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PART III

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PHOSPHORANE POLYMERS

R. A. Baldwin, M. T. Cheng, and C. O. Wilson, Jr.

American Potash & Chemical Corporation

TECHNICAL DOCUMENTARY REPORT ML-TDR-64-181, PART III

June 1966

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PHOSPHORANE POLYMERS

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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 research conducted from 1 April 1965 through 31 March 1966. The manuscript was released by the authors in April 1965 for publication as an RTD technical report. The work at American Potash & Chemical Corporation was carried out, under the supervision of Dr. K. R. Eilar, Manager, Research, by Dr. Roger A. Baldwin, who acted as project leader, Ming T. Cheng, C. O. Wilson, Jr., and, in part, Robert J. Mitchell.

This technical report has been reviewed and is approved.

William E. Gibbs

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Chief, Polymer Branch
Nonmetallic Materials Division
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ABSTRACT

A new route to bis tertiary phosphines, utilizing n-butyllithium, has been developed and has resulted in the improved syntheses of these vital intermediate compounds. As a result, the new bis-tertiary phosphine, 4,4'-bis(diphenylphosphino)diphenyl ether, has been successfully prepared and converted to the corresponding bis-azidophosphorane. The further polymerization of this bis-azidophosphorane has resulted in the first polyphosphorane from which long flexible fibers could be drawn. Other polyphosphoranes have been shown to have molecular weights of approximately 12,000 to 20,000.

Two new bis phosphinic acids, p-phenylene- and 4,4'-biphenylenebis-(phenylphosphinic acids) have also been synthesized via this n-butyllithium route. These compounds will be used in preparing a new type of polyphosphorane.

The new methylphenylphosphinic azide and its triphenylphosphine phosphorane were readily prepared and shown to be equally as stable to heat and to hydrolysis as were the fully phenylated homologues. Based on these results, a shortened route to the corresponding p-phenylenebis-(methylphosphinic acid) derivatives was successfully worked out. This series of compounds should result in more soluble polyphosphoranes.

It has been found that alkyl p-toluenesulfonates can be substituted for alkyl halides in certain of the Michaelis-Arbusov reactions and give high yields of pure dialkyl alkylphosphonates.

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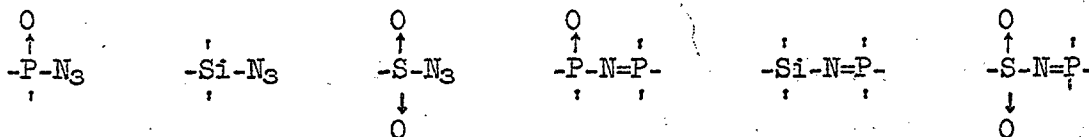
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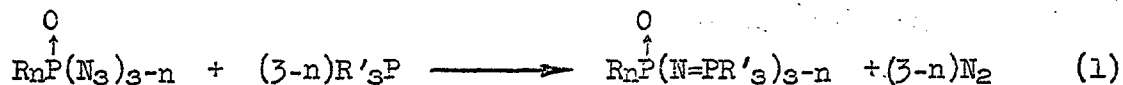
I. INTRODUCTION

As a result of exploratory research partially supported by the Air Force under Contracts AF 33(616)-6913 and -7810, it was discovered that a variety of stable organometalloid azides could be prepared. Furthermore, these organometalloid azides were found to react with tertiary phosphines to yield a series of metallo-nitrogen-phosphorus compounds generally having a high order of thermal and hydrolytic stabilities. A number of new compounds having the following bond systems were prepared and characterized:



This promising combination of chemical and physical properties suggested that polymers based upon these bonding systems would have hydrolytic, oxidative, and thermal stabilities.

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 phosphonic azides and tertiary phosphines.



Initial work designed to exploit these basic discoveries demonstrated that polyphosphoranes could indeed be synthesized via the reaction of phenylphosphonic 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.

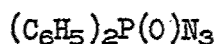
Further research resulted in an improved synthesis of phosphonic azides which has resulted in the preparation of a new class of phosphorane intermediate, the bis-azidophosphoranes. Utilization of these bis-azido-phosphoranes in polymer preparations resulted in polyphosphoranes from which brittle fibers and discs could be formed.²

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

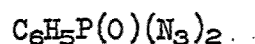
II. DISCUSSION

A. Nomenclature

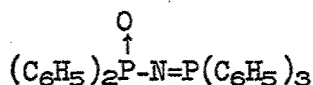
In order to attempt to provide more uniform and acceptable names for the variety of complex phosphorus-nitrogen compounds prepared in this investigation, the Chemical Abstract nomenclature will now be used when complete names are required. Thus Chemical Abstract names compounds containing more than one phosphorus atom by extension of the ACS rules for monophosphorus compounds [Chem. Eng. News, 30, 4515-22(1952)] or as derivatives of regularly named inorganic parents. The following examples will illustrate this changeover:



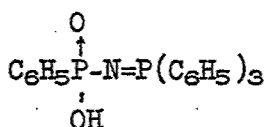
Old: Diphenylphosphonyl azide
CA: Diphenylphosphinic azide



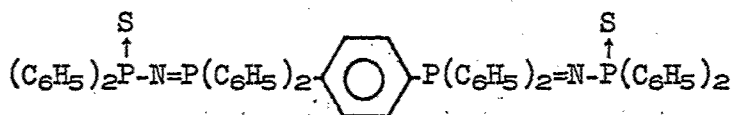
Phenylphosphonyl diazide
Phenylphosphonic diazide



Old: Diphenylphosphonimidotriphenylphosphorane
CA: P,P-Diphenyl-N-(triphenylphosphoranylidene)phosphinic amide



CA: P-Phenyl-N-(triphenylphosphoranylidene)phosponamidic acid



CA: N,N'-[p-Phenylenebis(diphenylphosphoranylidene)]-bis[P,P-diphenylphosphinothoic amide]

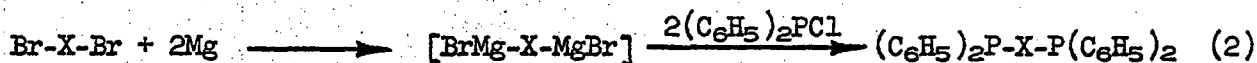
In the Chemical Abstract indexes the above names would be inverted at phosphinic amide, phosponamidic acid, and phosphinothoic amide, respectively.

B. Preparation of Intermediates

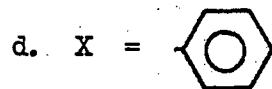
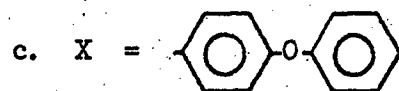
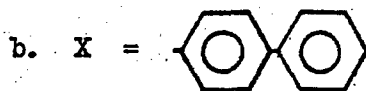
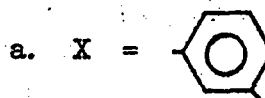
1. Bis Tertiary Phosphines

a. Via DiGrignard Reagents

The recent observation³ that a significant amount of isophthalic acid had been formed on carbonation of the monoGrignard reagent prepared from meta dibromobenzene as well as recent synthetic results by other workers,⁴ shows that the diGrignard reagents of meta dibromobenzene and of 3,3'-dibromobiphenyl can be prepared and successfully utilized. Although previous efforts in our work had only been successful with para-dibromobenzene, these new data suggested re-examination of the use of diGrignard reagents for the synthesis of bis tertiary phosphines. This reaction is illustrated in Equation 2.



I



Accordingly, 4,4'-bis(diphenylphosphino)biphenyl (Ib) has now been successfully prepared from the diGrignard reagent using tetrahydrofuran-benzene as the reaction solvent. In this synthesis the crude, viscous reaction product was solidified and partially purified by digestion with methanol to provide roughly 50% yields of crude Ib. The preparation of 1,4-bis(diphenylphosphino)benzene (Id) in the mixed tetrahydrofuran-benzene solvent mixture was also investigated in an effort to increase the yield of Id. However, the yield was only 24.6%, almost 50% less than the previous yields obtained using tetrahydrofuran alone.

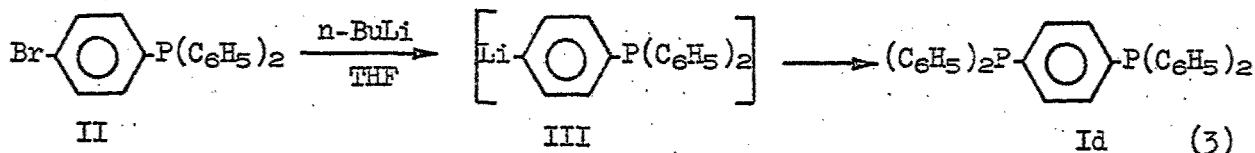
Unfortunately, additional attempts to prepare both 1,3-bis-(diphenylphosphino)benzene (Ia) and 4,4'-bis(diphenylphosphino)diphenyl ether (Ic) using tetrahydrofuran or tetrahydrofuran-benzene⁴ mixture as the

reaction solvent have resulted in amber-colored, viscous products. Attempts to crystallize and/or purify these materials have been unsuccessful. Examination of the infrared spectra of these materials has revealed the expected absorptions in addition to many extraneous absorptions due to PO, POP, and even PH. A possible source of this oxidation, peroxide containing tetrahydrofuran, was ruled out when all tetrahydrofuran in use was found to be peroxide free (starch-iodide method).

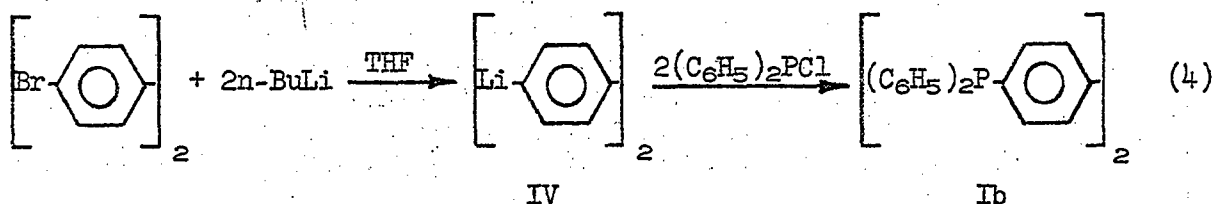
From the methanol extracts of Ib there was subsequently recovered diphenyl-4-hydroxybutylphosphine oxide. This material results from the interaction of the tetrahydrofuran solvent, diphenylchlorophosphine, and unreacted magnesium.⁵ Thus while it appears that this diGrignard route can result in the successful preparation of certain of the desired bis tertiary phosphines, the low yields of contaminated products make it a generally unattractive synthesis. However, a recent modification of this diGrignard preparation in tetrahydrofuran has been described by Chantrell and coworkers.⁶ After the diGrignard reagent had been prepared by refluxing magnesium and p-dibromobenzene in tetrahydrofuran for 18 hours, the insoluble diGrignard was filtered to remove the tetrahydrofuran and other soluble products. The spontaneously inflammable diGrignard was then slurried in low boiling petroleum ether for further use. Since this technique is reported to give a 75% yield of N,N,N',N'-tetraethyl-p-phenylene-bis-(phosphonous diamide),⁶ this appears to be a more useful synthesis for use in the preparation of bis tertiary phosphines.

b. Via Dilithioaromatics

The difficulties encountered in the syntheses and attempted syntheses of the polymer intermediates, the bis tertiary phosphines, have been described above and in detail in previous reports.⁷ Since both diGrignard reagents and lithium diphenylphosphinide reagents had failed to yield bis tertiary phosphines other than 1,4-bis(diphenylphosphino)benzene (Id) and more recently 4,4'-bis(diphenylphosphino)biphenyl (Ib) and since yields of 4,4'-bis(diphenylphosphino)biphenyl (Ib) via commercial 4,4'-dilithiobiphenyl were variable, an investigation of the preparation of the appropriate dilithium aryl derivatives from the corresponding dibromoaromatic compounds and n-butyllithium was begun. The potential utility of lithium aryls was demonstrated when it was found that 4-bromophenyldiphenylphosphine (II) could be first converted to the corresponding 4-lithio derivative III with n-butyllithium and then on to the known 1,4-bis(diphenylphosphino)-benzene (Eq. 3) (see below).



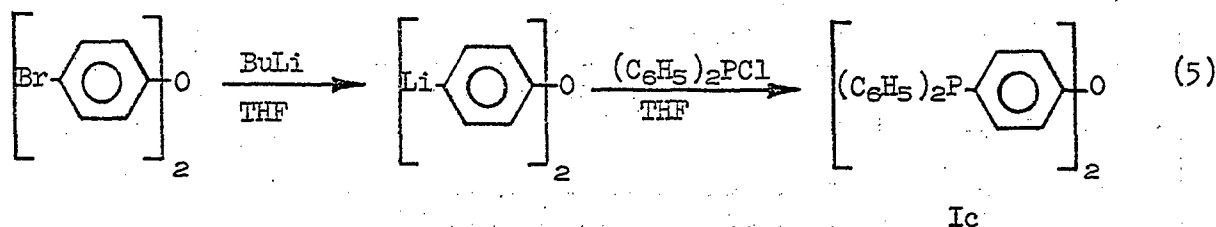
The first attempt to extend this technique was directed toward an improved synthesis of 4,4'-bis(diphenylphosphino)biphenyl (Ib). The



exothermic preparation of the dilithio intermediate IV was conveniently carried out by adding a hexane solution of n-butyllithium to the 4,4'-dibromobiphenyl in tetrahydrofuran at -60 to -70°C. After being allowed to warm to 0°C and then being cooled back to -70°C, the addition of two equivalents of diphenylchlorophosphine to IV was begun. It was found that the highest yield of high purity Ib (94%) was obtained by using two equivalents only of n-butyllithium per mole of 4,4'-dibromodiphenyl. Any excess of n-butyllithium apparently subsequently competed for the diphenylchlorophosphine and caused a decrease in yield. Thus a 250 g stock of 4,4'-bis(diphenylphosphino)biphenyl was prepared for further polyphosphorane studies. In addition to the high yields of pure product obtained via this technique, a considerable saving of time is affected when compared with the time consuming diGrignard method since a run can be completed in 8 hours or less.

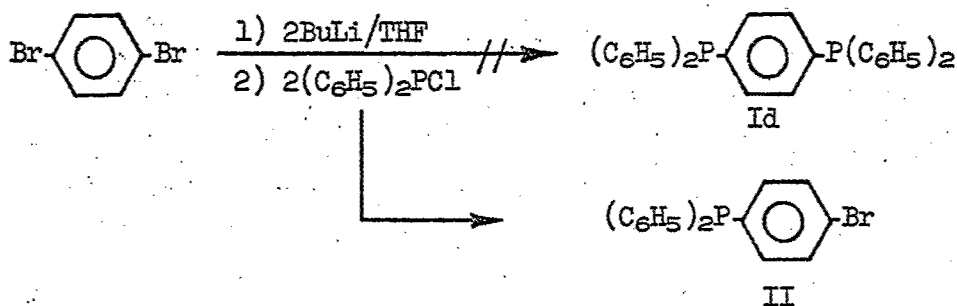
An additional quantity of 4,4'-bis(diphenylphosphino)biphenyl (Ib) was then prepared by this same general technique (Eq. 4). One slight change, however, in the reaction procedure was made. After the n-butyllithium had been added at -66°C to the 4,4'-dibromobiphenyl, the diphenylchlorophosphine was added immediately. Previously the reaction mixture had been allowed to warm to 0°C and then recooled to -66°C before the introduction of the diphenylchlorophosphine. This slight change in the reaction conditions resulted in only a 64% yield of somewhat impure Ib instead of a 94% yield of pure Ib.

In view of the above promising results, it was anticipated that a variety of new intermediates such as 4,4'-bis(diphenylphosphino)-diphenyl ether (Ic) and 1,3-bis(diphenylphosphino)benzene (Ia) could now be synthesized. Such new bis tertiary phosphines should result in phosphorane polymers having improved solubilities and physical properties such as fiber and disc-forming capabilities. Thus using this dilithio method, the ether-linked bis tertiary phosphine Ic was successfully synthesized in a survey



experiment in 75% yield when four equivalents of n-butyllithium were employed. Other experiments under slightly altered reaction conditions and also with only two equivalents of n-butyllithium generally resulted in oils which either failed to crystallize or which were crystallized only after many triturations with methyl alcohol and/or isopropyl alcohol. Reactions carried out in ether as the reaction solvent have also resulted in both oils and Ic. Thus while 4,4'-bis(diphenylphosphino)diphenyl ether (Ic) can now be prepared in yields ranging up to 50-75% in various preparations, this synthesis, however, still is not readily reproducible and requires additional study.

