a white solid, m.p. 73-75° C. Anal. calcd. for $C_{18}H_{14}BrP$: C, 63.36; H, 4.14. Found: C, 63.52; H, 4.34.

(3) Synthesis from p-Bromophenyldichlorophosphine (XI) (1943-63)

Under a nitrogen atmosphere p-bromophenyldichlorophosphine (p-bromophenylphosphonous dichloride), 4.16 g. (0.016 mole), and 10 ml. of anhydrous ethyl ether were placed in a 250 ml. flask. Phenylmagnesium bromide, 7.25 g. in 15 ml. ether was slowly added through an addition funnel. Although a slight exothermic reaction was observed, no cooling was necessary. Some solid settled out during the addition. The reaction mixture was cooled to room temperature before saturated ammonium chloride solution was added. After separation of the solids and extraction with ether, the organic extracts were dried over anhydrous sodium sulfate overnight. The solvents were removed at reduced pressure to yield 2.1 g. of white solid with a m.p. of 141-143°C. The infrared spectrum showed absorption bands at 8.40μ and 8.95μ which suggested that the product was a phosphine oxide. This spectrum was almost identical to that obtained for the p-bromophenyldiphenylphosphine oxide obtained in the previous experiment. A molecular weight determination of 354 (theory, 357) confirmed that this was the same oxide.

d. 3-Bromophenyldiphenylphosphine (XV) (1935-59 and 1945-46)

To a solution of 66.5 g. (0.282 mole) of m-dibromobenzene and 250 ml. of tetrahydrofuran were added small portions, over 2.5 hrs., of 6.85 g. (0.282 g-atom) of magnesium turnings. After 0.5 hr. at reflux, the reaction mixture was cooled to room temperature to give a clear, dark-green colored solution with all of the magnesium reacted. A solution of 62.3 g. (0.282 mole) of diphenylchlorophosphine dissolved in 100 ml. of tetrahydrofuran was then added slowly to the mono-Grignard solution. As the reaction progressed, the color gradually turned to a light tan. The reaction mixture was then refluxed for 1 hr. and cooled to room temperature before 50 ml. of saturated ammonium chloride solution was added. The organic phase was separated from the solids and concentrated to give 100 g. of a brown-colored liquid residue (n_D^{20} 1.6447) which did not solidify on standing.

A 7.0 g. portion of the oil was eluted through a column of alumina by means of 1:2 benzene-hexane to yield 5.0 g. of turbid, colorless liquid, n_D^{20} 1.6564. Anal. calcd. for $C_{18}H_{14}BrP$: Br, 23.42; P, 9.08; M.W., 341.2. Found: Br, 29.0; P, 8.43; M.W., 324. A second sample (~ 3 ml.) was distilled in a microdistillation apparatus at 165-170°C. and 0.005 mm. to give a colorless oil, n_D^{20} 1.6655. Anal. calcd for $C_{18}H_{14}BrP$: C, 63.37; H, 4.14. Found: C, 64.01; H, 4.54; Br, 22.7; P, 9.67; M.W., 333. The infrared spectra of both fractions were essentially identical with the spectrum of the distilled sample being somewhat more sharp. Neither of the spectra contained absorptions which would appear to be due to P-O absorption.

Further purification of the yellow liquid residue was attempted by means of a distillation through a short Vigreau column at about 0.01 mm. of pressure. A 56.9 g. quantity of the crude material gave the following fractions: (1) 10.8 g. of colorless liquid, b.p. 37-38°C., $n_D^{18.5}$ 1.6055, which was m-dibromobenzene (0.0458 mole, 16.2% of the starting m-dibromobenzene); (2) 1.4 g. to 96°; (3) 5.7 g. to 140°; (4) 9.2 g. at 131-143°C., $n_D^{18.8}$ 1.6724; (5) 9.0 g. at 143-145°C., n_D^{20} 1.6738; and (6) 1.4 g. at 143-173°C. A clear, brown-colored residue which was very viscous remained in the distillation flask.

The infrared spectrum of fraction 1 was identical to that of the starting m-dibromobenzene. Examination of fractions 4 and 5 by infrared indicated very little P-O contamination. Analysis of fraction 5: calcd. for $C_{18}H_{14}BrP$: Br, 23.42; P, 9.08; M.W., 341.2. Found: Br, 22.5; P, 10.1; M.W., 327.

The distillation residue was also examined by infrared spectroscopy which revealed strong absorptions associated with the P-O. Attempted crystallization of this residue was not successful.

e. Carbonation of MonoGrignard Reagents from meta- and para-Dibromobenzene (1945-53,54)

In similar experiments, 11.8 g. (0.05 mole) of meta- and para-dibromobenzene were dissolved in 80 ml. each of tetrahydrofuran under nitrogen. Small portions of the magnesium turnings, 1.2 g. (0.05 mole), were added over 3.5 and 6 hrs., respectively. In each experiment there was noted an initial formation of white solids (~ 5-10 min.) which then dissolved in the yellow-brown colored reaction mixture.

The addition of small pieces of solid carbon dioxide resulted in an exothermal reaction. This addition was continued until the reaction had subsided. The solvent was removed at reduced pressure before 20 ml. of water and 5 ml. of concentrated hydrochloric acid was added to the residual syrup. The resulting solids were filtered, washed with water, and vacuum dried briefly at 100°C. (~ 0.5 hr.) and 0.5 mm. and then for 18 hrs. at ambient temperature. In both runs, a strong odor of dibromobenzene was noted and during the drying at 100°C., these starting materials sublimed and distilled to the cooler portions of the drying pistol.

The crude acids were then redissolved in a slight excess of sodium hydroxide, treated with activated charcoal, filtered to remove any non-basic fractions and reacidified with concentrated hydrochloric acid to yield voluminous precipitates. Pertinate data for these experiments are shown in Table I. The low bromine values and wide melting ranges point to a significant

TABLE I

ACIDS OBTAINED ON CARBONATION OF
MONOGRIGNARD REAGENTS OF DIBROMOBENZENES

Acid	Yield of Acid, %	Melting Point		% Bromine		Melting Point of Dicarboxylic Acids
		Found	Reported	Found	Theory	
XVI a	78	240-260°	251-253°	34.1	39.75	Terephthalic acid, sublimes ~ 300°
XVI b	50	145-250°	155°	32.6	39.75	Isophthalic acid, 312-314°

contamination by the benzenedicarboxylic acids resulting from diGrignard formation.

The acid mixtures were then extracted with ether in an effort to separate the more soluble bromobenzoic acids from the contaminating phthalic acids XVIIa and b. The results are shown in Table II. During the drying of the ether soluble acids at 100° C. and 1 mm. of pressure it was noted that a very small quantity of a white sublimate was recovered, only enough for melting point determinations. The melting range of roughly 108-117° C. would suggest that these sublimates might be benzoic acid. Benzoic acid could result from the partial hydrolysis of any diGrignard reagent formed during the carbonation. The possibility that these sublimates are, instead, bromophenols is ruled out because of their very low melting points.

TABLE II

ACIDS OBTAINED VIA ETHER EXTRACTION

Acid	Percent Extracted	M.P., °C. Found	Percent Bromine	Neutralization Equivalent	
				Found	Theory
XVI a	82.1	251-53 but not clear to 285°	37.5	193	201
XVI b	80	145-150, solidified, remelted 155-195°	35.1	185	201

f. Separation and Purification of Tertiary Phosphines

A 100 ml. burette was filled to the 100 ml. level with 80-200 mesh activated alumina which had been oven-dried at 130° C. for 2 hrs. The column was filled with n-hexane before the compound(s) in benzene was placed on the column. Initial elution was with 1:1 benzene-hexane. After the phosphine had ceased to be collected (via index of refraction), the column was stripped with tetrahydrofuran or benzene.