As a result of the syntheses of Ib and Ic via the dilithio-aromatic intermediates, an attempt to also prepare 1,4-bis(diphenylphosphino)benzene (Id) via this new and facile method was initiated. However, under the same conditions that had given such high yields of 4,4'-bis(diphenyl-



phosphino)biphenyl (Ib), none of the expected bis tertiary phosphine Id was isolated. Instead the product was 4-bromophenyldiphenylphosphine (II) resulting from the reaction of only one of the bromine atoms of the starting material, 1,4-dibromobenzene. The yield of readily recrystallized II was a surprising 57%. The monobromo product was identified by comparison with authentic II obtained in earlier studies.⁸

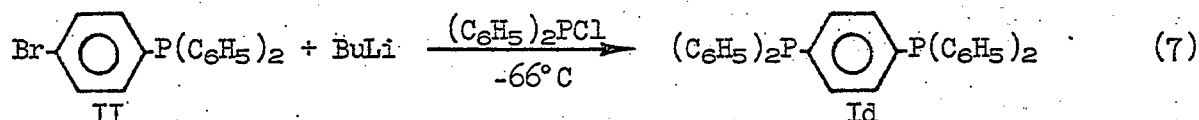
Because of this unexpected result, a study of the reaction of n-butyllithium and p-dibromobenzene in ether and in tetrahydrofuran was undertaken. The details of this study are contained in Table I. From the results of the various experiments, it is evident that the replacement of one of the bromine atoms of p-dibromobenzene takes place under a wide range of reaction conditions, i.e., -66°C to +32°C in either tetrahydrofuran or ether. However, subsequent replacement of the second bromine atom is difficult at best. This difficulty is readily reflected by the generally low yields of 1,4-bis(diphenylphosphino)benzene (Id), particularly when compared with the high yields of 4,4'-bis(diphenylphosphino)biphenyl obtained via this same reaction. Table I, thus, clearly demonstrates the marked effect of reaction conditions on the outcome of the reaction, i.e., mono- or disubstitution.

Since the yields of Id obtained from preparations in ether as the reaction solvent and using only two equivalents of n-butyllithium

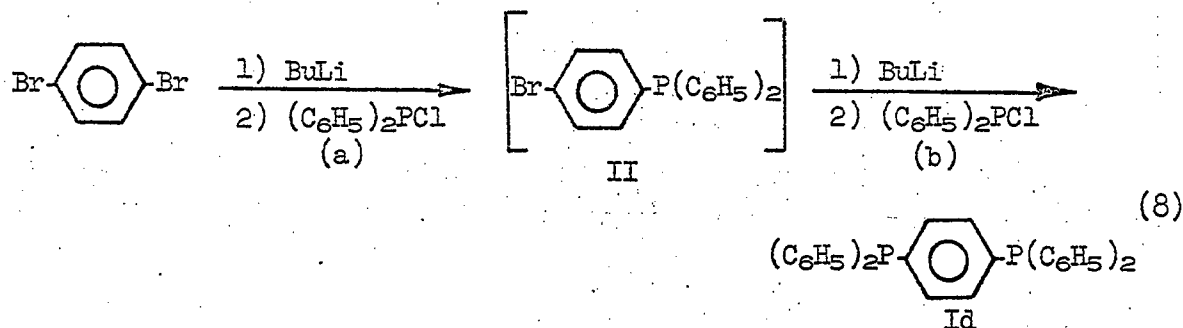
approached 50%, these data suggested that half of the n-butyllithium was being lost in some manner. Subsequent investigations utilizing four equivalents of n-butyllithium in refluxing ether for two and three-quarter hours gave a 58% yield of Id and an additional 11% of less pure product. Longer reflux lowered the yield of Id to 50%.

While the yields of Id obtained thus far via the n-butyllithium route can be equal to those via the diGrignard route, this newer route does have several advantages over the diGrignard route. Thus the reaction times are greatly reduced and the product is much more easily purified since it is not contaminated with the yellow oils and solids usually obtained from Grignard-phosphorus chloride reactions.

In view of the excellent yield and ease of synthesis of 4-bromophenyldiphenylphosphine (II) via the n-butyllithium route shown below in Equation 12, the further reaction of II with a second equivalent of butyllithium and of diphenylchlorophosphine to yield 1,4-bis(diphenylphosphino)benzene was suggested (Eq. 7). Again reaction conditions greatly



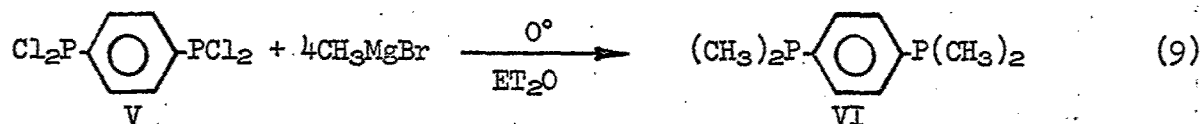
influenced the yields of Id. Attempted preparations in tetrahydrofuran at 5-15°C failed to yield any Id. The addition of a hexane solution of n-butyllithium to II in tetrahydrofuran at -66°C, and subsequent addition of the diphenylchlorophosphine also at -66°C resulted in a 64% yield of Id. The reversal of the initial addition sequence increased the yield of pure Id to 80%. The problems encountered on using tetrahydrofuran and n-butyllithium at or near room temperature may be due in part to the reported instability of the n-butyllithium in this solvent.⁹ Since on the one hand each of the steps leading to 4-bromophenyldiphenylphosphine (II) and thence to 1,4-bis(diphenylphosphino)benzene (Id) were found to readily give 80% yields, and since on the other, the direct preparations of Id via the dilithio intermediate were only moderately successful, it was of interest to attempt the two-step route without the intermediate isolation of II. Thus II was prepared in the usual manner and then dropped immediately into additional n-butyllithium at -66°. Subsequent addition of the second equivalent of diphenylchlorophosphine and workup gave 51.5 and 56.5% yields of slightly impure Id (Eq. 8).



While the yields were not as high as had been desired, they were not too far out of line when one considers that both steps a and b of Equation 8 individually result in only a 64% overall yield.

c. Via MonoGrignards

An additional synthesis of the new bis tertiary phosphine, 1,4-bis(dimethylphosphino)benzene (VI), was prepared as illustrated in Equation 9. Unfortunately, the yield of this compound in a preliminary

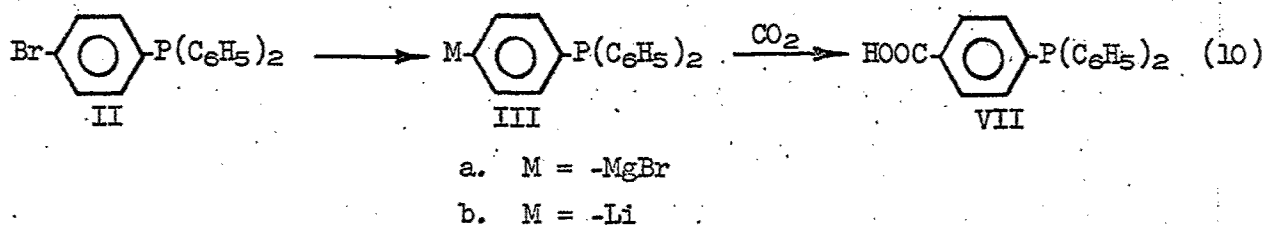


scale-up was very poor. Since the azide functions of the bis-azido-phosphoranes, now being used in the polyphosphorane preparations, have considerably diminished reactivity toward tertiary phosphines, it is expected that VI will react with the bis-azidophosphoranes more rapidly and completely than do the previously prepared bis tertiary phosphines containing diphenylphosphino functions, i.e., compounds Ia-d. The synthesis of the novel tetrachloro compound is described below in Section II.B.3.b.

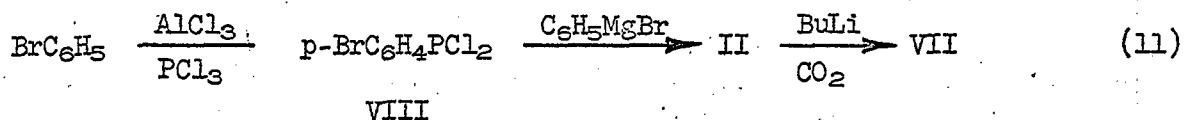
2. Monosubstituted Triphenylphosphines

The successful preparations of 3- and 4-bromophenyldiphenylphosphines via the inverse Grignard formation method⁸ have provided compounds for conversion to a variety of novel and useful intermediates for use in preparing polyphosphoranes. Such intermediates are mixed bis tertiary phosphines, tertiary phosphine-phosphinic acids, and even tris tertiary phosphines.

In an initial attempt to utilize these compounds, II was treated with magnesium in tetrahydrofuran-benzene in an attempt to form the mono-Grignard reagent IIIa, no reagent was formed. From the reaction mixture, there was subsequently recovered nearly all of the starting material II (Eq. 10).



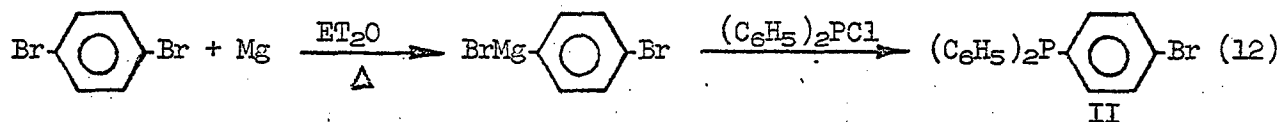
Previously Gilman and Brown¹⁰ reported that II could be prepared as shown in Equation 11. Treatment of II with n-butyllithium followed by



carbonation was reported then to give a 57% yield of the carboxylic acid VII. That the Friedel-Craft reaction in Equation 11 should yield pure para isomer VIII seems fortuitous in view of several recent studies concerning isomer distribution resulting from this reaction.^{11,12} In order to gain insight into the preparation of this potentially useful lithio derivative IIb and to confirm the identity of Gilman's para acid VII, the interaction of II and n-butyllithium was studied.

The preparation of VII as described by Gilman was repeated and none of the desired acid was obtained. However, when the reaction was carried out in tetrahydrofuran at -40 to -60°C, the yield of crude p-carboxyphenyldiphenylphosphine (VII) was 49%. Recrystallization from glacial acetic acid gave the acid VII with a melting point of 157°C, the same as had been previously reported by Gilman. However, comparison of the infrared spectrum of this acid with those of 3- and 4-bromophenyldiphenylphosphine failed to clearly confirm that product acid was the para isomer. Thus the two bromo derivatives contained strong para and meta absorptions at 12.35 and 12.85 μ , respectively, while the acid contained only weak, apparently para, absorption at 12.27 μ in addition to other weak absorptions at 11.75 (para?) and 13.1 μ (meta?) not present in either of the bromo compounds. Examination of the infrared spectrum of the meta acid may resolve this dilemma.

Since the earlier preparations⁸ of 4-bromophenyldiphenylphosphine (II) had resulted from the slow addition of aliquots of magnesium to 1,4-dibromobenzene in tetrahydrofuran at ambient temperature, it was also of interest to evaluate the use of diethyl ether in place of the tetrahydrofuran. The monoGrignard reagent was prepared by refluxing a mixture of one gram-atom of magnesium with one mole of 1,4-dibromobenzene in ether for three hours (Eq. 12). After the usual workup, a 73.6% yield of pale yellow-colored

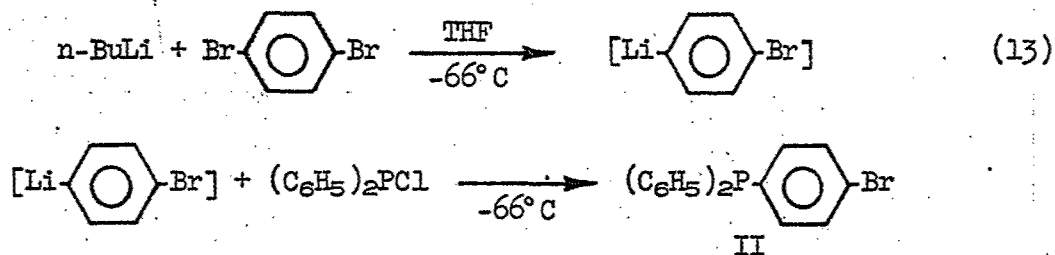


solid II, which required additional purification, was obtained.

It was inadvertently demonstrated in the previous section II.B.1.b., that n-butyllithium in tetrahydrofuran at -66°C will readily replace only one of the bromine atoms of p-dibromobenzene. Thus it appeared that the deliberate synthesis of 4-bromophenyldiphenylphosphine (II) via this route should be facile and should result in a great improvement over the earlier Grignard route.

The results of several experiments in tetrahydrofuran and in ether again reflect the effect of reaction conditions on the yield of II. The best

results (81% yield of high purity) were obtained by adding the p-dibromobenzene dissolved in tetrahydrofuran to the n-butyllithium at -66°C followed by the immediate introduction of the diphenylchlorophosphine (Eq. 13).



A comparison of the three routes to II, i.e., monoGrignard in ether, in tetrahydrofuran, or via n-butyllithium, clearly shows that the n-butyllithium approach results in the highest yields of more pure product.

A small quantity of p-bromophenyldiphenylphosphine (II) was oxidized by both hydrogen peroxide and potassium permanganate in acetone to provide the reference compound p-bromophenyldiphenylphosphine oxide (IX). The use of permanganate in acetone appeared to be the more facile synthesis for this phosphine oxide. The infrared spectrum of this compound was similar to that of the tertiary phosphine II with the exception of new, strong absorptions at 8.45μ (P-O) and at 9.0μ (Ar-PO). The combination of these two strong absorptions can be used as a qualitative identification of the presence of tertiary phosphine oxide impurity in a tertiary phosphine. Thus, absorptions at 8 to 8.5μ thought to be due to P-O groups must be accompanied by the second strong absorption at 8.9 to 9.1μ , at least in triarylphosphine oxides.

An additional quantity of 3-bromophenyldiphenylphosphine was obtained by the inverse addition of magnesium to meta-dibromobenzene in tetrahydrofuran. The apparently quantitative crude yield was reduced to only a 31.2% yield after distillation at reduced pressure. Conversion of this compound to the lithioderivative and then to the 1,3-bis(diphenylphosphino)benzene (Ia) will be studied as time permits.

This meta-bromo derivative has been isolated as a high boiling liquid which has not crystallized on standing for several months. Furthermore, since the para isomer II has been obtained as a solid melting at $75-77^{\circ}\text{C}$ and since the product thought to be II prepared by Gilman and Brown was reported to be liquid, it would now appear reasonable that the Friedel-Craft preparation of VIII did indeed yield an isomeric mixture of products (Eq. 11).

3. Phosphinic Acids

a. Bis Phenylphosphinic Acids

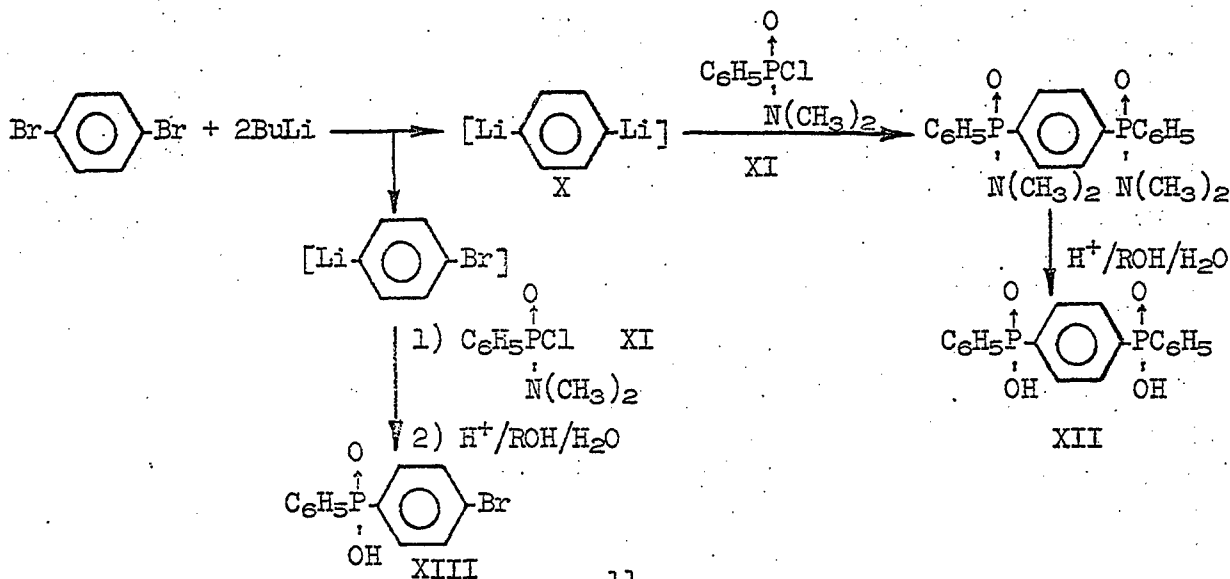
Previous differential thermal analysis data¹³ have suggested that polyphosphoranes linked via phosphinic-based phosphoranes may be more thermally stable than phosphonic-based phosphoranes, i.e.,



Necessary for the syntheses of polyphosphoranes having such phosphinic linkages are linked bis phosphinic acids, chlorides and azides. To this end, syntheses directed toward several arylenebis(phosphinic acids) were undertaken. Since the use of n-butyllithium to prepare dilithioaryls for conversion to bis tertiary phosphines had been relatively successful (see above, Section II.B.1.) the approach was via these same organometallic intermediates.

In the initial investigation, excess n-butyllithium was reacted at about -60°C with 1,4-dibromobenzene in an effort to insure a high conversion to 1,4-dilithiobenzene (X). Subsequently X was added to a slight excess of the phosphonic chloride XI at 0°C in order to minimize possible P-N cleavage instead of the desired reaction with the P-Cl. No attempt was made at this time to isolate the intermediate bis-phosphinic amide.

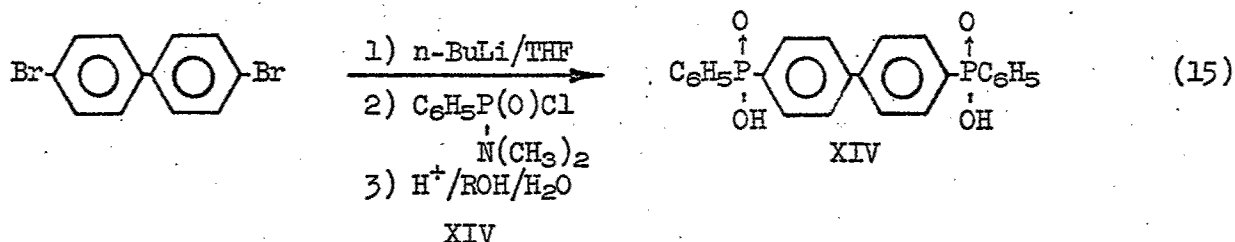
The crude bis phosphinic amide was then dissolved in isopropyl alcohol and hydrolyzed with 6N hydrochloric acid. The resulting crude bis phosphinic acid XII was purified by repeated solution in base and charcoal treatment to yield a small quantity of a white powder which was further extracted with methanol. The acid XII thus isolated has a melting point above 300°C and appears to have limited solubility in organic solvents. These properties are parallel to those of terephthalic acid. Analytical data fully agree with the calculated values.



Since the yield of p-phenylenebis(phenylphosphinic acid) (XII) was very low in the initial preparation, additional experiments have now been investigated under a variety of conditions in an effort to improve this yield. Again, as had been encountered during the synthesis of 1,4-bis(diphenylphosphino)benzene (Id), replacement of both bromine atoms was difficult. For example, after the n-butyllithium and p-dibromobenzene exchange was carried out in tetrahydrofuran at -66°C and the phosphonic chloride XI was added to this reaction mixture, acid hydrolysis gave a base and methanol soluble product. Further investigation revealed that this methanol soluble acid was 4-bromophenylphenylphosphonic acid (XIII) instead of the bis acid XII.

An increase in yield to 33% was obtained by allowing the exchange reaction mixture to warm to 32°C prior to adding it to the phosphonic chloride XI. Reactions carried out in ether yielded both XII and XIII. The infrared spectrum of the new bis phosphinic acid XII was difficult to obtain in a clear, sharp manner.

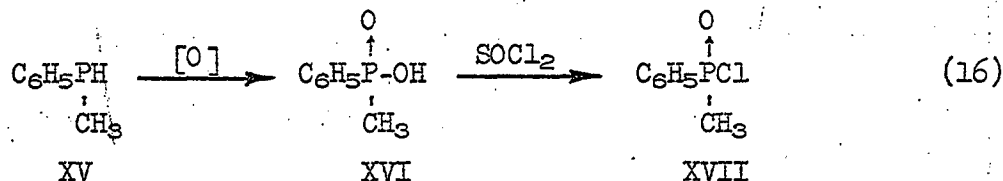
This line of investigation was also extended to the preparation of 4,4'-biphenylenebis(phenylphosphinic acid) (XIV). Since other recent data have shown that 4,4'-dibromobiphenyl can be converted to the dilithio-derivative much more easily than p-dibromobenzene (see Section II.B.1. above), it was anticipated that XIV should be more accessible than the phenylene-linked acid XII. Following the same procedure used for preparation of the 4,4'-bis(diphenylphosphino)biphenyl (Ib), the 4,4'-dilithiobiphenyl was prepared in tetrahydrofuran at -66°C , warmed to $+17^{\circ}\text{C}$ before being recooled to -66° and then added to an excess of the phosphonic chloride at -66°C . After acid hydrolysis, the new biphenylene-linked acid XIV was



isolated as a white powder, melting at about 195°C , in 32% yield. The identity of this powder was confirmed by analysis, neutralization equivalent and infrared analysis. The infrared spectrum of XIV was much more sharp and distinct than the phenylene acid XII. This new acid is, as expected, considerably more soluble in organic solvents and of a lower melting point than the p-phenylene homologue.

b. Bis Methylphosphinic Acids

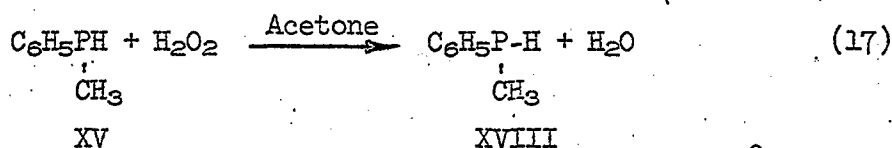
Concurrent with the above investigations of the syntheses of arylenebis phenylphosphinic acids, were a series of experiments designed to evaluate the potential utility of the methylphenylphosphinic grouping in phosphoranes. A part of this study was the syntheses of several methylphosphinic derivatives as shown in Equation 16.



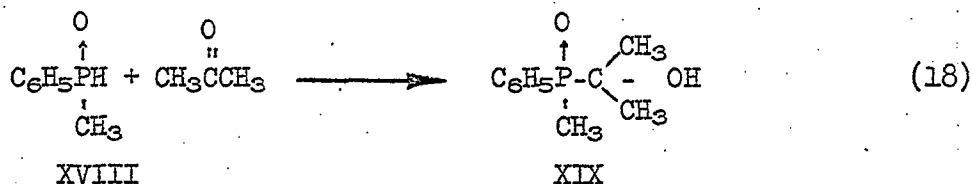
Methylphenylphosphine (XV), on hand in abundant supply, was oxidized by means of iodic acid to methylphenylphosphinic acid (XVI) (Eq. 16). The method was considered inadequate in that removal of the by-product iodine by aqueous distillation was extremely laborious and the yield of XVI was only 48%. As a result, the oxidation of the phosphine XV by means of hydrogen peroxide was undertaken in order that this oxidation be as facile and give as high a yield as possible so as to prevent undue loss of the hard-to-come-by bis phosphine XXI in the proposed route of Equations 19-20.

Oxidation of XV by means of 10% hydrogen peroxide in acetone resulted in the isolation of a product having the same melting point as the expected phosphinic acid XVI. However, further examination by infrared, neutralization equivalent, and mixture melting point revealed that the isolated material was not XVI.

Apparently, the oxidation of methylphenylphosphine in 10% hydrogen peroxide is a two-step process in which methylphenylphosphine oxide (XVIII) is the first product (Eq. 17). Then the rate of addition of the -P-H function of the oxide XVIII to the carbonyl group of the solvent,



acetone, is greater than the rate of the desired oxidation of the -P-H function to give the acid XVI (Eq. 16). Thus, P-methyl-P-phenyl-P-2-propanol-

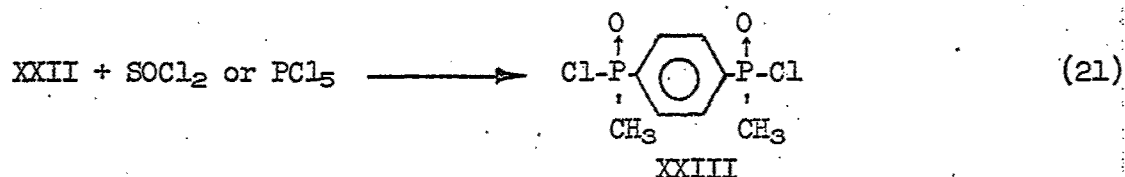
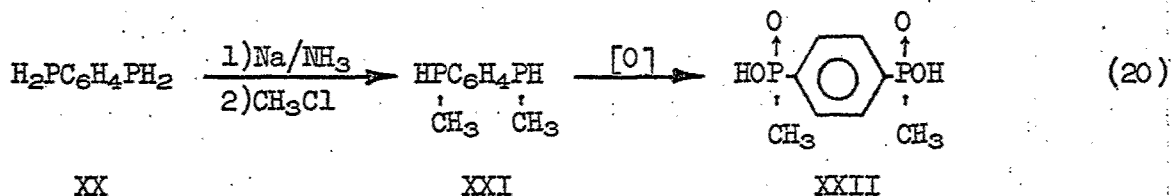
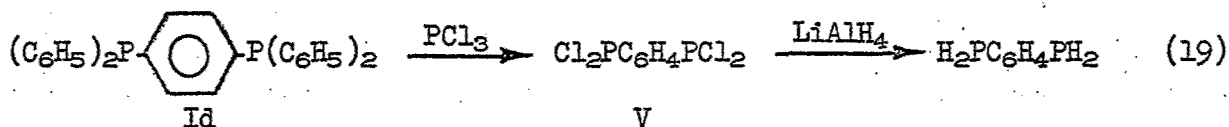


2-phosphine oxide (XIX), having a molecular weight of 198, appears to be the major product of this reaction. An infrared spectrum of this product indicated the presence of an alcohol O-H stretching band. Other data were obtained to indicate that this type of reaction occurred and efforts to confirm the identity of this product are in progress. Support for this hypothesis is a paper by Buckler and Epstein which describes the similar

reaction of primary phosphine oxides and carbonyl compounds.¹⁴

The methylphenylphosphinic acid (XVI) was then converted in carbon tetrachloride to the chloride XVII by reaction with thionyl chloride. The yield was an unexpectedly low 35%. Previous conversions of diarylphosphinic acids to the chlorides with thionyl chloride have, generally, resulted in much higher yields. Alternative routes to this methylphenylphosphinic chloride will be investigated in order that the planned conversion of XXII to the bis(methylphosphinic chloride) XXIII will be as efficient as possible (Eq. 21).

The second part of this investigation was concerned with an improved synthesis for p-phenylene bis(methylphosphinic acid) (XXII) via the sequence of reactions shown in Equations 19 and 20. It was anticipated that this method of synthesis of XXII would result in at least a 20-fold increase

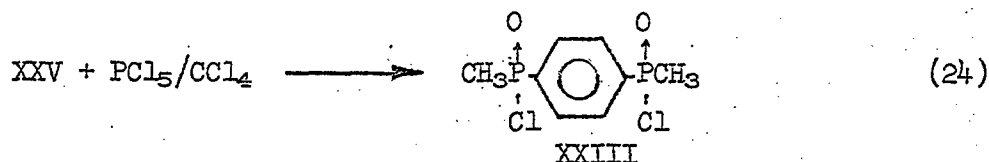
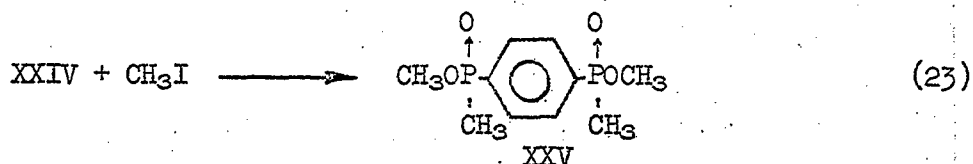
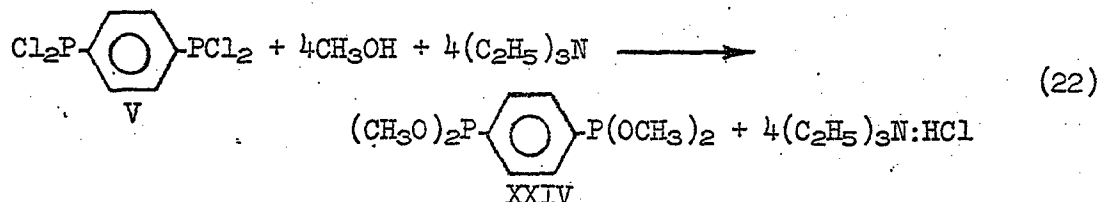


in the yield over the method of Eveleth and coworkers.¹⁵ This improved reaction sequence to compound XXI had been previously developed to provide intermediates for the preparation of thermoset polyborophane resins under Air Force Contract 33(657)-11296.¹⁶ Furthermore, it is also anticipated that the presence of methyl groups attached to the phosphorus atoms may result in several beneficial properties for the bis(phosphinic azide) of XXII. First, since the methyl groups are less bulky, greater polymer chain length might be realized due to less steric hindrance in the formation of the P=N bonds. Second, the bis(methylphosphinic azide) may have increased reactivity due to the inductive effect of the methyl group. In addition, the resulting polyphosphoranes may thus have modified physical and chemical properties.

The first step in this sequence, the preparation of p-phenylenebis(dichlorophosphine) V has been accomplished. On hand were several hundred grams of p-phenylenebis(diphenylphosphine) (Id) which were mixed with a large

excess of phosphorus trichloride in a large, heavy wall tube and sealed under a slight pressure of nitrogen. Benzene, having about the same critical pressure as phosphorus trichloride, was used as the pressure-equalizing medium within the steel reactor. The thermal reorganization reaction of Id to V was conducted at 300°C for 30 hrs. Although for some reason the tube ruptured, a quantitative yield of the by-product phenyl-dichlorophosphine was obtained indicating that the reaction proceeded satisfactorily. The crude tetrachloro compound was not isolated but was held in reserve for subsequent reaction steps.

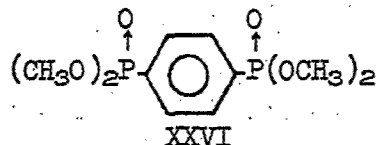
However, with the availability of this new bis dichloro-phosphine V, an alternate and shorter route to the bis(methylphosphinic chloride) XXIII was suggested. This route is outlined in the following equations.



In order to survey this new reaction sequence, approximately one-third of the crude tetrachloro intermediate V was reacted with methanol in the presence of triethylamine. The initial yield of XXIV was only 21%. This low yield for a reaction expected to give at least 70-80% yields can be easily rationalized. The explanation could be that during the preparation of V as a result of the breakage of the glass reaction tube in the steel pressure chamber that secondary reactions of the Friedel-Craft type took place on exposure of the phosphorus-chlorine compounds to the steel. The infrared spectrum of XXIV contained the expected absorptions, particularly a very strong absorption due to the presence of the methoxy group.

A higher boiling fraction was obtained following the distillation of the tetramethoxy product XXIV. This material had an infrared

spectrum which contained a strong P-O absorption. The P-O absorption suggested that this was simply the oxidized material XXVI. However, this



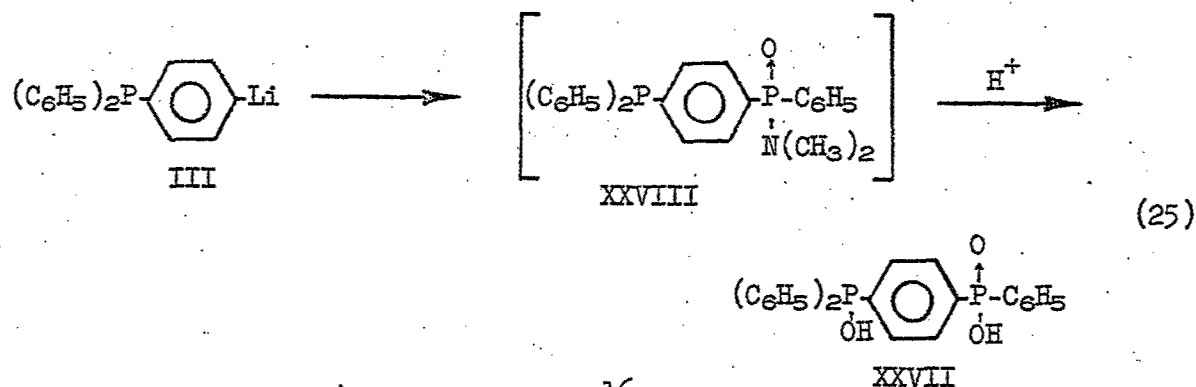
is not supported by phosphorus analysis which was only about two-thirds of that required for XXVI.

The subsequent step, the Michaelis-Arbusov reaction of the bis(dimethylphosphonite) XXIV with methyl iodide (Equation 23), was extremely exothermic when carried out in the absence of a solvent. When only one milliliter of methyl iodide had been added to neat XXIV, a rapid exotherm occurred which blew out both the thermometer and stopper in the condenser even though the system was attached to a mercury bubbler for pressure relief. However, a small quantity of a solid material was recovered from the reaction flask and isolated as a white powder. The infrared spectrum of this material was changed as expected with the principal development of absorptions due to P-O at 8.15 and 8.9 μ . Further, the analytical data are in good agreement with the calculated values for the expected Michaelis-Arbusov product dimethyl p-phenylenebis(methylphosphinate) XXV.