TABLE III

SEPARATION OF TERTIARY PHOSPHINES ON ALUMINA

Run	Mixture	1st Recovery	2nd Recovery
1943-68	2.37 g. $(C_6H_5)_3P^a$	2.20 g.[a]	-
	2.01 g. $(C_6H_5)_3PO^c$	-	2.0 g.[c]
1943-71	2.0 g. $(C_6H_5)_3P^a$	2.0 g.[a]	-
	2.0 g. $(C_6H_5)_3PS^d$	-	2.0 g.[d]
1943-74	2.0 g. $(C_6H_5)_3P^a$	2.4 g.[b]	-
	2.0 g. $(C_6H_5)_2P(O)NP(C_6H_5)_3$	-	None

(a) Melting point 80-82.5° C; (b) melting point 79-90° C; (c) melting point 154-156° C; (d) melting point 160-161° C.

4. Preparation of Azides

a. Attempted Synthesis of P-Hexamethyl-B,B′-diazidotriborophane (XLI) (1935-34)

A slight excess of sodium azide, 0.78 g. (0.012 mole), was added at ambient temperature to a stirred solution of 1.9 g. (0.005 mole) of P-hexamethyl-B,B′-dibromotriborophane (XL). At the end of 6 hrs., no azide was indicated by infrared spectroscopy. The mixture was then stirred for 72 hrs. at ambient temperature before a second infrared examination again showed no absorption due to the azide function. After 4 hrs. at reflux, no azide was again found in the infrared spectrum of the mixture but evolution of a gas was observed and was assumed to be nitrogen. The heating was continued, however, with the development of a yellow-orange color, now observed. After 7 hrs., gas evolution had stopped at about 100 cc. and still no azide absorptions were observed. These results suggest that decomposition of the azide was occurring more rapidly than the substitution reaction. No attempt was made at this time to identify the products of this unknown reaction.

b. Preparation of Diphenylphosphonyl Azide in Solvents Other Than Pyridine (1945-28,29,30,31; 1935-63)

In similar experiments, 2.4 g. (0.01 mole of diphenylphosphonyl chloride and 0.8 g. (0.012 mole) of sodium azide were stirred at ambient temperature in 35 ml. of solvent. The reaction was followed by observing the azide absorption at about 4.65μ. And where appropriate, reaction with triphenylphosphine was used to check the spectral evaluation.

TABLE IV

AZIDE FORMATION IN VARIOUS SOLVENTS

Time Hrs.	Azide Absorbance at 4.65μ			
	3,4-Lutidine	2,6-Lutidine[a]	α-Picoline	γ-Picoline[b]
0	-	-	-	-
2.5	Trace	Trace	0.48	0.26
4	-	Trace	0.48	-
6	0.094	Trace	0.48	0.475
11	0.18	-	-	-
22	0.30	-	(c)	-
31	0.33	-	-	-
72	-	0.42	-	-

Yield of diphenylphosphonimidotriphenylphosphorane: (a) 64.6%; (b) 89.6% of brown-colored product; (c) green-colored reaction mixture.

(1) Hexamethylphosphoric Triamide (1943-23,24)

A mixture of 4.8 g. (0.02 mole) of diphenylphosphonyl chloride, 1.3 g. (0.02 mole) of sodium azide, and 25 ml. of hexamethylphosphoric triamide (HPT) were stirred for 24 hrs. Samples withdrawn periodically for infrared examination showed erratic azide absorbances and are not shown as a result. After 24 hrs., the mixture was filtered under nitrogen pressure through a fine-glass sintered funnel. This clear solution was slowly added to 5.2 g. (0.02 mole) of triphenylphosphine. As there was no immediate nitrogen evolution, the reaction was heated to 90°C. to cause reaction. After 8 hrs. only about 41.5% of the expected nitrogen had been collected.

Dilution with water and ammonium hydroxide precipitated a yellow solid which was washed with ether to give 2.2 g. (~ 23.2%) of very impure diphenylphosphonimidotriphenylphosphorane, m.p. 135-138°C. (lit.,[24] m.p. 170-171°C.). From the ether wash were recovered 1.5 g. (0.0057 mole, 28.5%) of triphenylphosphine while acidification of the aqueous phase with concentrated hydrochloric acid yielded 3.0 g. (0.00137 mole, 6.8%) of diphenylphosphonic acid, m.p. 194-196°C.

(2) Benzene/Pyridine Mixtures (1943-159,160,163, and 1964)

Into a three-necked 100 ml. flask fitted with a condenser, gas inlet tube and septum was placed sodium azide, 1.95 g. (0.030 mole, 20% excess) in 50 ml. benzene. The mixture was stirred under a nitrogen atmosphere for 15 minutes before 6.0 g. (0.025 mole) of diphenylphosphonyl chloride was introduced through the septum by means of a syringe. To this reaction mixture 1.97 g. (0.025 mole) of pyridine was added. The mixture was stirred under static nitrogen atmosphere at room temperature, sampled periodically over 8 hrs. for infrared examination, and then allowed to stir overnight before addition of the triphenylphosphine was begun.

To the above reaction mixture, without filtering off the inorganic salts 6.55 g. (0.025 mole) of triphenylphosphine in 15 ml. of benzene was added. The conversion was found to be 63% based on the yield of the phosphorane.

Experiments using 2:1, 3:1, and 4:1 ratios of pyridine to diphenylphosphonyl chloride were similarly carried out and the results are shown in Table V.

(3) Pyridine/Dimethylformamide (1943-17)

The azide was prepared in the same manner as described in previous experiments. The inorganic salts, sodium chloride and azide, were filtered from the reaction mixture under nitrogen pressure. To the pink-colored filtrate was added 50 ml. freshly distilled DMF before the pyridine was removed from the mixed solvents under vacuum. The estimated quantity of the azide was 6.80 g. (0.028 mole).

TABLE V

AZIDE AND PHOSPHORANE FORMATION IN BENZENE/PYRIDINE SOLVENT

Mole Ratio				Azide Formation	Nitrogen Evolution	Phosphorane Formation[b] %
Pyridine: $(C_6H_5)_2P(O)Cl$	Pyridine (mole)	$(C_6H_5)_2P(O)Cl$ (mole)	Benzene (ml)	After 6 Hours[a]	at Midpoint of Theoretical Volume, hrs	$(C_6H_5)_2P(O)=N(C_6H_5)_3$
1:1	0.025	0.025	50	0.30	3.5	63
2:1	0.050	0.025	50	0.75	2	88
3:1	0.075	0.025	50	0.45	2.5	67
4:1	0.100	0.025	50	0.63	2	58

(a) Absorbance at 4.68μ; (b) Isolated yield.

The above solution was then added at ambient temperature to 6.24 g. (0.014 mole) of 1,4-bis(diphenylphosphino)benzene (IVa) in 25 ml. of dimethylformamide. After 5 hrs., although only 83% of the nitrogen had been collected, an infrared spectrum of the reaction mixture did not contain an azide absorption at 4.65µ.

Removal of the solvent at reduced pressure gave 14.1 g. of a yellow-colored, tacky residue. Washes with 50 ml. of ether, 50 ml. of dilute ammonium hydroxide solution, and 50 ml. of distilled water then gave 12.0 g. (0.0137 mole, 97.9% yield) of a cream-colored solid. An analytical sample recrystallized from isopropyl alcohol and water melted at 233-235° (reported[32] m.p. 233-235°C.). Anal. calcd. for $C_{54}H_{44}P_4N_2O_2$: P, 14.13; N, 3.20. Found: P, 13.7; N, 3.01.

c. Attempted Preparation of Phenylphosphonyl Diazide in Pyridine/Dimethylformamide (1943-19)

A mixture of 5.7 g. (0.029 mole) of phenylphosphonyl dichloride and 3.8 g. (0.058 mole) of sodium azide in 50 ml. of pyridine was stirred for 24 hrs. at ambient temperature before it was filtered to remove sodium chloride. After about one-half of the pyridine had been removed at reduced pressure, 50 ml. of DMF was introduced and concentration was resumed. An hour later an additional 25 ml. of DMF was added. Shortly thereafter it was observed that the reaction solution was bubbling. The mixture also slowly changed from yellow to a deep-red color.

When no more bubbles were observed (3 hrs.), the mixture was sampled for infrared examination. There was no azide absorption at 4.65µ at this point and the solution was not studied further at this time.