In spite of the initially low yield of XXIV and the uncontrolled exothermic nature of the initial Michaelis-Arbusov reaction, the use of more pure tetrachloro compound XX and more controlled reaction conditions are expected to make the reactions of Equations 22 and 23 an extremely attractive route to p-phenylenebis(methylphosphinic acid) and its derivatives. The conversion of the remaining two-thirds of the crude tetrachloro compound XX to XXIV is underway and this investigation will now be extended to the preparation of the p-phenylenebis(methylphosphinic azide).

c. Tertiary Phosphine-Phosphinic Acid

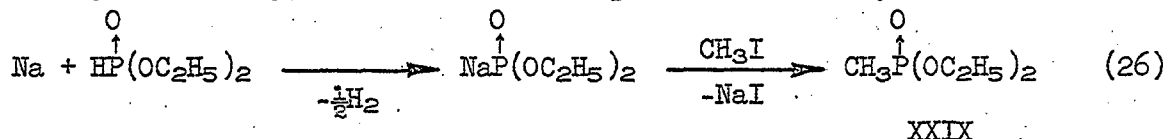
As a result of the above studies (Section II.B.2) which demonstrate the ease with which 4-bromophenyldiphenylphosphine (II) can be converted to the lithium derivative III, the study of the preparation of the novel, mixed tertiary phosphine-phosphinic acid XXVII was begun (Eq. 25).



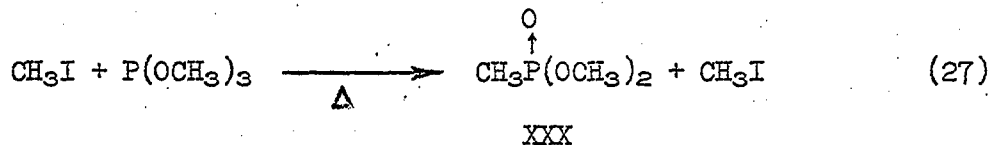
Such an acid as XXVII will lead to a phosphinic azide which will immediately polymerize in a head-to-tail fashion to yield a new type of polyphosphorane. No attempt was made at this time to isolate the intermediate phosphinic amide XXVIII. The crude XXVIII was hydrolyzed in alcoholic hydrochloric acid to yield a white, crystalline solid which was rather surprisingly insoluble in sodium hydroxide solution. However, infrared examination of this material revealed all of the expected absorptions in a very sharp spectrum, P-O at 8.33μ and 8.85μ , POH at 10.45 , and para substitution at 12.2 . Analyses for carbon and hydrogen were also in fair agreement with the theoretical values for XXVIII. Investigation of this novel tertiary phosphine-phosphinic acid is continuing.

4. Dialkyl Alkylphosphonates

Previous studies leading to arylenebis(phosphinic acids) via the corresponding diGrignard or dilithium reagents have been with the amine-blocked phenylsubstituted phosphonic chloride XI. In order to obtain similar methyl substituted phosphonic derivatives, several potential routes were surveyed. One approach is shown in Equation 26. The yield of ester XXIX



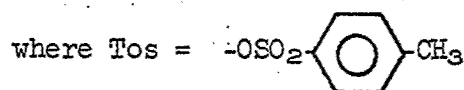
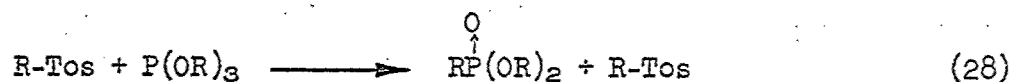
was only 34.8%. Apparently not all of the by-product sodium iodide had been removed and, as a result, caused decomposition during the distillation.¹⁷ The more direct Michaelis-Arbusov reaction of methyl iodide and trimethylphosphite resulted in an 81% yield of the homologous methyl ester XXX (Eq. 27).



These esters can be next converted to methylphosphonic dichloride by an initial hydrolysis to methylphosphonic acid followed by reaction with thionyl chloride. Then the dichloride will be treated with two equivalents of dimethylamine to obtain N,N-dimethyl methylphosphonamidic chloride to be used in preparing new methylphosphinic acids. Alternatively, the esters may be reacted directly with phosphorus pentachloride to obtain methylphosphonic dichloride. These routes will be surveyed to ascertain the best route with respect to both yield and reaction difficulties. (See Equation 30 below). This information will have added importance in that it may suggest the best way to convert dimethyl p-phenylenebis(methylphosphinate) (XXV) to p-phenylenebis(methylphosphinic chloride) (XXIII).

In reviewing the use of alkyl halides in the Michaelis-Arbusov reaction, it was considered to be of interest to evaluate the use of alkyl p-toluenesulfonates (tosylates) in place of the alkyl halides. As a part of

this study, methyl and ethyl tosylates were reacted with trimethyl- and triethylphosphites, respectively (Eq. 28). In these reactions, the mole



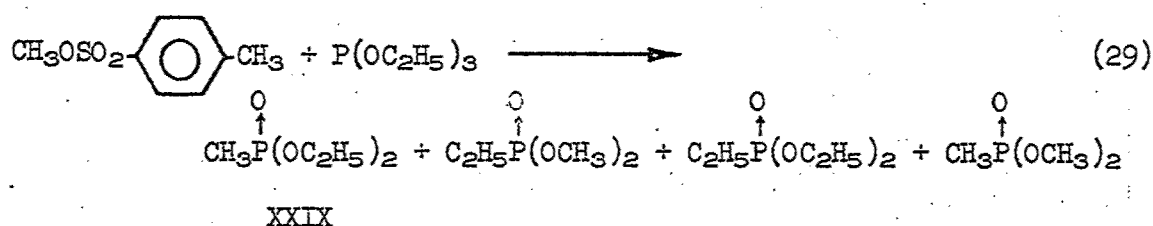
and

R = methyl (XXX) or ethyl (XXXI)

ratio of phosphite to tosylate was 10:1.

The reactants were mixed under nitrogen, sampled for an infrared spectrum, and heated rather rapidly. The result was a vigorous, exothermic reaction which subsided in 5-10 minutes. Infrared spectra of the reaction mixtures were now significantly changed and contained a strong P-O absorption indicative of the formation of the desired phosphonates. The reaction mixtures were then cooled and fractionally distilled at 18 mm pressure. No foreruns of unreacted phosphite were observed and the yield of distilled products XXX and XXXI were 98.8% and 92%, respectively. Infrared and vapor phase chromatographic comparisons of the dimethyl methylphosphonate obtained via Equation 28 showed that the product was identical to that obtained via the classical Michaelis-Arbusov reaction of Equation 27. That the esters were obtained in high purity was confirmed also by the vapor phase chromatograms. Methyl benzenesulfonate also yielded quantitative yields of XXX. In addition, the alkyl sulfonates were also recovered in high yields on distillation of residues remaining after the removal of the dialkyl alkylphosphonates. Furthermore, it was found that as little as one mole percent of alkyl tosylate will catalyze this reaction.

However, while these results were extremely encouraging, attempts to carry out a mixed reaction, i.e., methyl tosylate and triethylphosphite resulted in an extremely complex mixture of reaction products (Eq. 29).



In an attempt to insure only formation XXIX, a 1:1 ratio was employed. It was found that the best reaction correlations were obtained by not using excessive heating. This was achieved by carefully controlling the heat applied to the reaction and the subsequently fractionating the reaction products under high vacuum. During the gradual heating of the reactants, no

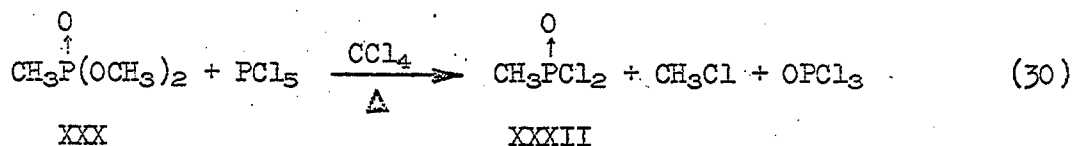
reaction was noted before the pot temperature reached 105°C. As soon as it reached 105°C, the reaction mixture began to reflux, and within 3 minutes the pot temperature had reached 210°C, accompanied with vigorous refluxing. The reaction, however, subsided immediately. After cooling to room temperature, the reaction mixture was fractionated under vacuum to yield 29.7 g (91.4% of theory) of colorless liquid boiling at 54°C/2.5 mm.

This product, however, was found by vapor phase chromatography to contain only 74% of XXIX and tentatively, 21.5% of the unexpected product dimethyl ethylphosphonate. A more likely by-product, diethyl ethylphosphonate (XXXI), was present in only 2.7%.

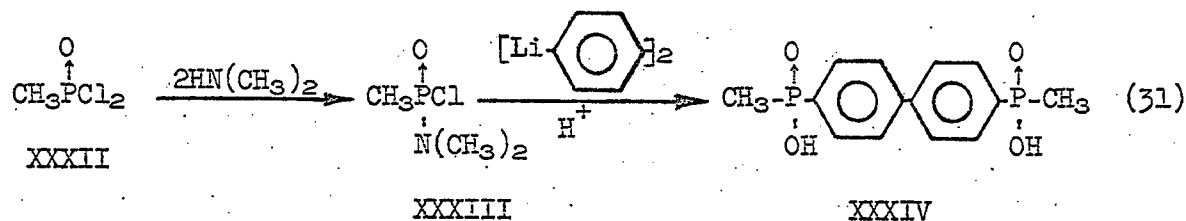
Similarly, trimethylphosphite and ethyl tosylate gave a mixture of products identified as containing 43.5% dimethyl ethylphosphonate and 42.1% dimethyl ethylphosphonate as well as several minor components. Thus, the use of alkyl tosylates to prepare mixed dialkyl alkylphosphonates, where the alkyl groups are different, is not practical due to the scrambling of the alkyl groups of the reactants.

Attempts to further extend this reaction to other types of esters were not successful. Thus, ethyl diphenylphosphinate and methyl toluate failed to react with triethylphosphite and trimethylphosphite, respectively, and were quantitatively recovered. Similarly, an attempt to transfer a phenyl group from phenyl tosylate to triethylphosphite also failed. Since aryl halides also fail to undergo the Michaelis-Arbusov reaction,¹⁸ the failure of this latter reaction is not too surprising.

Subsequent reaction of dimethyl methylphosphonate (XXX) with phosphorus pentachloride in carbon tetrachloride resulted in a 78% yield of methylphosphonic dichloride (Eq. 30) which readily solidified into



beautiful crystals. The methylphosphonic dichloride (XXXII) will next be treated with two equivalents of dimethylamine to give the monoamino compound XXXIII which will in turn be used to prepare bis(methylphosphinic acids) such as XXXIV. Such acids as XXXIV are not currently available via the new Michaelis-Arbusov route of Equations 22 and 23. Work on this series of compounds as illustrated in Equation 31 is underway.

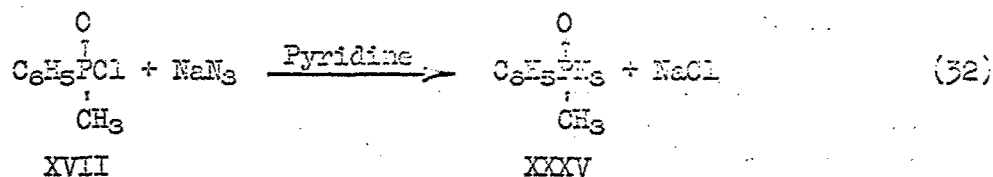


5. Organometalloid Azides

a. Phosphinic Azides

As a part of the program to prepare and evaluate the potential utility of the methylphenylphosphinic group in a prototype phosphorane, the synthesis of methylphenylphosphinic chloride (XVII) from methylphenylphosphine (XV) has been described in an earlier section of this report (Section II.B.3). Furthermore, since alkyl-arylphosphinic azides had not been previously investigated, it was also considered prudent from a safety point of view to determine the thermal and shock stabilities of methylphenylphosphinic azide (XXXV).

Methylphenylphosphinic azide (XXXV) was prepared from the chloride XVII by simply stirring the chloride with sodium azide in pyridine (Eq. 32).

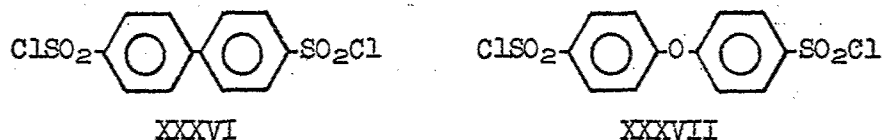


A small quantity of this new azide, the first example of a mixed alkyl-arylphosphinic azide, was distilled at low pressure without incident to give a high yield of XXXV. It was also found to not be detonated in a drop-weight test and to burn only slowly in air. Thus, this mixed phosphinic azide appears to be as stable as the previously prepared diarylphosphinic azides.¹⁹ The azide asymmetric stretching absorption was found at about 4.68μ , also the same as observed for the diaryl homologues. Therefore, approximately 10 grams of pure XXXV were isolated by means of the low pressure distillation. The azide was then used to prepare the new phosphorane XXXIX (see Section II.C.1).

b. Sulfonyl Azides

Earlier studies of sulfonyl azides and sulfonimidophosphoranes were both encouraging and discouraging.²⁰ While several monosulfonimidophosphoranes were easily prepared and showed promising thermal stabilities, attempts to form a bis-phosphorane from 1,3-benzene-di(sulfonyl azide) were completely unsuccessful.

To further investigate this area, the syntheses of the two di(sulfonyl chlorides) XXXVI and XXXVII from the corresponding aromatic hydrocarbons and excess chlorosulfonic acid was carried out. However, only

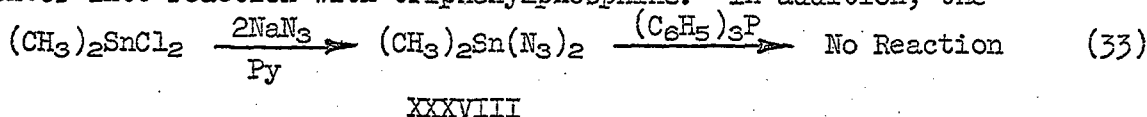


the diphenyl ether derivative XXXVII was readily separated and purified; undoubtedly XXXVII was obtained as an isomeric mixture.

The isomeric mixture of XXXVII was subsequently allowed to stir with sodium azide in tetrahydrofuran for 24 and 64 hours before two equivalents of triphenylphosphine was added. In both runs, the nitrogen evolutions were very low and medium azide absorptions were still observed in the reaction mixtures. The addition of a third equivalent of triphenylphosphine to the 64-hour run resulted in additional nitrogen evolution. Thus these results are similar to the erratic data obtained in the earlier studies and appear to rule out completely this system for use in polyphosphorane formation.

c. Tin Azides

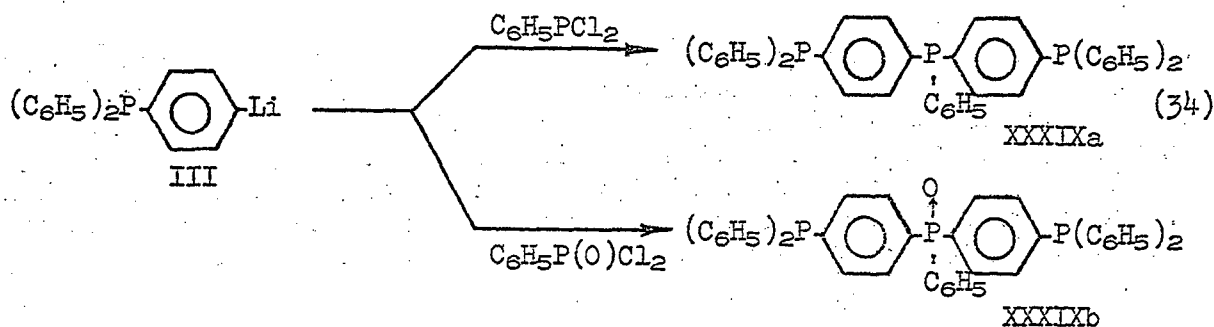
It had been observed in earlier works that triphenyltin azide did not react with triphenylphosphine to liberate nitrogen or form the phosphorane.^{21,22} In an additional survey reaction, dimethyltin dichloride was reacted with sodium azide in pyridine to form the tin diazide XXXVIII (Eq. 33). It had been expected that the presence of methyl groups in XXXVIII might change the chemistry of the azide groups attached to tin so that they might enter into reaction with triphenylphosphine. In addition, the



presence of two azide groups was also expected to result in enhanced reactivity as had been noted previously as being true for the phosphonic diazides.^{1,23} However, no nitrogen was liberated after 24 hours at the reflux temperature in pyridine with triphenylphosphine and the infrared spectrum of the mixture still contained a strong azide absorption. Thus, these data are in agreement with the earlier findings; organotin azides do not react with triphenylphosphine. At the present, there is not any ready explanation for this lack of reactivity of the tin azides with triphenylphosphine.

6. Tris Phosphines

In view of the ease with which 4-bromophenyldiphenylphosphine (II) can be converted to its lithium derivative III, investigation of the syntheses of a new series of phosphines, the tris tertiary phosphines, has been initiated (Eq. 34). The new tris tertiary phosphine XXXIXa will be used

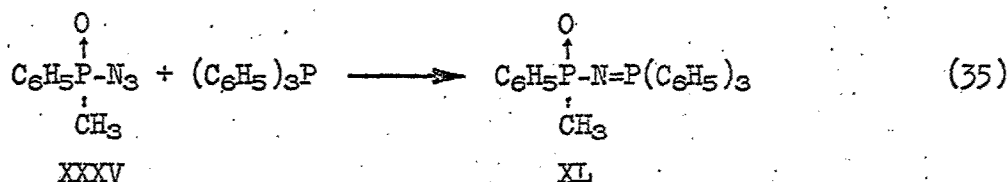


to crosslink the polyphosphoranes while the mixed bis tertiary phosphine-phosphine oxide XXXIXb will provide an additional compound for preparing linear polyphosphoranes. In addition, it is expected that XXXIXb will impart added flexibility to the linear polyphosphoranes and thus provide better fibers than are currently being drawn from the p-phenylene and p-biphenylene linked polyphosphoranes. Isolation and characterization of these new compounds are in progress.

C. Preparation of Phosphorane Prototypes

1. Phosphoranes

The new and stable methylphenylphosphinic azide (XXXV) was reacted with triphenylphosphine in pyridine to yield the prototype phosphorane XL (Eq. 35). This new prototype was desired in order to compare its thermal,



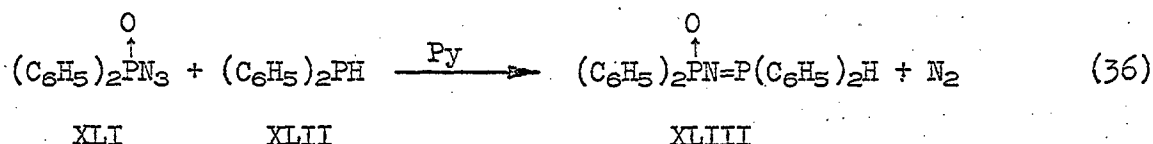
hydrolytic, and solubility properties with those of the fully phenyl-substituted prototype and thus evaluate the potential of the methylphenylphosphinic group in polyphosphoranes. Further evidence of the stability of the new azide XXXV was obtained when it was found that the reaction with triphenylphosphine proceeded very slowly at room temperature.

A quantitative yield of nitrogen gas was obtained from the reaction at reflux in pyridine, and the solid product was analyzed and proved to be the expected P-methyl phosphorane XL. While the molecular weight value was found to be 395 instead of the theoretical 415, this low value may be related to our limited use of chloroform as the solvent in the Neumeyer molecular weight apparatus. In spite of a wide melting range, other analytical data were in good agreement with the calculated values. This wide melting range for an otherwise, essentially pure product might be related to the presence of an enantiomeric mixture due to the presence of an asymmetric-phosphorus atom in XL. A small-scale reaction was carried out in a sealed tube at 125°C for several hours and the nitrogen was measured quantitatively on the vacuum line. This sealed tube reaction vacuum line analysis technique is the basis for the quantitative analyses of the bis-azidophosphoranes (see below).

Attempted recrystallization of XL was made difficult by its general tendency to "oil out" from alcohol-water mixtures which had previously been useful for the recrystallization of the phenyl-substituted phosphoranes. It would seem then that the substitution of a methyl group for a phenyl group in XL certainly changed the solubility characteristics. While the solubility of the P-diphenyl compounds in polar solvents like ether had proved to be very limited, the P-methyl phosphorane XL seems to have considerable

solubility in ether, indicating possibly a change in the position of electronic charge within the molecule. Benzene or toluene, relatively nonpolar solvents, proved to be suitable for use as recrystallization media for the alkyl-aryl compound. In addition, thermogravimetric analysis data for XL indicate that it is also qualitatively as thermally stable as the fully phenyl-substituted prototype. Thus, the methylphenylphosphinic system appears to be a potential linking unit for polyphosphoranes. As a result, investigation of the route to and the properties of p-phenylene-bis(methylphosphinic azide) will be continued.

Two exploratory experiments expected to provide a new class of phosphoranes having a reactive functional group, a P-H, were briefly surveyed. In this survey, diphenylphosphinic azide (XLI) was reacted with diphenylphosphine (XLII) in refluxing pyridine to yield varying quantities of nitrogen (Eq. 36). Although infrared examination of the reaction mixture



indicated that most of the azide had reacted, as evidenced by the extremely weak azide absorption, it also revealed no absorption due to P-H.

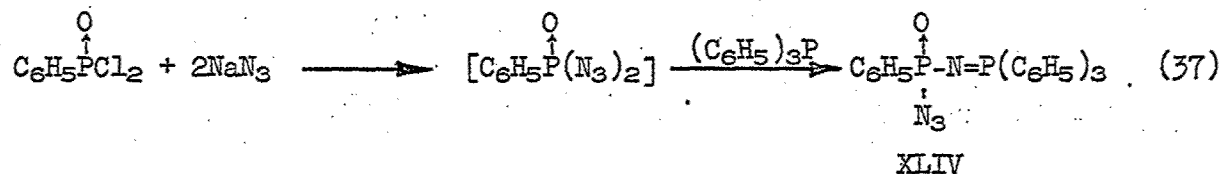
A second run at room temperature was also inconclusive since only a small quantity of nitrogen was collected and the infrared spectrum of the reaction mixture also failed to show either azide or PH absorptions. These results were somewhat surprising in view of ease with which most azide runs are monitored by means of infrared spectroscopy and nitrogen evolution. However, in view of the number of other conceivable reaction routes, perhaps these results are then not too surprising. No further study of this interesting reaction system is planned for the present.

2. Azidophosphoranes

It has previously been pointed out that in order to fully characterize and thus to take advantage of the potential of the recently discovered bis-azidophosphoranes, it would be necessary to develop an analytical technique which would distinguish between the azide and imido nitrogen of these compounds.²⁴ Initially, the use of the standard Kjeldahl method resulted in nitrogen analyses which did 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 was not clear then whether the difficulty was due to impurities in the sample or to incomplete analysis.

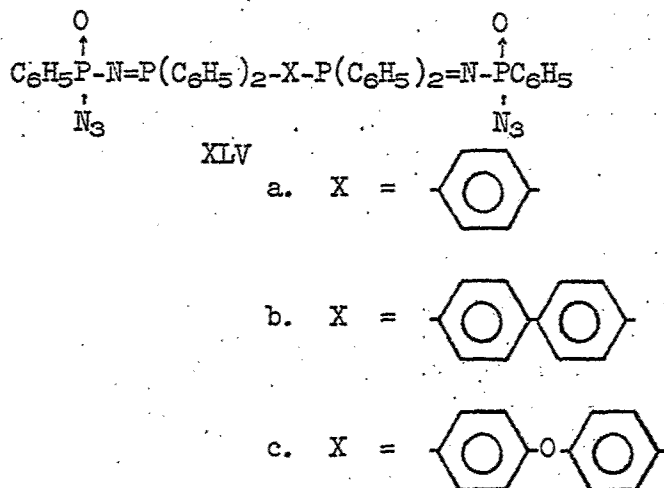
As was pointed out in Section II.C.1 above, the sealed tube reaction of methylphenylphosphinic azide and triphenylphosphine and subsequent quantitative measurement of the by-product nitrogen on the vacuum line suggested a convenient method for the analysis of the bis-azidophosphoranes.

A quantity of the azidophosphorane XLIV, which has been well characterized previously,²⁵ was prepared to provide material developing an analytical method for the azide nitrogen (Eq. 37). This known azidophosphorane XLIV was then submitted for analysis by both the sealed tube-vacuum line



technique and by a combination of wet chemical methods. Thus, the vacuum line technique measured 98.6% of the theoretical nitrogen gas and the wet chemical methods yielded 106% of the azide, 101% of the total nitrogen, and 100% of the phosphorus content. Therefore, either method will give a useful assay of the azidophosphoranes; however, in view of the simplicity of the sealed tube-vacuum line technique, it will usually be the method of choice in the future. Thus this vacuum-line technique appears to be a facile and reliable technique for assaying the azide content of azidophosphoranes and also of phosphinic azides. It should lead to better control of stoichiometry in future polymer preparations.

Additional quantities of the bis-azidophosphoranes XLVa and b were prepared for use in polymer preparations. Examination of these two bis-azidophosphoranes by the vacuum-line technique indicated XLVa and b to have



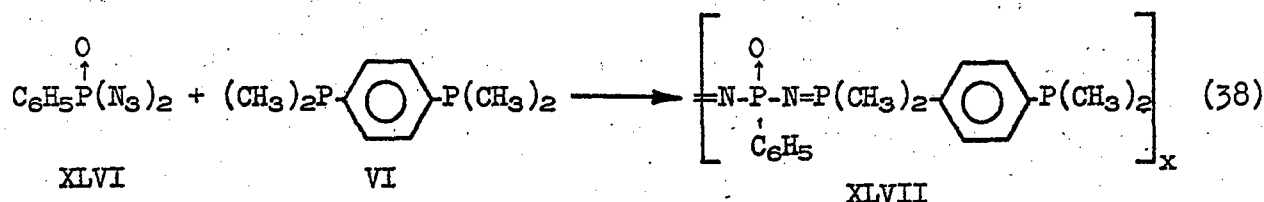
88-89% and 100% of the theoretical azide content, respectively.

As a result of the successful synthesis of 4,4'-bis(diphenylphosphino)-diphenyl ether (Ic), it was also possible to prepare the new ether-linked bis-azidophosphorane XLVc. This new intermediate was readily isolated as a white powder which melted over the range 120-125°C. It was anticipated that this new ether-linked compound would impart more flexibility to polyphosphoranes prepared from it than had the p-phenylene and biphenylene-linked intermediates XLVa and b.

D. Preparation of Phosphorane Polymers

1. Reaction of Phenylphosphonic Diazide and 1,4-Bis(dimethylphosphino)benzene

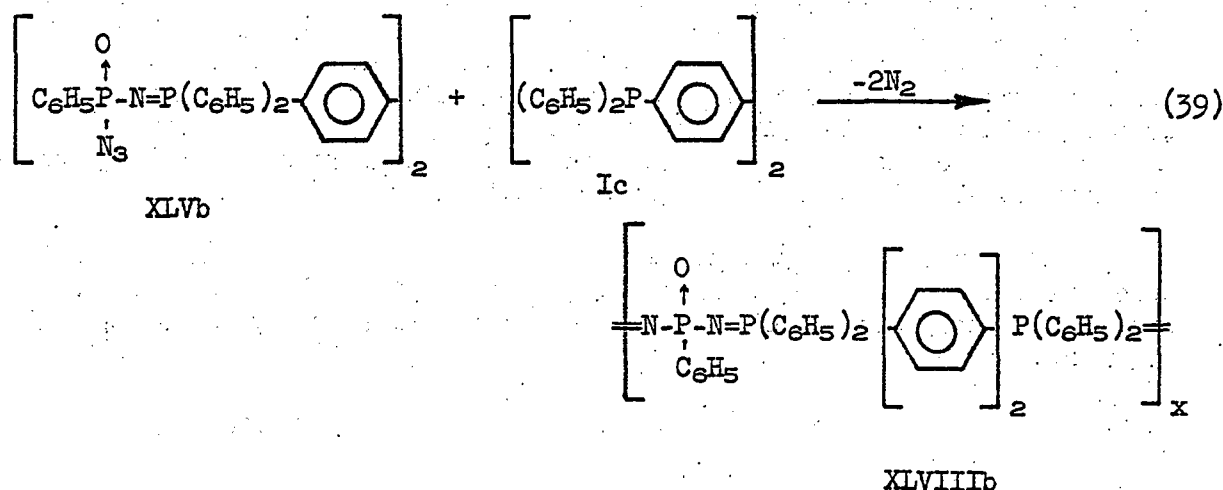
The interaction of phenylphosphonic diazide and 1,4-bis(dimethylphosphino)benzene (VI) in dimethylformamide was carried out at 70°C in view of the anticipated increase in reactivity of the new bis(tertiary phosphine)VI.



The volume of nitrogen collected was approximately 89% of theory after only four hours. The resulting crude polymer XLVII was found to have a low melting range of only 60-70°C, considerably below the melting ranges observed for the fully phenylated polyphosphoranes. The infrared spectrum of XLVII contained the expected absorptions in the region of 7 to 9μ; no azide absorption was observed and only a weak absorption at 10.5μ due to possible POP was observed. Attempts to pull fibers from XLVII in water at 60-70°C were not successful.

2. Reaction of 4,4'-Bis(diphenylphosphino)-biphenyl and the Bis-Azidophosphorane XLVb

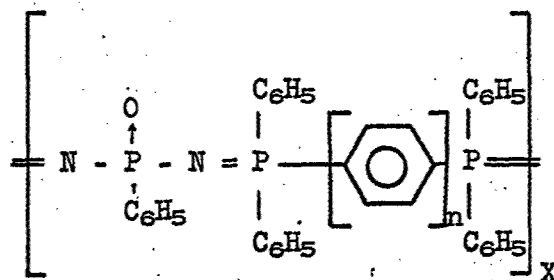
The reaction of 1,4-bis(diphenylphosphino)benzene (Ia) and the bis-azidophosphorane XLVb to yield a polyphosphorane from which the first fibers and disks were formed has been described.²⁶ In an extension of this work, the biphenylene homologues were reacted under similar conditions in refluxing dimethylformamide as shown in Equation 39. The reaction had



approached completion after 7 hours at the reflux temperature. After the usual workup long (4-5 ft), brittle fibers were pulled from the crude polymer XLVIII in water at about 65°C. An attempt to determine the viscosity of this material in chlorobenzene was apparently not successful as no increase in the observed viscosity of chlorobenzene solutions were noted. These viscosity measurements will be continued with other samples of the various polyphosphoranes.

A sample of this p-phenylene-linked polyphosphorane which had been prepared via the bis-azidophosphorane XLVa and which yielded the first brittle fibers of this study, was submitted to thermalgravimetric analysis. Examination of the data revealed that there was no difference in the thermal properties of this sample of the polyphosphorane; i.e., 10% weight loss and a 38% residue which was then stable from about 600-825°C.

Independent molecular weight values for the p-phenylene (XLVIIIa) and 4,4'-biphenylene (XLVIIIb) linked polyphosphoranes have now been



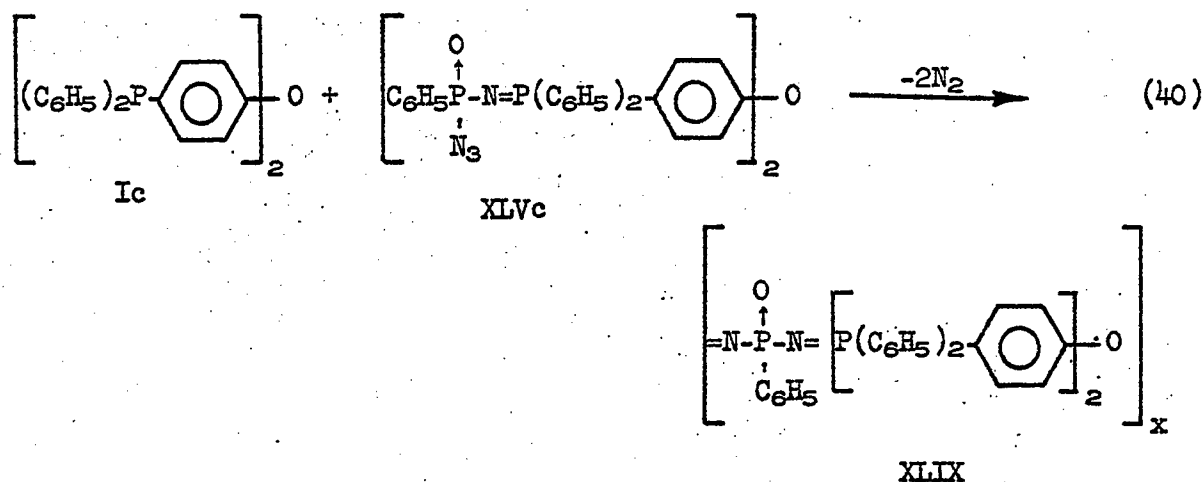
XLVIII

a. $n = 1$

b. $n = 2$

determined at the U. S. Rubber Company.²⁷ These samples are reported to have molecular weight values, by light scattering, of 20,000 and 13,000, respectively. These values correspond to degrees of polymerization of about 33 and 20. This is very encouraging data. Furthermore, since these polymers were not prepared by our newer bis(azidophosphorane) route which is now yielding flexible fibers, we can infer that our more recent polymers have even higher degrees of polymerization. The preparation of new samples for additional molecular weight determinations is underway.