5. Preparation of Phosphorane Prototypes

a. Diphenylsilyl-bis(imidotriphenylphosphorane) (XXVI)

(1) In Situ Synthesis (1935-27)

To a mixture of 2.6 g. (0.04 mole) of sodium azide and 10.5 g. (0.04 mole) of triphenylphosphine in 200 ml. of refluxing pyridine was slowly added a solution of 5.2 g. (0.02 mole) of diphenylsilyl dichloride in 20 ml. of pyridine. The nitrogen evolved was 828.5 cc. (92.5% of theory). The initially green-colored reaction mixture turned to a pink color on standing overnight. Examination of the mixture at this point by infrared spectroscopy showed no azide absorptions at about 4.65µ. The yellow-colored, gummy residue obtained on removal of the solvent at reduced pressure was dissolved in hot benzene and isopropyl alcohol was added to precipitate an off-white solid. Recrystallization from benzene-isopropyl alcohol yielded 7.4 g. (0.010 mole, 50% yield) of white, crystalline diphenylsilyl-bis(imidotriphenylphosphorane), m.p. 191.5-193°C. (lit.,[20] m.p. 194-195°C.).

A 0.4597 g. quantity of the bis-phosphorane was stirred at ambient temperature for 16 hrs. in aqueous pyridine. After filtration and drying, 0.4511 g. (98.1%) of the white XXXVI, m.p. 192-193.5°C. was recovered. A second quantity was heated on a steam bath for 2 hrs., cooled, filtered, and vacuum dried. The recovered product, m.p. 192-193.5°C., weighed 0.3975 g. (92.9%). The loss here was attributed to mechanical losses.

(2) Stepwise Synthesis (1945-4)

One hundred ml. of pyridine and 2.6 g. (0.041 mole) of sodium azide were placed in a 300 ml. round-bottom flask fitted with a condenser, addition funnel, and sampling septum and attached to a nitrogen collection system. Then 10.9 g. (0.041 mole) of diphenylsilyl dichloride was added through the septum by means of a syringe. After stirring overnight at ambient temperature, the mixture was sampled for infrared examination. A strong azide asymmetric stretching absorption at 4.64µ and a medium azide symmetric absorption at 7.57µ were observed.

Subsequently, 10.8 g. (0.041 mole) of triphenylphosphine dissolved in 25 ml. of dry pyridine was added so as to maintain a study evolution of nitrogen. A total of 921 cc. of nitrogen was collected which corresponds to a yield of 102.6%. Infrared examination at this point showed only a very weak azide absorption at 4.68µ and a stronger, broader doublet at 7.38 and 7.70µ, due to P=N had replaced the symmetric azide absorption. A 35 ml. quantity of the reaction solution was withdrawn for use in studying the chemistry of the intermediate chlorophosphorane XXXIV.

Assuming that approximately 25% of the chlorophosphorane had been removed, 2 g. (0.03 mole) of sodium azide was then added to the reaction mixture. Infrared examination of the red-colored reaction mixture after 4 and 6 hrs. showed no increase in the azide absorbance at 4.68µ after 4 hrs. Another 35 ml. quantity of the reaction solution was removed in order to study the chemistry of the azidophosphorane XXXV and to compare it with the preceding chlorophosphorane XXXIV.

To the remaining pyridine solution of the azidophosphorane XXXV (about 0.02 mole) at gentle reflux was slowly added 5.2 g. (0.02 mole) of triphenylphosphine in enough pyridine to give 25 ml. of solution. The reaction evolved 456 cc. of nitrogen (101.8% of theory) and was pale-yellow in color. Although on cooling, the red color returned, after standing over the week end, the mixture had again become yellow in color.

The pyridine was removed at reduced pressure to give a yellow-green residue which was washed with ether and dilute ammonium hydroxide. After drying, 12.5 g. (0.17 mole, 85% yield) of the crude bis-phosphorane was obtained.

Digestion of a 1.1 g. quantity of the crude product with 10 ml. of isopropyl alcohol gave 0.8 g. bis-phosphorane melting at 192-194°C. (lit.,[20] m.p. 194-195°C.).

b. P,P'-Bis(diphenylphosphonimido)-4,4'-bis(diphenylphosphino)biphenyl (XLVIII) (1887-177,185)

The reaction of 2.4 g. (0.1 mole) diphenylphosphonyl azide (XXX) with 2.6 g. (0.05 mole) of 4,4'-bis(diphenylphosphino)biphenyl (II) in 30 ml. of toluene at reflux resulted in the evolution of only about 86% of the theoretical quantity of nitrogen. The addition of about 0.3 ml. of additional azide did not cause additional nitrogen evolution.

Removal of the solvent at reduced pressure gave a tacky, off-white solid. The material became more granular after washing with dilute ammonium hydroxide and drying at reduced pressure and had a melting range of 120-200° C. (reported[33] m.p. 241-243° C.). Recrystallization of the crude bis-phosphorane from acetonitrile resulted in a white powder which still had a wide melting range, 140-190° C. However, infrared examination of this material showed that the principle absorptions at 6.97(m), 8.0(sb), 8.56(s), 8.96(vs) and 12.25μ were identical to those of the previous preparation.[33]

Anal. calcd. for $C_{60}H_{48}N_2O_2P_4$: C, 75.62; H, 5.08; N, 2.94; P, 13.0. Found: N, 2.99; P, 12.2.

In a second run, the addition of 3.4 g. (0.014 mole) of diphenylphosphonyl azide to 3.7 g. (0.007 mole) of 4,4'-bis(diphenylphosphino)-biphenyl (II) in 35 ml. of refluxing pyridine resulted in the evolution of 279 cc. (313 cc. theory, 89.1%) of nitrogen after 1.5 hrs. An infrared examination of the pyridine reaction mixture at this point indicated a weak azide absorption at 4.64μ.

After cooling to room temperature and standing for about 1 hr., a white precipitate began to form. After standing overnight, the solids were filtered and dried at reduced pressure to give 5.2 g. of white powder which melted and resolidified at about 170-175° C. and remelted at 238-242° C. Recrystallization from acetonitrile provided a white, crystalline powder, m.p. 241-242° C., reported[33] m.p. 241-243° C., (sealed tube, uncorrected) which was used for thermogravimetric analysis. Anal. Found: C, 75.91; H, 5.35.

c. N,N'-[p-Phenylene-bis(diphenylphosphoranylidyne)]-bis(P-azido-P-phenylphosphonic Amide) (XLIVa)

(1) In Pyridine (1945-24 and 1943-115)

To a pink-colored pyridine solution of phenylphosphonyl diazide, prepared by stirring 3.1 g. (0.0162 mole) of phenylphosphonyl dichloride and 1.1 g. of sodium azide and 20 ml. of dry pyridine for 18 hrs. at room temperature, was added a slurry of 3.6 g. (0.0081 mole) of 1,4-bis-(diphenylphosphino)benzene (IVa) and 50 ml. of pyridine. The initial reaction rate is rapid and exothermic and essentially complete in 0.5 hr. The nitrogen collected was 356 cc. (98.1% of theory). Infrared examination of the reaction mixture at this point showed a strong asymmetric azide stretching at 4.70μ as well as P=N absorption at 8.0μ. The spectrum was identical to that previously obtained for phenylazidophosphonimidotriphenylphosphorane (XLII) in pyridine solution.[22]

Attempted isolation by pouring a portion of the reaction mixture into ice water resulted in only partial solidification of the resulting oil. Filtration of the solid-oil suspension gave 0.9 g. of a white solid which was vacuum dried at 100° C. for 1 hr. Infrared inspection of the solid now showed strong absorptions at 4.72μ ($-N_3$), 7.75-8.0μ (P=N), 8.37μ (P-O), and at 9.00μ ($=P(O)-C_6H_5$). There was not any evidence for hydrolytic products as shown by the lack of any absorption at 10.3-10.65μ. This spectrum was also essentially that of the previously isolated azidophosphorane XLII.

The remaining pyridine solution was first filtered under dry nitrogen pressure to remove sodium azide and sodium chloride and then concentrated at reduced pressure to give a friable, tan-colored powder. However, on drying at 100° C., the material melted and formed a glass on cooling which was found to melt at 65-70° C. A molecular weight value of 880 (theory, 807; 109%) was obtained for this fraction. The total yield of crude diphosphoranediazide XLIVa was 6.9 g. Attempted crystallization from various solvents has resulted in oils which would not crystallize.

In the second experiment, to approximately 16.6 g. (0.08 mole) of phenylphosphonyl diazide (XLIII) dissolved in 240 ml. of pyridine was slowly added 14.7 g. (0.033 mole) of 1,4-bis(diphenylphosphino)benzene (IVa) slurried in 120 ml. of pyridine. After only two hours, 1475 cc. (quantitative) of nitrogen was collected. Infrared inspection showed a strong azide absorption at 4.72μ. After the salts had been removed by filtration through a fine glass sintered funnel, removal of the pyridine at reduced pressure gave a syrup-like, amber-colored residue. Addition of ether to the residue precipitated a yellow-colored tacky residue and the liquid phase became cloudy. The ether layer was decanted and washed with dilute ammonium hydroxide which caused a white solid to separate from the ether phase. After filtration, washing with water, and vacuum drying, 5.1 g. of white solid melting at 136-138° C. was isolated. The infrared spectrum of this material showed a strong azide at 4.72μ as well as the typical phosphorane spectrum from 7-9μ. In addition, there was a marked absence of any absorption at 10.4-10.9μ which might have been ascribed to POP absorption as a result of hydrolysis. A molecular weight determination in benzene using the Neumeyer method gave a value of 821 (theory 806).

Similar treatment of the yellow, tacky fraction resulted in the isolation of 18.0 g. of light-yellow colored solids with a melting range of 125-130° C. This material had a very similar infrared spectrum which however contained an absorption at 10.8μ due POP. Further purification was achieved via recrystallization from a water-ethanol-pyridine to yield white, hydrolysis product free, XLIVa, m.p. 144-146° C., in only 30% recovery.

Anal. calcd. for $C_{42}H_{34}O_2N_8P_4$: C, 62.54; H, 4.25; N, 13.89; P, 15.36. Found: C, 61.70; H, 5.75; N, 4.42; P, 15.60.

The solvents were concentrated, treated with dilute ammonium hydroxide and filtered to remove insolubles. Acidification with concentrated hydrochloric acid precipitated white solid XLIVb which melted over the range 245-254° C. The infrared spectrum of this material was very similar to the spectrum of the previously prepared and identified acid XLV.

Anal. calcd. for $C_{42}H_{36}O_4N_2P_4$: N, 3.70; P, 16.38. Found: N, 3.4; P, 16.4.

(2) In Benzene/Pyridine Solvent (1972-2)

The phenylphosphonyldiazide (0.065 mole), prepared in the benzene/pyridine solvent system with a molar ratio of 2:1 for the pyridine and phenylphosphonyldichloride, was reacted with one-half equivalent of 1,4-bis(diphenylphosphino)benzene in benzene at room temperature. It took about three hours to complete the nitrogen evolution (98.5%). The mixture was filtered and the solvent removed from the filtrate under reduced pressure to yield a pale-yellow solid. It was washed several times with ethanol to yield white XLIVa with the melting range of 126-130° C. The yield was quantitative. The infrared spectrum resembled the spectrum of pure compound prepared in pyridine.

Anal. calcd. for $C_{42}H_{34}O_2N_8P_4$: P, 15.34%. Found: P, 15.5.

Several additional preparations of XLIVa were carried out in a similar manner to provide material for the other studies.

d. N,N‴-Bis(triphenylphosphoranylidene)-N′,N″-[p-phenylene-bis(diphenylphosphoranylidyne)]-bis(P-phenylphosphonic diamide) (XLVII)

(1) In Toluene (1945-33)

A 3.9 g. (app. 0.00483 mole) quantity of the crude bis-azidophosphorane XLIVa was partially dissolved in 20 ml. of toluene and brought to refluxing before the addition of 2.5 g. (0.00954 mole) of triphenylphosphine dissolved in 30 ml. of toluene was begun. After 8.5 hrs., the nitrogen collected was only approximately 180 cc., only 84% of theory. The mixture was sampled for infrared examination at this point. The azide absorption at 4.70μ was now absent but typical phosphorane absorptions were present at 7.5-8.1, 8.3, 8.5, and 9.0μ.

The toluene was decanted from solids on the wall of the reaction flask and concentrated to yield an off-white colored residue which weighed 5.4 g. The infrared spectrum contained the expected absorptions as well as probably POP absorption at 10.4-10.95μ. A 3.0 g. quantity of this material was dissolved in benzene and refluxed with activated charcoal for 0.5 hr. After filtration to remove the charcoal the benzene was removed by means of a Rinco evaporator and water aspirator pressure to give 1.1 g. friable, white solids. The infrared spectrum of this fraction was unchanged from that of the crude reaction product. Anal. calcd. for $C_{78}H_{64}O_2N_4P_6$: N, 4.39; P , 14.57; M.W. 1275. Found: N, 3.30; P, 13.7; M.W., 826.

Ether was stirred with the solids on the wall of the reaction flask for 4 hrs. to give 1.4 g. of a white powder which melted over the range 114-180° C. These solids also had an infrared spectrum which was similar to those of the previous fractions. Comparison with the spectrum of the previously prepared[23] acid-phosphorane XLV shows that the absorption at 10.7-10.95μ which was thought to be due to a POP absorption was also present in XLV. Due to the grossly impure nature of this tetraphosphorane as evidenced by the wide melting point range, infrared spectra, and elemental analyses, this synthesis was repeated using more pure bis-azidophosphorane XLIVa.

(2) In Pyridine (1943-153)

A 2.6 g. (0.01 mole) quantity of triphenylphosphine in 30 ml. of pyridine was brought to reflux before 4.0 g. (0.005 mole) of the bis-azidophosphorane XLIVa in 10 ml. of pyridine was slowly added. The nitrogen collected was 215 cc. (96% of theory). Removal of the solvent at reduced pressure and work-up yielded 5.8 g. (0.00454 mole, 90.8%) of light-yellow crystals melting at 101-103° C. Anal. calcd. for $C_{78}H_{64}O_2N_4P_6$: N, 4.39; P, 14.57. Found: N, 3.70; P, 14.3.

e. N,N′-[p-Biphenylene(diphenylphosphoranylidyne)]-bis(P-azido-P-phenylphosphonic Amide) (XLVI)

(1) In Pyridine (1945-50)

A mixture of 2.0 g. (0.031 mole) of sodium azide, 3.1 g. (0.0157 mole) of phenylphosphonyl diazide, and 50 ml. of pyridine were allowed to stir at ambient temperature for 18 hrs. The addition of 4.1 g. (0.0078 mole) of 4,4′-bis(diphenylphosphino)biphenyl suspended in 100 ml. of pyridine was carried out in increments over 2.5 hrs. The rate of nitrogen evolution was very slow at ambient temperature. After 3.25 hrs., an infrared examination of the reaction mixture showed an intense azide absorption at 4.72μ. An additional 0.8 g. of sodium azide and 0.4 ml. of phenylphosphonyl dichloride was added to the reaction after 6 hrs.

After stirring for 72 hrs. at ambient temperature the nitrogen evolved was only 300 cc. (not corrected, theory 352 cc.) and the solution infrared spectrum was essentially the same as that of the earlier sample.

Approximately 48 cc. of the reaction solution was withdrawn and concentrated at reduced pressure to give a tacky, green-colored residue. The addition of ether precipitated a white solid which was examined in the infrared and was found to have a strong azide absorption at 4.73μ, phosphorane absorptions at 7-8.2μ, phenyl-PO at 8.75μ as well as a possible P-O-P absorption at 10.75. There was no evidence for other acid absorptions in the 4-6μ region or for 1,4-disubstitution at 12.2μ.