The two new, diphenyl ether linked polymer components Ic and XLVc were reacted in refluxing dimethylformamide to yield the diphenyl ether linked polyphosphorane XLIX (Eq. 40). The polyphosphorane XLIX was isolated



as a yellow-colored tacky material. Long, flexible fibers were drawn from both the neat polymer and from the polymer in warm water. Although a molecular weight value, via the Neumayer thermistor method,²⁸ of only 1185 was obtained which represents a degree of polymerization of two, the fiber forming characteristics suggest a somewhat higher degree of polymerization. These new fibers retained their flexibility in air for at least a week. This flexibility of XLIX is in marked contrast to the previously prepared phenylene and biphenylene linked polyphosphoranes from which only brittle fibers and discs have been formed. It is of considerable interest to speculate about the possible properties of polyphosphorane copolymers in which the bis(azidophosphorane) and the bis(tertiary phosphine) contain different linking groups, especially the case in which only one is a diphenyl ether linked unit. Considerably more work is now planned for the polyphosphorane preparation and evaluation phase of this investigation.

3. Prepolymerization Study

A preliminary experiment designed to study the effect of preparing a phosphorane prepolymer was investigated. A mixture of 1,4-bis(diphenylphosphino)benzene (Id) and the bis-azidophosphorane XLVa was reacted in a refluxing benzene-dimethylformamide solvent. After 24 hours, only 43.5% of the nitrogen had been evolved and the phosphorane prepolymer was isolated as a flaky, white solid which softened at 80°, foamed at 125° and melted at about 140°C. The infrared spectrum contained, as expected, a medium strong azide absorption at 4.65μ.

When placed in hot water long fibers, still brittle however, were drawn out from the tacky ball of prepolymer. The remaining white solid now softened at 115°, foamed at 125°, and now did not melt until about 250°C. When a sample of this water-treated material was placed in an aluminum die and heated at 125°C and 520 psi, a hard, yellow disk was obtained. This disk had more structural integrity than had previous disks. Infrared examination

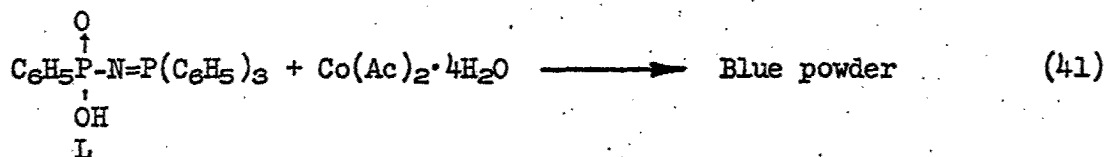
of the disk showed that the intensity of the azide absorption at 4.65μ had decreased considerably. Now the polymer softened at 150° , foamed at 165° , and showed only a trace of melting to 260°C . This appears to be a possibly rewarding area of study and will be continued. Perhaps laminate composites can be fabricated from this phosphorane prepolymer.

4. Phosphorane Polymer Fraction

In an effort to gain insight into possible chain length distributions in both p-phenylene and 4,4'-biphenylene-linked polyphosphoranes prepared thus far, fractionation of these materials using chlorobenzene and n-hexane was undertaken. The sample was dissolved in boiling chlorobenzene and n-hexane was added to the cloud point. The mixture was then cooled, the solids removed, and the filtrate was again brought to reflux before additional hexane was added. This was repeated five to six times. The preliminary data on these various fractions are shown in Tables IV, V, and VI. Infrared examination of the fractions showed all to be essentially identical. Attempts to determine the molecular weights of the various fractions will now be made. To this end, calibration of the molecular weight apparatus with chloroform and/or chlorobenzene is underway.

E. Miscellaneous

Recent investigations by Rose and Block have demonstrated that linear polymers can be readily prepared from phosphinic acids and metal ions such as cobalt (II), zinc (II), and beryllium (II).²⁹ Since a variety of phosphorane-phosphinic acid compounds can be readily prepared, it was of interest to briefly investigate the reaction of one of these phosphorane-phosphinic acids L and cobalt (II) acetate tetrahydrate. If successful



such a reaction could be used to crosslink linear polyphosphoranes having phosphinic acid groups. Initially, rose-colored powders were obtained which then were converted to bright blue-colored powders on exposure to air and heating. In a melting point capillary tube the blue powder appeared to be stable to about 280°C at which point a gas was noted to be evolving. Thermal gravimetric analysis data for the blue powder indicate about 4% weight loss at 300°C , 44% loss at 400°C , and then a gradual loss to yield a residue of 44% at 800°C . This appears to be a potentially rewarding area of investigation and may be continued as time permits.

F. Experimental

CAUTION! Certain of the phosphonic diazides used in this study are extremely sensitive to heat and shock and should be handled with care.^{1,23} All azide and organolithium reactions were carried out under a dry, inert atmosphere and in anhydrous solvents.

Infrared spectra of liquid samples were determined on a Beckman IR5 spectrophotometer as thin films. The spectra of solids were determined as potassium bromide pellets on a Perkin Elmer Model 21 spectrophotometer. Molecular weights were determined using the Neumayer thermistor method.²⁸ Nitrogen gas volumes are always corrected unless otherwise noted. Boiling and melting points are not corrected. Vapor phase chromatography was done on a Perkin Elmer 801 gas chromatograph using 6-foot glass columns packed with 10 percent tricresolphosphate on 60-80 mesh Gas Pack F.

1. Preparation of Intermediates

a. Commercial 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:

	<u>m. p. °C</u>	<u>Recrystallized from</u>
Triphenylphosphine	80.5-82	Isopropyl Alcohol
4,4'-Dibromobiphenyl	162-164	Benzene
4,4'-Dibromodiphenyl Ether	57-59	Ethanol
	<u>b. p.</u>	<u>n_D²⁰</u>
Diphenylchlorophosphine	76-89° C/0.3 mm	1.6362
Phenylphosphonic Dichloride	140-142° C/20 mm	1.5580-1.5590
Diphenylphosphinic Chloride	128-132° C/0.1 mm	1.6100

b. p-Phenylenebis(phosphonous dichloride) (V) (W-1893-121)

Into a heavy wall glass tube (cap. about 2700 ml) were placed 378 g (0.849 mole) of p-phenylenebis(diphenylphosphine) (Id) and 2602 g (18.94 moles, 744% excess) of phosphorus trichloride. The tube was sealed under about 20 mm dry nitrogen gas. Then the tube was submerged in about 2 liters of benzene within a large high pressure steel reactor which was sealed and heated for 30 hrs at 300°C.

For some reason the glass tube ruptured during the heating cycle. Nevertheless the benzene solution containing the products was subjected to fractional distillation first at atmospheric pressure to

remove the benzene and excess phosphorus trichloride. The residue was then subjected to vacuum distillation and 465.0 g (3.396 moles, 100.0%) of phenyldichlorophosphine was removed, b.p. 91°C/13 mm. Based on the yield of this by-product the conversion was quantitative; the liquid residue presumably containing 0.85 mole of p-phenylenebis(phosphonous dichloride) was held in reserve for subsequent conversions to other intermediates.

c. P-(N,N-Dimethylamino)-P-phenylphosphonic Chloride (XI) (1945-94,95)

Into a solution consisting of a one-mole quantity (195 g, 162 ml) of phenylphosphonic dichloride and one mole of pyridine (79 g, 80 ml) dissolved in 400 ml of dry toluene was slowly distilled 45 g (1 mole, 65 ml) of dimethylamine. The reaction temperature was held at 5°C or less by means of an ice-salt bath. The by-product pyridine hydrochloride was removed by filtration through a fine glass-sintered funnel and washed thoroughly with toluene.

The combined toluene solutions were concentrated at reduced pressure to give a yellow oil which was then fractionally distilled. The forerun yielded 20.6 g (.106 mole, 10.6%) of unreacted phenylphosphonic dichloride. The product, obtained as a colorless liquid distilling at 87-93°C and 0.2 mm, weighed 120.4 g (0.589 mole, 65.9% yield based on consumed dichloride) and was sealed in small vials.

A second similar preparation carried out in 600 ml of diethyl ether and using two moles of dimethylamine resulted in the isolation of 134 g (0.657 mole, 89.9% yield based on consumed dichloride) of P-(N,N-dimethylamino)-P-phenylphosphonic chloride. The product was distilled into small storage vials and sealed for storage until needed.

d. Ethyl Diphenylphosphinate (1945-138)

A mixture of 16.2 g (0.206 mole) of pyridine, 9.5 g (0.206 mole) of ethanol, and 250 ml of ether was cooled to 10°C before slow addition of 48.6 g (0.206 mole) of diphenylphosphinic chloride was begun. After stirring overnight, the pyridine hydrochloride was carefully removed by filtration through a fine glass-sintered funnel. The ether filtrate was concentrated and distilled through a short Vigreux column at 0.3 mm of pressure to yield 9.3 g (n_D^{20} 1.5719) boiling at 139-141°C and 29.5 g (n_D^{20} 1.5726) boiling at 140-141°C. The combined yield was 76.5%.

The second fraction solidified on standing overnight to give a solid melting at 35-37°C (lit³⁰ m.p. 165). Kosolapoff has previously questioned this older, high melting point for ethyl diphenylphosphinate.³¹

Anal. calcd. for $C_{14}H_{15}O_2P$: P, 12.58. Found: P, 12.7.

e. Phenyl p-Toluenesulfonate (Phenyl Tosylate) (1972-195)

To 103.2 g (0.5 mole) of p-toluenesulfonyl chloride and 47.4 g (0.6 mole) of pyridine slurried in 350 ml of ethyl ether was slowly added 56.4 g (0.6 mole) of phenol in 200 ml of ether. After 4 hrs at the reflux temperature the reaction mixture was cooled and allowed to stand for 48 hrs. The ether was decanted from the mixture of white crystals and tan solids and the solids were then washed with cold water to yield a white crystalline material. The ether was removed at reduced pressure and the resulting solids were also washed with cold water. The combined solids weighed 118 g (0.476 mole, 95.2% yield) and melted at 93-95°C.

f. Preparation of Arylene-di(sulfonyl chlorides)

(1) Diphenylether-4,4'-di(sulfonyl chloride) (XXXVII)
(1945-93)

Into a 3-neck flask fitted with a stirrer, condenser, addition funnel, and thermometer were added 200 ml of chloroform and 40 g (0.235 mole) of diphenyl ether. The flask and its contents were then cooled to 0°C by means of an ice-salt bath. The chlorosulfonic acid, 200 g (1.72 mole, 113 ml), was slowly added over 1 hr while maintaining the reaction temperature at 0°C.

After 1 hr at room temperature, the clear reaction mixture was poured into ice-water. The chloroform layer was separated with difficulty and subsequently washed with water, dilute sodium carbonate, and water until neutral. The still cloudy chloroform was dried over anhydrous sodium sulfate, decanted, and concentrated at reduced pressure to yield 76.2 g (0.208 moles, 88.5%) of a white powder melting incompletely at 120-126°C.

A sample recrystallized from chloroform-hexane melted over the range 110-129°C. Anal. calcd. for $C_{12}H_8Cl_2O_5S_2$: Cl, 19.18; S, 17.48%. M.W., 366.7. Found: Cl, 19.8; S, 17.4; M.W., 373.5. Recrystallization of the remaining product from chloroform-hexane gave two crops of crystalline powder: (a) 21.9 g having a melting range of 112-128°C, and (b) 7.5 g which softened at 100°C and melted at 105-113°C. The infrared spectra of these fractions were essentially identical. However, fraction b contained some impurity as was indicated by its analysis (found: Cl, 20.5; S, 16.9).

(2) Attempted Synthesis of Biphenyl-4,4'-di(sulfonyl chloride) (XXXVI) (1945-91)

In a similar fashion, 30.8 g (0.2 mole) of biphenyl dissolved in 200 ml of chloroform was reacted at 0°C to 5°C with 116 g (0.8 mole) of chlorosulfonic acid. However, after the reaction was completed and poured into ice-water, an emulsion formed. It was therefore extremely difficult to separate the aqueous phase. The solids subsequently isolated

were largely insoluble in glacial acetic acid which is reported to be a solvent suitable for the recrystallization of the di(sulfonyl chloride).³² As a result, this experiment was discontinued for the present.

2. Preparation of Bis Tertiary Phosphines

a. 4,4'-Bis(diphenylphosphino)biphenyl (Ib)

(1) Via DiGrignard Reagent (1945-61,64, and 89)

The diGrignard reagent was formed from 31.2 g (0.1 mole) of 4,4'-dibromodiphenyl and 4.8 g (0.2 g-atom) of magnesium turnings in 125 ml of tetrahydrofuran and 50 ml of benzene. The reflux period was 13 hrs. The subsequent addition of 44.1 g (0.2 mole) of diphenylchlorophosphine in 30 ml of tetrahydrofuran was initially exothermic. The reaction mixture was further refluxed for 1.5 hrs.

Hydrolysis by means of 55 ml of saturated ammonium chloride solution, separation of the yellow-colored organic phase, and subsequent concentration of the organic phase yielded a bright yellow-colored, tacky residue. Digestion with methanol yielded 22.9 g of crude 4,4'-bis(diphenylphosphino)biphenyl, having a wide melting range.

Similar yields were obtained from two additional runs with only minor procedural modifications. From the methanol extracts was recovered a yellow oil which precipitated some white solids. Infrared examination of the yellow oil indicated it to be the same cleavage product of the tetrahydrofuran which had been previously identified by Garner and Tedeschi⁵ to be diphenyl-4-hydroxybutylphosphine oxide. Exhaustive purification of these impure fractions of Ib by recrystallization from ethylene glycol dimethyl ether and/or tetrahydrofuran-methanol was necessary in order to obtain Ib melting at 191-193°C.

(2) Via n-Butyllithium (1972-129,132,136,138,143,152, and 1997-35)

A 74.5 g (0.24 mole) quantity of 4,4'-dibromobiphenyl and 200 ml of tetrahydrofuran were cooled to -66°C before 0.48 mole of n-butyllithium in 300 ml of hexane was added slowly through an addition funnel. After warming to 0°C and recooling to -66°C, 105.4 g (0.48 mole) of neat diphenylchlorophosphine was added. The reaction mixture was warmed to room temperature and filtered to remove the majority of the product. After washing with water and digestion with methanol, 117 g (0.224 mole, 94% yield) of Ib melting at 190-191° was recovered.

Several runs using a 20% excess of n-butyllithium resulted in average yields of Ib of 82% while one experiment employing a 30% excess of the n-butyllithium gave a 73.5% yield of 4,4'-bis(diphenylphosphino)biphenyl.

The following experiment was studied in order to determine the possible effect of eliminating the warm-up to 0°C before adding the

diphenylchlorophosphine.

Thus, to 39.0 g (0.125 mole) of 4,4'-dibromobiphenyl dissolved in 150 ml of tetrahydrofuran which was held at -66°C by an external Dry Ice-acetone bath, was slowly added 160 ml of a hexane solution of n-butyllithium (0.25 mole). Immediately after the addition of the n-butyllithium had been completed, 55.2 g of diphenylchlorophosphine was slowly added so as to maintain the reaction temperature at or below -62°C . The reaction mixture was allowed to warm to ambient temperature and the white solids were removed by filtration. The solids were washed with water and with methanol to yield 19.7 g of crude 4,4'-bis(diphenylphosphino)-biphenyl melting at $185-190^{\circ}\text{C}$. The filtrate was concentrated and similarly worked up to yield an additional 22 g of somewhat less pure product. The combined yield was 63.8%.

In one further study, only the addition sequence for the reactants was altered. Thus, the addition of 31.2 g (0.1 mole) of 4,4'-dibromodiphenyl dissolved in 200 ml of tetrahydrofuran to 125 ml (0.2 mole) of n-butyllithium held at -66°C was followed by warming to 0°C . Subsequent addition of 44 g (0.2 mole) of diphenylchlorophosphine and the usual workup resulted in isolation of only 35 g (0.067 mole, 67% yield) of Ib melting at $188-191^{\circ}\text{C}$.

In a comparison run, 0.05 mole of 4,4'-dibromobiphenyl, 0.2 mole of n-butyllithium, and 225 ml of ether were held at reflux for two and three-fourths hours before 0.2 mole of diphenylchlorophosphine was introduced. After the usual workup, a 65% yield of Ib melting at $185-188.5^{\circ}\text{C}$ was obtained.