This reaction was discontinued as a result of the more promising of results obtained via the mixed solvent method (see below).

(2) In Benzene/Pyridine Solvent (1943-170,171)

The phenylphosphonyl diazide (0.03 mole) prepared in the benzene/pyridine solvent system with a molar ratio of 2:1 for the pyridine and phenylphosphonyl dichloride, was reacted with one-half equivalent (7.8 g., 0.015 mole) of 1,4-bis(diphenylphosphino)biphenyl (II) in benzene at room temperature. It took about one and one-half hours to complete the nitrogen evolution. It was filtered and the solvent was removed from the filtrate to yield a pale-yellow solid with a melting range of 180-200° C. The yield of this crude product was quantitative. It was then washed several times with acetone to yield a white XLVI (75% yield) with a melting point of 210-212° C. The infrared spectrum resembled the spectrum of the product made in pyridine including a strong azide absorption in the region of 4.70μ. Anal. calcd. for $C_{48}H_{38}O_2N_8P_4$: P, 14.03%. Found: P, 14.1.

6. Preparation of Phosphorane Polymers

a. Reaction of Phenylphosphonyl Diazide and 4,4'-Bis(diphenylphosphino)biphenyl (1887-187 and 1943-107)

A mixture of 1.15 g. (0.0059 mole) of phenylphosphonyl dichloride and 0.77 g. (0.0118 mole) of sodium azide in 15 ml. of pyridine were allowed to stir at ambient temperature for 18 hrs. before the addition of 3.1 g. (0.0059 mole) of 4,4'-bis(diphenylphosphino)biphenyl (II) as a slurry in 35 ml. of pyridine was begun. The evolution of nitrogen was slow during the addition of the slurry. After the solids in the addition funnel were washed into the reaction flask with an additional 10 ml. of pyridine, the reaction mixture was brought to reflux and held there for 5.5 hrs. The nitrogen evolved was only 155 cc. (uncorrected, theory 264 cc.). Although the pyridine solution still contained azide (infrared absorption at 4.65μ), the pyridine was removed at reduced pressure to yield a tan-colored solid. The solid was washed with dilute ammonium hydroxide (25 ml. water to 5 ml. concentrated ammonium hydroxide), with water, filtered, and vacuum dried.

The tan powder, which weighed 3.9 g. (theory 4.0 g.), was found to have infrared absorptions due to azide at 4.70μ and probably P-O-P at 10.7-10.8μ as well as the typical phosphorane absorptions at 6.95, 7.5-8.6, and 8.98μ. A sample of this impure material was submitted for differential thermal analysis to provide reference data.

In a second preparation under similar conditions, 3.9 g. (0.019 mole) of phenylphosphonyl diazide (XLIII) and 9.9 g. (0.019 mole) of 4,4'-bis(diphenylphosphino)biphenyl (II) were reacted at reflux in pyridine. After removal of the salts and solvent, 12.0 g. of yellow-colored powder was isolated. After being dried at 100° C/0.5 mm., the solid softened at 165° C., foamed at 175° C., and melted at 225-230° C. The differential thermal analysis curve for this biphenylene linked polyphosphorane XLIXb contained an endotherm which began at 476° C. and peaked at 556° C. as well as an endotherm which began at about 187° C. and which peaked at 258° C. The infrared spectrum of this material contained all of the expected absorptions. A sample was also submitted for thermal gravimetric analysis.

From the salts filtered from the reaction mixture, an additional 1.4 g. of white solid was recovered after the salts had been dissolved in dilute ammonium hydroxide. This powder softened at 210-215° C. and appeared to decompose at 300° C. The infrared spectrum was similar to that of the first fraction.

b. Reaction of Phenylphosphonyl Diazide and 1,4-Bis(diphenylphosphino)benzene

(1) Sequential Reaction (1943-130 to 135)

In a 2000 ml. three-necked flask equipped with a condenser, septum, and addition funnel and which had been well dried and purged with dry nitrogen was placed 23 ml. of a pyridine solution containing 0.012 mole of phenylphosphonyl diazide. 1,4-Bis(diphenylphosphino)-benzene (IVa) 2.6 g. (0.006 mole) dissolved in 100 ml. of pyridine was added slowly, at ambient temperature, to the diazide solution. After two hrs., 250 cc. of nitrogen, 93% of theory, had been collected. A strong azide absorption was present at 4.72μ in the spectrum of the mixture.

Without isolation of the bis-azidophosphorane XLIVa, a second quantity of 1,4-bis(diphenylphosphino)benzene (IVa), 5.2 g. (0.012 mole, in 200 ml. of pyridine was slowly added to the reaction mixture and then allowed to stir at ambient temperature for 18 hrs. As only 30 cc. of nitrogen was collected during the period, the reaction mixture was brought to reflux in order to force the reaction to proceed. The nitrogen evolved was measured at 420 cc. in contrast to the theoretical volume of only 269 cc. The error can be ascribed to the difficulty in measuring volume expansion due to the heating of the reaction mixture. However, infrared inspection showed the absence of any azide absorption in the region 4.65-4.75μ.

Assuming that the previous reaction had proceeded as expected to the bis-tertiary phosphine terminated L, an additional 0.012 mole of phenylphosphonyl diazide (XLIII) in 23 ml. of pyridine was added within two minutes to the reaction mixture. As there was no evidence of nitrogen evolution, the reaction mixture was heated at 100° C. for 6 hrs. Then another 0.012 mole of 1,4-bis(diphenylphosphino)benzene (IVa) added directly to the reaction mixture. After 5.5 hrs. at a mantle temperature of 180° C., a total of 580 cc. (not corrected) was collected which agrees well with the theoretical value of 538 cc. The infrared spectrum of the reaction solution showed the absence of azide absorption at 4.65-4.75μ. After removal of the pyridine at reduced pressure, 17.0 g. of brown-colored solids, which softened at 120° and foamed at 155° C. were recovered. Further characterization is underway. *Anal.* calcd. for $C_{36}H_{29}ON_2P_3$: P, 15.49. Found: P, 14.2.

(2) In Situ in Pyridine (1943-102)

Under an atmosphere of dry nitrogen, a mixture consisting of 6.5 g. (0.1 mole) of sodium azide, 8.1 g. (0.041 mole) of phenylphosphonyl dichloride, and 75 ml. of pyridine were allowed to stir for 24 hrs. at ambient temperature. To the gently refluxing solution of the resulting phenylphosphonyl diazide (XLIII) was slowly added 18.3 g. (0.041 mole) of 1,4-bis(diphenylphosphino)benzene (IVa) in 150 ml. of pyridine. After 8 hrs. at reflux, about 1643 cc. (90% of theory) of nitrogen had been collected. Infrared inspection of the reaction mixture showed that there was no azide absorption at 4.7µ. After the by-product sodium chloride and excess sodium azide were removed by filtration, the pyridine was removed at reduced pressure to give 26.5 g. of a straw-colored solid. After drying at 100° C. and 0.5 mm. of mercury for two hours, the polyphosphorane softened at 145° C., foamed at 164° C., and melted at 200° C. *Anal.* calcd. for $C_{36}H_{29}N_2P_3$: N, 4.68; P, 15.52. Found: N, 3.89; P, 17.6. Differential thermal analysis indicated only a small exotherm beginning at about 406° C. which peaked at 429-438° C. and then an endotherm which peaked at about 527-537° C.

A second portion was heated at 140° C. and 10^{-3} mm. for 2 hrs. This sample now softened at 165-170° C., foamed at 190-230° C. and melted at 255-260° C. The differential thermal analysis curve was essentially the same as the above sample. *Anal.* Found: N, 3.89; P, 17.6.

(3) In Situ in γ-Picoline (1945-34)

A mixture of 16 g. (0.082 mole) of phenylphosphonyl dichloride, 11.8 g. (0.182 mole, 11% excess) of phenylphosphonyl dichloride, and 40 ml. of γ-picoline which was allowed to stir at ambient temperature for 72 hrs. became dark red-brown in color.

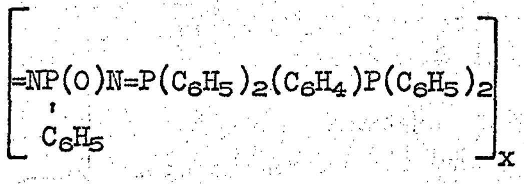
To a refluxing solution of 8.9 g. (0.02 mole) of 1,4-bis-(diphenylphosphino)benzene in 35 ml. of γ-picoline was slowly added 13 ml. of the above diazide solution. Although the evolution of nitrogen was essentially quantitative, infrared examination of the reaction mixture showed a weak azide absorption at 4.70µ. An additional 6.5 hrs. at reflux did not cause a decrease in the azide absorption. Twenty-five ml. (25 g.) of the reaction solution was withdrawn and the solvent removed at reduced pressure to give 5.8 g. of brown-colored powder which softened at 87° C. and partially melted and foamed to 160° C. A 2.8 g. portion of the powder was washed with two 15 ml. portions of ethyl ether, then dilute ammonium hydroxide solution, and water to give 2.7 g. of tan-colored powder after drying at 10^{-3} mm. and room temperature. *Anal.* calcd. N, 4.68; P, 15.52. Found: N, 4.59; P, 14.4. This fraction still contained a relatively strong azide absorption at 4.72µ (potassium bromide pellet). A 0.6291 g. sample of the unwashed powder was subsequently heated over the temperature of 110-220° C. during 3.5 hrs. The resulting dark-brown colored glass weighed 0.5684 g. and no longer contained any azide absorption at 4.70µ. The glass softened at 170-220° C. but did not flow to 240° C. Anal. Found: N, 4.47; P, 15.4.

As a result of the continued presence of azide absorptions in the various fractions obtained from the initial aliquot, small quantities of 1,4-bis(diphenylphosphino)benzene were added to a refluxing reaction mixture until there no longer was any azide absorption. Removal of the picoline solvent resulted in the isolation of 6.8 g. of a dark-brown colored powder. The infrared spectrum of this powder contained only a trace azide at 4.70µ as well as the typical phosphorane absorptions at 7-9µ. Anal. Found: N, 4.38; P, 14.4. A 2.6 g. portion of this powder was slurried with 25 ml. of benzene and refluxed for 3 hrs. The benzene was decanted from a tacky residue and concentrated to yield 1.6 g. (61.6%) of a tan-colored powder. When heated in the air on a watch glass, the powder softened at approximately 200° C. and was unaffected to 265° C. There was no fiber formation from the melt while the brown glass which formed on cooling did not adhere to the surface of the watch glass. Heating of a 2.2999 g. quantity of the crude polyphosphorane at 10^{-4} mm. from 95 to 205° C. for 2 hrs. resulted in the isolation of 2.1576 g. (93.8% recovery) of a brown glass. This recovery duplicated the result obtained from the heating of the first fraction of this polyphosphorane.

(4) In Pyridine/Dimethylformamide Mixture (1943-34)

Into a 500 ml., 2-necked flask equipped with a condenser and addition funnel 8.92 g. (0.020 mole) of 1,4-bis(diphenylphosphino)-benzene (IVa) in 100 ml. of DMF was placed. It was heated in a hot water bath until all solids were dissolved. A gas collecting device was then connected to the condenser before phenylphosphonyl diazide (XLII), 4.16 g. (0.020 mole), in 23 ml. of pyridine was added slowly through the addition funnel to the hot solution with stirring. Within 10 minutes 520 cc. of nitrogen gas was collected. After one hour an additional 100 cc. was collected. A total of 665 cc. (or 614 cc. at STP) of nitrogen gas (68% conversion) was collected over a period of 6 hrs. The infrared spectrum of the reaction mixture showed no azide absorption in the region of 4.65µ. The solvents were removed at reduced pressure to yield 13 g. of crude yellow-colored gummy polymer.

A portion of the gummy yellow solid was washed with acetone and filtered to isolate 2.8 g. white solid which decomposed at 275° C. To this filtrate water was added to precipitate 4.0 g. of a light-yellow solid which also decomposed at 272-275° C. The infrared spectra of both solids were identical and did not contain any absorption due the azide. Anal. calcd. for the unit of



$$\left[\underset{C_6H_5}{=NP}(O)N=P(C_6H_5)_2(C_6H_4)P(C_6H_5)_2 \right]_x$$

$C_{36}H_{29}P_3N_2O$: P, 15.5%; N, 4.70%. Found: P, 14.4%; N, 2.13%.

c. Reaction of 1,4-Bis(diphenylphosphino)benzene (IVa) and the Bis-Azidophosphorane (XLIVa)

(1) In Dimethylformamide (1972-9)

In a 250 ml. 3-necked flask fitted with a condenser, thermometer, and gas inlet and outlet tubes was placed 4.50 g. (0.01 mole) of 1,4-bis(diphenylphosphino)benzene (IVa) and 50 ml. of dimethylformamide. This solution was then brought to reflux under nitrogen before the addition of 8.0 g. (0.01 mole) of the bis-azidophosphorane XLIVa in 50 ml. of dimethylformamide was begun. The nitrogen evolved was 448 cc. (90.9% of theory).

After removal of the solvent at reduced pressure, the light-yellow colored tacky residue (~ 14 g.) was washed with distilled water and dried to give 12 g. (96% yield) of a white powder which softened at 125°, foamed at 205° and darkened at 245° C.

When the powder was placed in water and heated to about 65°, it balled to a gummy mass from which long fibers (brittle) could be pulled repeatedly. When the powder was placed in a small die and heated to 90° C. with about 4800 psi a clear, amber-colored disk was formed. However, this disk was also brittle. Anal. calcd. for $C_{36}H_{34}ON_2P_3$: N, 4.6; P, 15.5. Found: N, 3.7; P, 15.2.

(2) In Dimethylsulfoxide (1972-6)

A similar preparation run in dimethylsulfoxide at 85° C. resulted in only a 66% collection of the nitrogen. The powder, precipitated from the dimethylsulfoxide by the addition of water, was washed with ethyl ether to yield 8.5 g. (67% yield) of light-yellow colored powder. This powder softened at 85°, foamed at 98° to 130°, became clear at 170°, and darkened at 230° C. When placed in water at 65° C, long brittle threads could be drawn out. Anal. Found: N, 3.19; P, 14.6.

(3) In Hexamethylphosphoric Triamide (1972-11)

Since it had been observed that 1,4-bis(diphenylphosphino)-benzene (IVa) is oxidized in hexamethylphosphoric triamide at the reflux temperature, this run was carried out at 85° C. However, the nitrogen evolution was only 67.8% of theory and only 7.7 g. (61.5% yield) of polyphosphorane was isolated after washing with water and with ethyl ether. The powder softened at 95°, foamed at 125°, and darkened at about 250° C. Similar long, white, brittle fibers could be drawn from this product polyphosphorane. Anal. Found: N, 4.03; P, 14.3.

d. Reaction of Diphenylsilyl Diazide and 1,4-Bis(diphenylphosphino)benzene

(2) In Pyridine (1943-94)

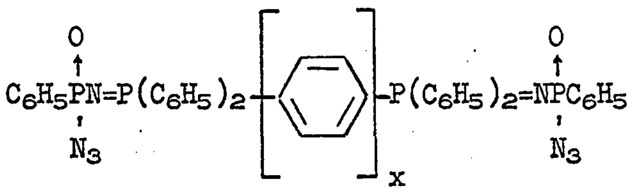
Into a 3-necked, 500 ml. flask equipped with condenser, rubber septum, and addition funnel were placed 3.12 g. (0.048 mole) of sodium azide and 100 ml. of pyridine. The system was flushed with nitrogen for 5 mins. before 4.0 g. (0.02 mole) of diphenylsilyldichloride was introduced through the septum into the flask. The reaction was continued at room temperature under static nitrogen atmosphere with stirring for 24 hrs. After 24 hrs. a sample was taken for infrared inspection and showed a strong azide absorption at 4.72µ.