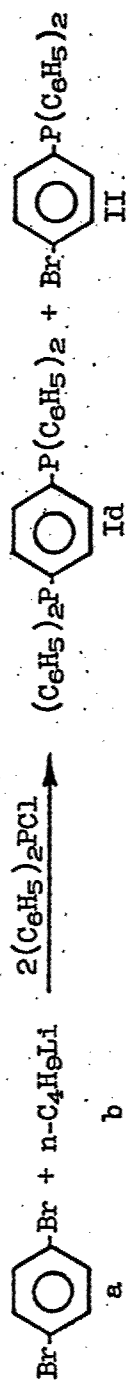
b. 1,4-Bis(diphenylphosphino)benzene (Id)

(1) Via n-Butyllithium and p-Dibromobenzene

A number of experiments have been carried out under a variety of reaction conditions in an effort to improve upon the yield 1,4-bis(diphenylphosphino)benzene (Id) obtained directly from p-dibromobenzene and n-butyllithium. The pertinent data for most of these experiments are shown in the following table. Three runs in tetrahydrofuran over the temperature range -66° to $+32^{\circ}\text{C}$ are not included since only traces of 4-bromophenyldiphenylphosphine (II) were isolated.

TABLE I

PREPARATION OF 1,4-BIS(DIPHENYLPHOSPHINO)BENZENE



Run No.	Moles of		Solvent ¹	Reaction Temperature	Time Hrs	Yield %	
	a	b				Id	II
1972-158	0.12	0.24	Ether	Ambient	1	15	24.4
1972-161	0.18	0.36	Ether	Ambient	3	36	-
1972-163	0.18	0.36	Ether	Ambient	6	24	-
1972-165	0.18	0.36	Ether	Reflux	3	47.3 ²	-
1945-152	0.05	0.2	Ether	Reflux	2-3/4	57.8	-
1935-91	0.05	0.2	Ether	Reflux	4	50	-
1935-95	0.05 ³	0.1	THF	-66° to 0°	0.5	25	-
1935-97	0.05 ³	0.2	THF	-66° to 0°	0.5	42	-
1972-141	0.24 ⁴	0.478	THF	-66° to 0°	0.5	-	57
1935-107	0.05 ⁴	0.2	THF	-66° to 0°	2/3 at -66° 1-1/3 at 0°	33.2	-

1. The n-butyllithium is in hexane
2. An additional 11.2% of impure product also isolated
3. n-Butyllithium added to dibromobenzene
4. Dibromobenzene added to n-butyllithium

(2) Via n-Butyllithium and 4-Bromophenyldiphenylphosphine (II)

(a) Tetrahydrofuran at 10° (1945-113 and 114)

A mixture of 50 ml of 1.6M n-butyllithium in hexane and 50 ml of tetrahydrofuran was cooled to 10°C before beginning the addition 27.3 g (0.08 mole) of 4-bromophenyldiphenylphosphine dissolved in 50 ml of tetrahydrofuran. The reaction mixture soon became dark-brown or black in color, was stirred at 10°C for 1-1/2 hrs and then stirred at 18°C for another 30 min. The addition of 17.6 g (0.08 mole) of diphenylchlorophosphine at 18-20°C resulted in a gradual color change from black to yellow. After the addition was completed, the mixture was first held at 50°C for 30 min and then concentrated at reduced pressure to yield a yellow-colored, oily residue. The oil failed to solidify on treatment with methanol and was soluble in ethanol and 2-propanol. The expected product, 1,4-bis(diphenylphosphino)benzene, would have not been soluble in these solvents and would have solidified on treatment with the methanol.

In a second experiment, a 14.7 g (0.0431 mole) quantity of 4-bromophenyldiphenylphosphine was dissolved in 100 ml of tetrahydrofuran and cooled to 5°C before beginning the addition of 27 ml (0.0431 mole) of n-butyllithium in hexane. The temperature was held at 5-10°C during the 20-minute addition during which the mixture color slowly changed to black. After stirring at 5°C for 5 minutes, the addition of 9.5 g (0.0431 mole) of diphenylchlorophosphine was completed in 10 minutes. The color of the reaction mixture again changed from black to yellow. The concentration of the mixture, after 1-1/2 hours at 4°C, yielded a yellow-colored oil which was largely soluble in methanol. None of the expected bis-tertiary phosphine could be separated.

(b) Tetrahydrofuran at Low Temperature (1945-115 and 116, 1972- 83 and 177)

In a preliminary survey experiment, to 0.023 mole of n-butyllithium and 25 ml of tetrahydrofuran at -66°C, was slowly added 0.01 mole of 4-bromophenyldiphenylphosphine (II) dissolved in 25 ml of tetrahydrofuran. After 1 hour at -66°C, 0.01 mole of diphenylchlorophosphine was slowly introduced. The reaction mixture was slowly warmed to room temperature, treated with methanol to destroy unreacted n-butyllithium and/or diphenylchlorophosphine, and concentrated to give a yellow, gummy residue. Digestion with methanol then gave 2.0 g (40% yield) of impure Id melting at 155-160°C.

In this experiment, 19 g (0.0557 mole) of 4-bromophenyldiphenylphosphine and 100 ml of tetrahydrofuran were cooled to about -74°C prior to the addition of a deficiency of n-butyllithium, 27 ml of a hexane solution of n-butyllithium containing 0.043 mole of the n-butyllithium. The reaction temperature was held below -66°C during the 25-minute addition period by means of an external Dry Ice-acetone bath. The mixture slowly

turned black in color and was then stirred at -74°C for 1 hour.

The subsequent addition of 12.3 g (0.056 mole) of diphenylchlorophosphine and 10 ml of tetrahydrofuran was completed in 6 minutes. The color of the reaction mixture was brown at the end of the addition but turned to yellow on warming to -25°C . After warming at $50-60^{\circ}\text{C}$, 10 ml of methanol was added with no observable reaction. Concentration of the reaction mixture yielded a white solid and a yellow oil. Digestion with methanol resulted in the recovery of 9.8 g (0.022 mole) of crude 1,4-bis(diphenylphosphino)benzene melting over the range $152-162^{\circ}\text{C}$. The yield based on n-butyllithium was 51% but only 39.5% when based on the bromophosphine.

A second experiment was carried out at -70°C by adding 18.3 ml (0.0293 mole) of n-butyllithium solution to 10 g (0.0293 mole) of 4-bromophenyldiphenylphosphine. After only 5 minutes at -70°C , 6.5 g (0.0293 mole, 5.3 cc) of diphenylchlorophosphine in 10 ml of tetrahydrofuran was added over a 4-minute interval. The resulting mixture was allowed to warm to room temperature (18°C), heated at $50-60^{\circ}\text{C}$ for 15 minutes, and then was treated with 10 ml of methanol. Concentration at reduced pressure yielded a semi-solid residue which was then digested with 50 ml of methanol and filtered. After an ether wash on the filter, 8.4 g (0.0188 mole, 64.2% yield) of free-flowing, granular 1,4-bis(diphenylphosphino)benzene (Id) melting at $160-164^{\circ}\text{C}$ was isolated.

In a third similar run, to 18.3 ml (0.029 mole) of a hexane solution of n-butyllithium at -66°C was added 10 g (0.029 mole) of 4-bromophenyldiphenylphosphine dissolved in 100 ml of tetrahydrofuran. Without further delay or warming, 6.5 g (0.029 mole) of diphenylchlorophosphine was slowly added. On warming to room temperature, white solids separated and were removed by filtration under nitrogen. After washings of the solids with methanol and with water, 10.4 g (0.0233 mole, 80.3%) of 1,4-bis(diphenylphosphino)benzene (Id) melting at $161-162^{\circ}\text{C}$ was recovered.

(3) Via Two Step in Situ Reaction (1935-84 and 88)

The following experiments describe attempts to effect the two conversions of p-dibromobenzene to 1,4-bis(diphenylphosphino)benzene (Id) without the intermediate isolation of 4-bromophenyldiphenylphosphine (II).

In the first step, 4-bromophenyldiphenylphosphine (II) was formed in a reaction flask fitted with a bottom take-off. Thus, to 0.15 mole of n-butyllithium in hexane at -66°C was added 35.4 g (0.15 mole) of p-dibromobenzene in 100 ml of tetrahydrofuran. Without further delay, 11 g (0.05 mole) of neat diphenylchlorophosphine was introduced.

The cooling bath was removed and a second reaction flask was attached to the bottom take-off of the original reaction flask. The solution of II was then dropped into a second equivalent of n-butyllithium

and 30 ml of tetrahydrofuran at -66°C . A viscous brown-colored material quickly formed and made magnetic stirring of the reaction mixture impossible. Subsequent addition of the second equivalent of diphenylchlorophosphine resulted in a clear, yellow-colored reaction mixture which was concentrated to give a yellow, semisolid residue. Digestion with methanol and ether resulted in the isolation of 34.5 g (approximately 51.5% yield) of Id melting over the range $159-170^{\circ}\text{C}$.

A second, essentially identical run except for mechanical stirring of the second flask resulted in a 56.5% yield of Id melting over the range $163-172^{\circ}\text{C}$.

(4) Via DiGrignard Reagent (1972-47)

Into a dry 500-ml, 4-neck Morton flask fitted with a nitrogen inlet and a condenser, high speed mechanical stirrer, thermometer, and an addition funnel were placed magnesium turnings, 4.86 g (0.2 g-atom), and 100 ml of tetrahydrofuran. p-Dibromobenzene, 23.6 g (0.1 mole), in 50 ml of benzene was added slowly through the addition funnel to the reaction mixture. After the addition was completed in 15 minutes, the reaction mixture was heated at reflux with stirring for a total of 23 hours.

The reaction mixture was cooled to room temperature and diphenylchlorophosphine, 45.8 g (0.208 mole), was added. After one hour at reflux, the system was cooled to ambient temperature, and 60 ml of saturated ammonium chloride solution was introduced. The tetrahydrofuran-benzene layer was decanted from the white solid and concentrated at reduced pressure to yield 40.0 g of crude product. The solids were digested with methanol and filtered to yield 23.0 g of white solid which was then recrystallized from toluene and methanol to yield 11.0 g (24.6%) white powder with a melting point of $164-166^{\circ}\text{C}$ as compared to a melting point of $166-168^{\circ}\text{C}$ for the known 1,4-bis(diphenylphosphino)benzene.

c. 1,4-Bis(Dimethylphosphino)benzene (VI) (1972-22)

Into a 3-liter, 4-neck Morton flask fitted with a mechanical stirrer, addition funnel, condenser, and thermometer and well flushed with dry nitrogen was transferred, by nitrogen pressure, 398 g (3.34 mole) of methyl magnesium bromide in 1200 ml of ether. Approximately 234 g (0.836 mole) of 1,4-bis(dichlorophosphino)benzene (V) dissolved in 300 ml of anhydrous ether was placed in the addition funnel and slowly added to the Grignard reagent held at $0-5^{\circ}\text{C}$. After one hour at reflux, the reaction was cooled and treated with about 200 ml of saturated ammonium chloride solution. The ether was decanted from the solids which were subsequently broken up under nitrogen and further extracted with additional ether. The combined ether was concentrated to yield a small quantity of a black-colored liquid residue. It was fractionated at 0.01 mm pressure to yield only 11 g of colorless product boiling at $66-70^{\circ}\text{C}$ and $n_D^{24} 1.5890$.

Anal. calcd. for $C_{10}H_{16}P_2$: P, 31.62; M.W., 198.2. Found P, 29.2; M.W., 193. The infrared spectrum did not contain any P-O absorptions in the 8.5-9.0 μ region.

d. Attempted Preparation of 1,3-Bis-(diphenylphosphino)benzene (Ia) (1945-59,62, and 67)

Under an atmosphere of nitrogen, 4.8 g (0.2 g-atom) of magnesium turnings were slowly added over two hours to 23.6 g (0.1 mole) of meta-dibromobenzene in 100 ml of anhydrous tetrahydrofuran. The initial reaction was exothermic. After the magnesium addition was completed, the mixture was heated to reflux and the formation of a yellow-brown colored insoluble material was observed. After approximately 17 hours at the reflux temperature, 44.0 g (0.2 mole) of diphenylchlorophosphine was quickly added to the suspension of the diGrignard and the reaction mixture was held at the reflux temperature for an additional two hours to complete the reaction.

The addition of 50 ml of saturated ammonium chloride solution to the reaction mixture at ambient temperature resulted in the formation of a gelatinous precipitate. The yellow tetrahydrofuran phase was decanted, the precipitate washed with two 50 ml portions of tetrahydrofuran, and the combined organics were concentrated to yield a tacky, amber-colored residue. Attempts to induce this residue to crystallize were unsuccessful. A small quantity of the residue was dissolved in benzene and eluted through a column of activated alumina with 1:1 benzene-hexane. Concentration of the eluate resulted in the isolation of white, tacky residue which did not crystallize. This residue had n_D^{21} of 1.6618 which is close to that observed for p-bromophenyldiphenylphosphine (II), n_D^{20} 1.6680, before it solidifies. However, infrared examination of this material shows strong absorptions at 8.4 and 8.95 μ which are associated with aromatic phosphine oxides. Coupled with the strong absorption at 12.7 μ assigned to a meta substituted benzene, one concludes that this material is probably an oxide of the desired 1,3-bis-(diphenylphosphino)benzene or even meta-bromophenyldiphenylphosphine.

Additional efforts to effect the purification and solidification of this material by means of extraction of the tertiary phosphine by means of concentrated hydrochloric acid also resulted in the isolation of the same tacky residue. This technique had previously worked well for the purification of 4,4'-bis(diphenylphosphino)biphenyl.³³

A second experiment was carried under similar conditions, except that the reflux period for the diGrignard formation was only 12 hours. After the usual workup, the residue was the same tacky, amber-colored material as had been obtained previously. Infrared examination surprisingly indicated a P-H absorption at 4.38 μ in addition to absorptions due to P-O at 8.48 and meta-substituted phenyl at 12.7 μ . This residue was set aside for further study at a later date.

The third experiment was carried out on the same scale and in a similar manner to the previous attempted preparations. The only changes were the addition of 50 ml of benzene to the tetrahydrofuran used in the Grignard formation and a longer reflux period (45 hrs) for this formation. Workup again yielded the tacky, brown residue after the ammonium chloride hydrolysis.

e. 4,4'-Bis(diphenylphosphino)diphenyl Ether (Ic)

(1) Attempted Preparation Via the DiGrignard Reagent

(1945-66, 72, 73, and 90)

After only five hours at reflux, a mixture of 32.8 g (0.1 mole) of 4,4'-dibromodiphenyl ether, 4.8 g (0.2 g-atom) of magnesium turnings, 50 ml of benzene and 50 ml of tetrahydrofuran contained only a trace of the magnesium. In this system, the diGrignard reagent was soluble in contrast to all previous diGrignard preparations. Addition of 44 g (0.2 mole) of diphenylchlorophosphine in 25 ml of tetrahydrofuran was exothermic and the reaction temperature was held at 20°C by means of an ice water bath. After 1 hour at reflux and the usual workup, concentration of the tetrahydrofuran-benzene phase yielded a clear, amber-colored residue. Infrared examination of the crude product revealed the expected absorptions for the expected product.

Solution of a sample of the crude product in concentrated hydrochloric acid followed by filtration through charcoal and dilution with ice water precipitated a white solid. However, on exposure to the air or on vacuum drying, the material became extremely tacky and impossible to handle. Digestion with methanol failed to cause the oil to solidify. Similar products were obtained from additional preparations under varying reaction conditions.

(2) Via n-Butyllithium

A number of experiments were run under varying reaction conditions in attempting to obtain a high yield of pure 4,4'-bis(diphenylphosphino)diphenyl ether (Ic). Pertinent details of these investigations are given in Table II.

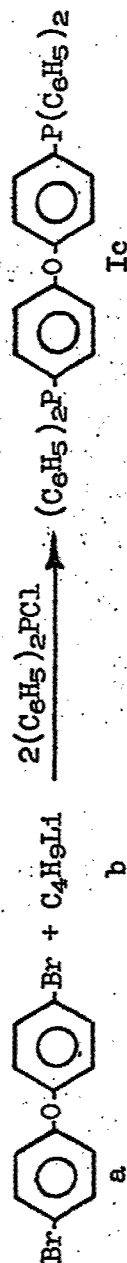
The crude reaction products are solidified by digestion with methanol or by solution in ether, filtration to remove insolubles, concentration and digestion in methanol depending on the purity of the crude reaction product. Analytical samples, melting at 115-116°C, were obtained by recrystallization from benzene-methanol and/or ethyl acetate.

Anal. calcd. for $C_{36}H_{28}OP_2$: P, 11.50; M.W., 538.8.
Found: P, 11.30; M.W., 513.