Without filtering off the sodium chloride and the unreacted sodium azide, 1,4-bis(diphenylphosphorus)benzene, 8.92 g. (0.02 mole) suspended in 100 ml. of pyridine, was slowly added to the gently refluxing pyridine solution. Due to a leak in the nitrogen collection system, no measurement of the volume of gas evolved was made. After 3 hrs. an infrared examination of the reaction mixture indicated the reaction to be complete as there was no longer any azide absorption at 4.72µ. The pyridine was then removed under reduced pressure to yield 9.00 g. of yellow-colored solids. An infrared spectrum showed characteristic broad absorption of -P=N- at 7.25 to 7.75µ. The product softened at 110° C. and darkened at 215° C. The molecular weight determined by Neumeyer Method in benzene was found to be 1130. Anal. calcd. for $C_{42}H_{34}SiN_2P_2$: P, 9.42; N, 4.26; Si, 4.26. Found: P, 9.74; N, 3.15; Si, 3.94. Differential thermal analysis of this material indicated a small endotherm at 476° C. which peaked at 500-539° C.

III. SUMMARY AND CONCLUSIONS

Work carried out in a variety of areas, all of which are directed to the ultimate syntheses of thermally stable polyphosphoranes, has resulted in the syntheses of new and useful tertiary phosphines, phosphonic acids, and phosphorane intermediates such as the bis-azidophosphoranes. This work included the investigation of both phosphorus and silicon containing organometallic azides.

It was found that the synthesis of phosphonyl azides can be readily carried out in benzene by using a 2:1 molar ratio of pyridine to phosphonyl chloride. By using this method, two new bis-azidophosphoranes, XLIVa and XLVI, were



XLIVa. X = 1

XLVI. X = 2

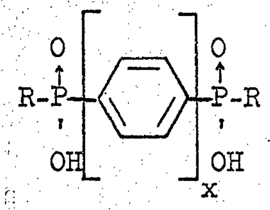
successful prepared in high yield and purity. The stability and ease of synthesis of these compounds now makes it unnecessary to handle or purify the unstable phenylphosphonyl diazide. The bis-azidophosphorane XLIVa was subsequently reacted with 1,4-bis(diphenylphosphino)benzene in several solvents to give the polyphosphorane from which, for the first time, fibers and disks (brittle, however) could be formed. Further exploitation of this discovery is planned.

Thermal gravimetric analysis studies of para-phenylene and 4,4'-biphenylene linked polyphosphoranes indicated a thermal stability to 400° C. The residue of 40-45 percent was then observed to be stable to 700-800° C. Since these values were obtained from <u>in situ</u> prepared polyphosphoranes, further studies on thermal stability will be carried out with samples obtained via the bis-azidophosphoranes such as XLIVa and XLVI.

The bis-phosphorane XLVIII containing the 4,4'-biphenylene linking unit has been shown by thermogravimetric analysis to undergo no weight loss to 410° C. and only a 10% loss at 460° C. As a result, additional preparations of the intermediate 4,4'-bis(diphenylphosphino)biphenyl will be made to meet the needs of further studies.

The successful syntheses of 3- and 4-bromophenyldiphenylphosphines (IX and XV) via an inverse Grignard technique provides access to the syntheses of several highly desired intermediates such as meta-bis-tertiary phosphines and a mixed tertiary phosphine-phosphonic acid. In connection with this work has been the development of two methods for the purification of tertiary phosphines--one by solution in concentrated hydrochloric acid, the other by column adsorption chromatography on alumina. A second part of the continuing research on polyphosphoranes will be on the preparation of the intermediates described.

The initial studies of the preparations of two para-arylene linked phosphonic acids, XXV and XXIX, were also investigated. Further efforts will be directed to the synthesis of larger amounts of these acids and to their conversion to the corresponding phosphonyl chlorides and azides.



XXV
X = 2; R = C_6H_5-

XXIX
X = 1; R = CH_3-

A preliminary survey of silyl diazides has suggested that the chemistry of various silyl azide-phosphorane systems analogous to the previously described bis-azidophosphoranes can be developed. As time permits, this new area will also be further studied. In addition, the first synthesis of a silicon containing polyphosphorane was carried via the <u>in situ</u> technique. Since differential thermal analysis indicated thermal stability to approximately 450° C., additional work is warranted.

An attempt to prepare a triborophane diazide was not successful. No further work is planned in this field.

IV. REFERENCES

1. R. A. Baldwin and F. A. Billig, Technical Documentary Report, No. ML-TDR-64-181, Part I, July, 1964.

2. Ibid., p. 16.

3. R. E. Buckles and N. G. Wheeler in N. Rabjohn, Organic Synthesis, Coll. Vol. IV, John Wiley & Sons, Inc., New York, 1963, p. 257.

4. A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, J. Org. Chem., 28, 2091(1963).

5. C. O. Wilson, Jr. and F. X. Maggio, Technical Documentary Report No. ML-TDR-64-183, Part I, June, 1964, p. 25.

6. R. I. Wagner, R. M. Washburn, and A. B. Burg, Technical Documentary Report No. WADC-TR-57-126, Part VI, July, 1962, p. 108.

7. R. A. Baldwin, K. A. Smitheman, and R. M. Washburn, J. Org. Chem., 26, 3547(1961).

8. J. J. Newmayer, Anal. Chim. Acta., 20, 519(1959).

9. J. G. Hartley, L. M. Venanzi, and D. C. Goodall, J. Chem. Soc., 3930 (1963).

10. L. D. Quin and J. S. Humphrey, Jr., J. Am. Chem. Soc., 83, 4124(1961).

11. T. Weil, B. Prijs, and H. Erlenmeyer, Helv. Chim. Acta., 36, 1314(1953); CA 48, 10642a(1954).

12. M. Davis and F. G. Mann, J. Chem. Soc., 3786(1964).

13. R. A. Baldwin and F. A. Billig, Technical Documentary Report No. ML-TDR-181-64, Part I, July, 1964, p. 64.

14. Ibid., p. 5.

15. E. M. Eveleth, L. D. Freeman, and R. I. Wagner, J. Org. Chem., 27, 2192(1962).

16. C. O. Wilson, Jr. and F. X. Maggio, Technical Documentary Report ML-TDR-64-183, Part II, April, 1965, p.

17. R. I. Wagner, A. B. Burg, and D. L. Mayfield, WADC Technical Documentary Report 57-126, Part V, January, 1961, p. 104.

REFERENCES (CONT)

18. R. A. Baldwin and F. A. Billig, Technical Documentary Report No. ML-TDR-64-181, Part I, July, 1964, p. 4.

19. Ibid., p. 44.

20. W. T. Reichle, Inorg. Chem., 3, 402(1964).

21. R. A. Baldwin and F. A. Billig, Technical Documentary Report No. ML-TDR-181-64, Part I, July, 1964, p. 2.

22. Ibid., p. 11.

23. Ibid., p. 17.

24. R. A. Baldwin and R. M. Washburn, J. Am. Chem. Soc., 83, 4466(1961).

25. R. A. Baldwin and F. A. Billig, Technical Documentary Report No. ML-TDR-64-181, Part I, July, 1964, p. 14.

26. Ibid., p. 26.

27. L. Parts, M. L. Nielsen, and J. T. Miller, Jr., Inorg. Chem., 3, 1261(1964).

28. R. I. Wagner, R. M. Washburn, and A. B. Burg, Technical Documentary Report No. WADC-TR-57-126, Part VI, July, 1962, p. 58.

29. G. Schiemann and W. Winkelmüller in A. H. Blatt, Organic Synthesis, Coll. Vol. II, John Wiley & Sons, Inc., New York, 1943, p. 188.

30. R. A. Baldwin and F. A. Billig, Technical Documentary Report No. ML-TDR-64-181, Part I, July, 1964, p. 39.

31. M. F. W. Dunker, E. B. Starkey, and G. L. Jenkins, J. Am. Chem. Soc., 58, 2308(1936).

32. R. A. Baldwin and F. A. Billig, Technical Documentary Report No. ML-TDR-64-181, Part I, July, 1964, p. 52.

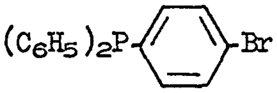
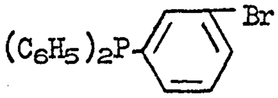
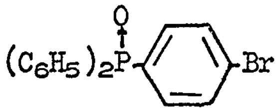
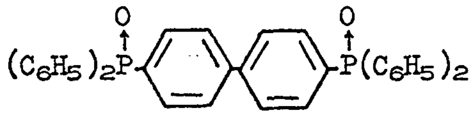
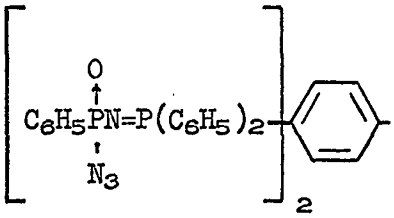
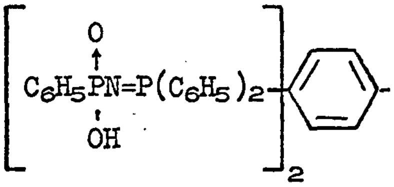
33. Ibid., p. 53.

APPENDIX

Listed in Table VI are the new compounds prepared during the period 1 April 1964 and 1 April 1965, under Air Force Contract No. AF 33(657)-11129. References indicate page numbers of this report.

TABLE VI

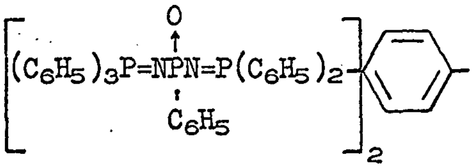
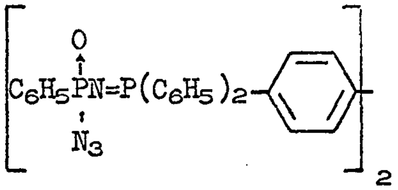
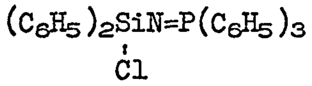
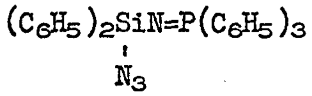
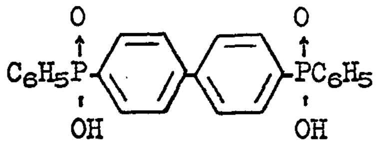
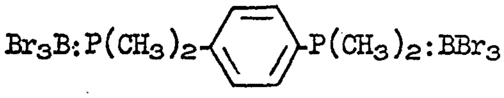
NEW COMPOUNDS

Name (Text Number)	Structural Formula
Tertiary Phosphines and Derivatives	
4-Bromophenyldiphenylphosphine (IX)	
3-Bromophenyldiphenylphosphine (XV)	
4-Bromophenyldiphenylphosphine oxide (XIV)	
4,4′-Bis(diphenylphosphino)biphenyl (II)	
4,4′-Bis(diphenylphosphino)biphenyl-bisoxide (IIa)	
1,4-Bis(dimethylphosphino)benzene (III)	
Arylene-Linked Phosphoranes	
N,N′-[p-Phenylenebis(diphenylphosphoranylidyne)]-bis(P-azido-P-phenylphosphonic amide) (XLIVa)	
N,N′-[p-Phenylene(diphenylphosphoranylidyne)]-bis(P-hydroxy-P-phenylphosphonic amide) (XLIVb)	

Melting Point, °C	Boiling Point	Remarks	Reference
73-75	165-175°/10^{-3} mm		6, 41
-	165-170°/.005 mm		8, 43
141-143	-	Strong P-O absorption at 8.4µ	7, 43
191-192	-		2, 31
299-301.5	-	Strong, sharp P-O absorption at 8.5µ	3, 32
-	80°/10^{-3} mm		3, 39
144-146	-	Strong, sharp N_3 absorption at 4.72µ	17, 52
245-254	-		17, 54

TABLE VI (CONT)

NEW COMPOUNDS

Name (Text Number)	Structural Formula
N,N‴-Bis(triphenylphosphoranylidene)-N′,N″-[p-phenylenebis(diphenylphosphoranylidyne)]-bis(P-phenylphosphonic diamide) (XLVII)	
N,N′-[p-Biphenylene(diphenylphosphoranylidyne)]-bis(P-azido-P-phenylphosphinic amide) (XLVI)	
Silicon Phosphoranes	
Chlorodiphenyl-N-(triphenylphosphoranylidene)silyl amide (XXXIV)	 $(C_6H_5)_2\underset{Cl}{Si}N=P(C_6H_5)_3$
Azidodiphenyl-N-(triphenylphosphoranylidene)silyl amide (XXXV)	 $(C_6H_5)_2\underset{N_3}{Si}N=P(C_6H_5)_3$
Miscellaneous	
Diphenylsilyl azidochloride (XXXIII)	$(C_6H_5)_2Si(N_3)Cl$
4,4′-Biphenylenebis(phenylphosphinic acid) (XXV)	
1,4-Bis(dimethylphosphino)benzene-bis-(tribromoborane)	

Melting Point, °C	Boiling Point	Remarks	Reference
103	-	No N_3 absorption	19, 54
210-212	-	Strong N_3 absorption at 4.70μ	18, 55
-	-	Not isolated; observed via products and/or infrared	14, 50
-	-	Not isolated; observed via products and/or infrared	14, 50
-	-	Not isolated; observed via products and/or infrared	14, 50
-	-	Partially characterized	11, 27
-	-	Stable adduct	4, 39

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

American Potash & Chemical Corporation
Whittier, California

2a. REPORT SECURITY CLASSIFICATION
Unclassified

2b. GROUP
--

3. REPORT TITLE

PHOSPHORANE POLYMERS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Summary Technical Report - (April 1964 - March 1965)

5. AUTHOR(S) *(Last name, first name, initial)*

Baldwin, Roger A. and Cheng, Ming T.

6. REPORT DATE
June 1965

7a. TOTAL NO. OF PAGES

7b. NO. OF REFS
33

8a. CONTRACT OR GRANT NO. AF 33(657)-11129

b. PROJECT NO. 7340

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

ML-TDR-64-181, Part II

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
--

10. AVAILABILITY/LIMITATION NOTICES DDC release to CFSTI not authorized. Qualified requesters may obtain copies of this report from DDC. Dissemination outside the Department of Defense or to recipients other than Government defense contractors is prohibited.

11. SUPPLEMENTARY NOTES
--

12. SPONSORING MILITARY ACTIVITY
Nonmetallic Materials Division, Air Force Materials Laboratory, Research & Technology Div., Air Force Systems Command, WPAFB, O.

13. ABSTRACT

An improved method for the synthesis of phosphonyl azides has resulted in the synthesis of a new class of phosphorane intermediate, the bis-azidophosphorane. Subsequent reaction of these bis-azidophosphoranes with bis-tertiary phosphines has resulted in polyphosphoranes from which, for the first time, fibers and disks (brittle, however) could be formed.

Thermal gravimetric analysis studies continue to indicate that the biphenylene linking unit provides phosphoranes (prototypes as well as polymers) which are more thermally stable than are those with p-phenylene units. An initial thermal evaluation of polyphosphoranes indicated thermal stability to 400°C. and a residue of 40-45 percent which was then stable to 700-800°C.

Additional synthetic effort has resulted in the preparation of two new and useful intermediates, the 3- and 4-bromophenyldiphenylphosphines as well as two bis-phosphonic acids.

A survey of silyl azides and phosphoranes was conducted and the promising results suggest additional studies. An attempt to prepare a triborophane diazide was unsuccessful.

DD FORM 1 JAN 64 1473

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Inorganic Polymers						
Phosphoranes						
Bis-phosphines						
Polyphosphoranes						
Bis-azides						
Bis-azidophosphorane						
Bis-organometallic intermediates						
Phosphorus compounds						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2*a*. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7*a*. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8*a*. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
_______________________________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through
_______________________________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through
_______________________________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, *or (U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.