For further characterization of Ic, a 5-g sample of the semipure Ic was dissolved in acetone and titrated with potassium permanganate

TABLE II

PREPARATION OF 4,4'-BIS(DIPHENYLPHOSPHINO)DIPHENYL ETHER (Ic)



Run No.	Moles of		Addition Sequence	Solvent(s) ¹	Reaction Temperature	Time Hrs	% Yield of Ic ²
	a	b					
1997-12	0.2	0.4	a to b	THF	-66° to 0°	1.5	-
-16	0.1	0.2	a to b	THF	-66° to 0°	2	64.5
-19	0.18	0.4	b to a	benzene	20° to reflux	18	-
-20	0.18	0.4	b to a	benzene	20°-30°	1	-
-23	0.18	0.4	b to a	benzene	20° to 69°	2	-
-25	0.18	0.4	b to a	benzene	20° to 36°	2	-
-28	0.05	0.16	b to a	ether	Ambient	3/4	-
-31	0.05	0.2	a to b	THF	-66° to +20°	1.3	56
-33	0.05	0.2	a to b	ether	28° to 44°	3.0	-
-38	0.05	0.2	a to b	THF	-66° to 0°	1.5	68
-41	0.05	0.2	a to b	THF	-66° to 0°	1.5	53
-44	0.05	0.2	a to b	THF	-66° to 0°	2.0	84
-45	0.05	0.1	a to b	THF	-66°	4.5	64.5

1. The n-butyllithium is in hexane

2. Yield of solid Ic melting about 105-110°C

in acetone until a faint pink color was maintained. The manganese dioxide was washed well with acetone and benzene and the organics were concentrated to give a white semisolid. Further digestion with ether solidified the product and 2.8 g (about 53%) of the bis oxide of Ic was recovered. Recrystallization from ethanol-water gave a white crystalline bis oxide melting at 191-193°C. The infrared spectrum contained strong P-O absorptions at 8.4 and 8.96 μ , aromatic ether at 8.0 μ , and para substitution at 12.1 μ .

Anal. calcd. for $C_{36}H_{28}O_3P_2$: P, 10.86. Found: P, 10.8.

3. Preparation of Monosubstituted Triphenylphosphines

a. 3-Bromophenyldiphenylphosphine (1945-52)

To 100 g (0.424 mole) of m-dibromobenzene dissolved in 750 ml of tetrahydrofuran was slowly added, over a 6-hr period, increments of 10.3 g (0.424 g-atom) of magnesium turnings. The temperature of the reaction mixture which increased exothermically to 42°C during the initial additions was then held at 34°C by means of a water bath. The diphenylchlorophosphine, 93.5 g (0.424 mole), was added without dilution with solvent. The resulting clear, yellow-colored solution was refluxed for 1 hour to complete the reaction before the mixture was cooled and 60 ml of saturated ammonium chloride was added.

The clear tetrahydrofuran solution was decanted from the tacky, white-colored residue and then concentrated to yield 102.5 g of a tan, viscous residue. Distillation at reduced pressure gave the following fractions:

	<u>b.p. (°C)</u>	<u>Press. (mm)</u>	<u>Wt.</u>	<u>n_D</u>
1.	to 40°	0.01	8.4	1.6034 at 24°
2.	40-113	0.01	2.5	
3.	113-142	0.01	16.6	White solid in distillate
4.	142-157	0.01	11.1	1.6744 at 22°
5.	157-162	0.001	24.7	1.6754 at 21.8°
6.	157-165	0.001-0.1	5.3	1.6736 at 21

and a distillation residue of 21.2 g.

Anal. calcd. for $C_{18}H_{14}BrP$; Br, 23.4; P, 9.08. Found: Fraction 4 Br, 23.7; P, 9.27, and Fraction 5 Br, 23.7; P, 9.27. Fraction 1 was unreacted m-dibromobenzene (0.0356 mole, 8.4%). Fractions 4, 5, and 6 represent a 31.2% yield based on consumed m-dibromobenzene.

b. 4-Bromophenyldiphenylphosphine (II)

(1) Via n-Butyllithium (1972-141, 169, 172, and 174)

Into a 4-neck, 1-liter Morton flask fitted with a thermometer, condenser, stirrer, and an addition funnel was placed 300 ml of a hexane solution containing 0.478 mole of n-butyllithium. This was cooled to -66°C prior to the slow addition of 56.4 g (0.24 moles) of 1,4-dibromobenzene dissolved in 200 ml of dry tetrahydrofuran. By means of an external Dry Ice-acetone bath and vigorous stirring, the reaction temperature was held at -60°C or less throughout the addition.

The reaction mixture was allowed to warm to 0°C and then was recooled to -66°C before the addition of 105.4 g (0.0478 mole) of diphenylchlorophosphine was begun. After the addition was completed, the reaction mixture was warmed to ambient temperature and filtered to give 14.5 g of lithium chloride. The solvents were removed from the filtrate to give 70.0 g of solids melting at $74-78^{\circ}\text{C}$. These were further recrystallized from ethanol to yield 47.0 g (0.137 mole, 57% yield) of pure 4-bromophenyldiphenylphosphine (I) melting at $75-76.5^{\circ}\text{C}$.

Anal. calcd. for $\text{C}_{18}\text{H}_{14}\text{BrP}$: C, 63.38; H, 4.13; Br, 23.42; P, 9.05. Found: C, 63.95; H, 4.70; Br, 22.5; P, 9.30.

The following procedure appears to be the best route to II: To 0.30 mole of n-butyllithium in hexane which had been prechilled to -66°C was slowly added 70.7 g (0.30 mole) of p-dibromobenzene dissolved in 200 ml of tetrahydrofuran. The reaction temperature was held at -60°C or less throughout this addition. As soon as the p-dibromobenzene had been added, 66.1 g (0.3 mole) of diphenylchlorophosphine was slowly introduced from a second addition funnel. The reaction mixture was allowed to warm to room temperature and then filtered under nitrogen to remove salts. The filtrate was concentrated at reduced pressure to yield a semisolid residue which was triturated with methanol to yield a white, crystalline solid (quantitative crude yield). After two additional washings with methanol, 83 g (0.243 mole, 81% yield) of 4-bromophenyldiphenylphosphine melted at $75-77^{\circ}\text{C}$. The infrared spectrum of this material was identical to that of previously prepared II. Using this route, 500 g of II has been prepared for use in future research.

In a second duplicate experiment, only the addition sequence was changed with the n-butyllithium in hexane being added to the p-dibromobenzene in tetrahydrofuran at -66°C . Following the usual workup, only 46 g (0.135 mole, 45% yield) of p-bromophenyldiphenylphosphine was isolated.

(2) Via Grignard Reagent in Ether (1945-97)

A 118-g (0.5 mole) quantity of p-dibromobenzene was dissolved in 400 ml of diethyl ether and a small portion of the magnesium turnings (12 g, 0.5 mole) was added in an effort to initiate the reaction. However, the reaction was begun by adding Grignard which had been prepared externally in tetrahydrofuran. The remaining magnesium was added over two hours to the refluxing reaction mixture. After the reaction had been at reflux for 3 hours, it was cooled to 5°C by means of an ice-water bath before the addition of 110.3 g (0.5 mole) diphenylchlorophosphine was begun. After the addition was complete, the reaction mixture was allowed to stir overnight at ambient temperature.

The subsequent addition of 75 ml of saturated ammonium hydroxide solution was exothermic and required external cooling. The resulting yellow ether phase was decanted from the white solids which were subsequently washed with 50 ml of ether, 50 ml of tetrahydrofuran, and a second 50 ml of ether. The organic phases were combined and concentrated to yield a yellow-colored viscous oil. After the oil had been heated at 100°C and 0.1 mm until no further p-dibromobenzene sublimed from the oil, a yellow-colored residue was stored under nitrogen and slowly crystallized over two weeks. The solid was then broken up and digested with methanol to yield 125.4 g (0.368 mole, 73.6% yield) of pale yellow-colored 4-bromophenyldiphenylphosphine, melting at 65-69°C. The use of ether, then, results in better yields than were originally obtained using tetrahydrofuran,³⁴ but less than the newly developed route utilizing n-butyllithium (see above).

c. p-Bromophenyldiphenylphosphine Oxide (IX) (1945-70,71)

Approximately 2.0 g (0.0059 mole) of p-bromophenyldiphenylphosphine was dissolved in 20 ml of acetone. Subsequent addition of 50 ml of a 3% solution of hydrogen peroxide in acetone was weakly exothermic. The acetone was allowed to boil off on a water bath to yield an oil which was redissolved with more acetone. This procedure was repeated three times. After the final boil off and standing for 2 days, the residual oil had solidified. After a thorough washing with water, filtration, and vacuum drying, the solid melted at 140-146°C.

To a second 2-g sample dissolved in 20 ml of acetone was slowly added an acetone solution of potassium permanganate. The dark-purple color immediately disappeared and a brown precipitate formed. It was necessary to remove this solid twice during the oxidation by filtration. When one drop of the permanganate solution gave a pink coloration, a small crystal of the phosphine was given a colorless solution. After removal of the last of the brown precipitate, the acetone solution was concentrated to yield a semi-solid residue. The crystals were washed well with ether to yield 1 g of oxide melting at 151.5-153.5°C. Infrared examination of the crystals revealed strong absorptions at 8.45 and 9.0 μ due to the P-O as well as a strong absorption at 12.29 μ assigned to the para-substituted benzene.

Anal. calcd. for $C_{18}H_{14}BrOP$: Br, 22.39; P, 8.67; M.W., 357.2.
Found: Br, 21.9; P, 8.8.

d. 4-Carboxyphenyldiphenylphosphine (VII)

(1) Via the Grignard Reagent (1972-44)

Into a 250 ml, 3-neck Morton flask fitted with a condenser, high speed stirrer, and addition funnel were placed 0.486 g (0.02 g-atom) of magnesium turnings and 15 ml benzene. The system was flushed with nitrogen gas for 5 minutes and a mercury bubbler was connected to the condenser to assure an air-free system. p-Bromophenyldiphenylphosphine, 6.82 g (0.02 mole), in 15 ml of tetrahydrofuran was added slowly at room temperature. After the addition was completed the reaction mixture was held at its reflux temperature for a total of 15 hours. No Grignard reagent was formed and all of the p-bromophenyldiphenylphosphine was recovered after filtration to remove the unreacted magnesium and concentration of the filtrate.

(2) Via n-Butyllithium (1972-56)

Into a 300 ml, 3-neck flask fitted with a condenser, thermometer and rubber septum was placed 25 ml of dry tetrahydrofuran. The system was flushed with nitrogen gas for 5 minutes to remove traces of oxygen. n-Butyllithium, 1.92 g (0.03 mole), in 18.7 ml of n-hexane was introduced through the septum. Under nitrogen atmosphere, the septum was replaced by an addition funnel in which p-bromophenyldiphenylphosphine, 6.4 g (0.02 mole), in 25 ml of tetrahydrofuran had been placed. The n-butyllithium solution was cooled to $-40^{\circ}C$ with stirring by means of a Dry-Ice-acetone bath before the p-bromo compound was added slowly. The addition was thus completed in 30 minutes. The color of the reaction mixture changed from yellow to red. The stirring was continued at $-40^{\circ}C$ for one additional hour.

Under nitrogen atmosphere an excess quantity of Dry Ice powder was added. The carbonated reaction mixture was warmed up to room temperature and the solvent was removed under reduced pressure to yield a sticky, yellow material. Water was added and filtered to obtain a red-colored alkaline aqueous solution. Dilute hydrochloric acid solution was slowly dropped in to precipitate a gummy, white solid. The color of the solution turned to light-yellow as soon as it became acidic. The crude solid, 3.0 g (49%), was recrystallized from glacial acetic acid to yield white crystals with a melting point of $157^{\circ}C$ (lit., ^{10} m.p. $157^{\circ}C$).

Anal. calcd. for $C_{18}H_{15}O_2P$: P, 10.09. Found: P, 10.5%.
A weak para absorption was noted at 12.27μ while no meta absorption was observed at 12.85μ . Comparison with 3- and 4-bromophenyldiphenylphosphines showed a strong para absorption at 12.35 and a strong meta absorption at 12.85μ , respectively.

4. Preparation of Phosphinic Acids

a. Methylphenylphosphinic Acid (XVI) (1893-122 and 157)

(1) Via Iodic Acid Oxidation

A mixture of 98.0 g (0.79 mole) of methylphenylphosphine (XV) and 100 ml of absolute ethanol was put into a 1000-ml flask equipped with a magnetic stirring bar. To the stirring solution immersed in an ice bath was added an aqueous solution containing 115.0 g (0.65 mole, 3.5% excess) of iodic acid dissolved in about 600 ml of water. The product-iodine was removed from the reaction mixture very laboriously by repeated distillation of the water-iodine mixture and replenishment of the water. Finally, the light-brown solution was treated with charcoal to yield a colorless solution.

The aqueous residue was reduced in volume and on cooling yellow crystals precipitated. The product, 58.7 g (0.38 mole, 48.1%), was recrystallized from ethanol as white needles, m.p. 136.2-137.0°C. An infrared spectrum showed an absorption pattern which was expected for methylphenylphosphinic acid.

In a second larger preparation, the crude methylphenylphosphine (XV) was purified by distillation in a spinning band apparatus, b.p. 90.6°C/50.4 mm. From this distillate, 154.9 g (1.248 moles) of the pure methylphenylphosphine was dissolved in 300 ml of absolute ethanol and added dropwise to a solution of 195.2 g of iodic acid dissolved in 750 ml of distilled water. The exothermic reaction produced iodine immediately and was controlled by means of an ice bath placed around the reaction flask.

A voluminous amount of iodine was removed when first the ethanol-water mixture was removed by distillation at 85-99°C. The addition of more water (about 6 l.) was followed by additional distillation until the iodine was removed. The resulting yellow solution was treated with bone charcoal and the first crop of product was allowed to crystallize. This product, which was recrystallized as white needles from absolute ethanol, m.p. 135.5-137.0°C, weighed 58.0 g (0.372 mole, 30.0%) and was determined to be methylphenylphosphinic acid.

Anal. calcd. for $C_7H_9PO_2$: N.E., 156. Found: N.E. 154.

(2) Via Attempted Hydrogen Peroxide Oxidation (1893-147)

In a 1-liter flask were mixed 172.1 g of 30% hydrogen peroxide (51.6, 1.518 moles) and 334.5 g of acetone to form a 10.2% solution. A second solution consisting of 99.1 g (0.798 mole) of methylphenylphosphine dissolved in 100 ml of acetone was added dropwise to the oxidizing agent maintained at or near 0°C. After addition, the reaction mixture tested positive for the presence of excess peroxide by the iodine-starch method. The reaction mixture then was refluxed for 1.5 hours.

Acetone and water were removed by distillation and replacement water was added until the head temperature was 100°C. The aqueous solution containing the product was reduced in volume, and the first crop of a white powder was crystallized, washed with absolute ethanol and dried, m.p. 134-135°C. Three other crops of products were collected and treated in the same fashion and were found to have melting points of 134-135°C, 133-136°C, and 138-140°C, respectively. A total of 72.5 g of the white solid was collected.

A portion of the higher melting fourth crop was examined for its equivalent weight value by titration with standard base. It was found to have very little acid character, an equivalent weight of 5.00. A check by infrared analysis revealed gross differences when a comparison was made with the standard spectrum for methylphenylphosphinic acid. A mixed melting point was checked with a sample of the pure acid and the melting point range was lowered from 135.5-137°C to 109-134°C. Thus, this product was not methylphenylphosphinic acid.

A molecular weight value of 238 was obtained (Neumeyer, chloroform), and an elemental analysis gave values of 62.75% C, 9.39% H, 15.8% P, and 12.06% O (by difference). By calculation an empirical formula of $C_{10}H_{18}PO_2$ was obtained. An infrared spectrum showed a strong band at 3200 cm^{-1} which might be interpreted as the O-H stretching bond of an alcohol function. Additional efforts are underway in order to identify this unknown.

b. Methylphenylphosphinic Chloride (XVII) (1893-127)

To a slurry of 58.4 g (0.37 mole) of methylphenylphosphinic acid and 300 ml of carbon tetrachloride was added in small increments 104.6 g (0.88 mole, 138% excess) of thionyl chloride. Evolution of sulfur dioxide and hydrogen chloride was detected by litmus paper and odor. The resultant solution was refluxed for several hours.

The reaction mixture was distilled at atmospheric pressure over a temperature range of 73-76°C to remove the carbon tetrachloride and unreacted thionyl chloride.

Then the mobile yellow residue, noticeably viscous, was subjected to distillation under reduced pressure. The first product to distil, b.p. 85°C/1.5 mm, turned to a low-melting solid in the water-cooled receiver and as yet has not been characterized. The second fraction remained a liquid, 22.9 g (0.131 mole, 35.0%), b.p. 95°C/< 1 mm. An infrared spectrum displayed the expected absorption bands for methylphenylphosphinic chloride.

Anal. calcd. for C_7H_9POCl : Cl, 20.31. Found: 19.64
(Volhard).

c. p-Phenylenebis(phenylphosphinic acid) (XII)

(1) In Tetrahydrofuran (1945-88 and 105)

In a survey experiment, under an atmosphere of dry nitrogen, 4.8 g (0.02 mole) of p-dibromobenzene dissolved in 10 ml of tetrahydrofuran was slowly added to a solution of 50 ml of n-butyllithium in hexane (0.08 mole, 100% excess) and 25 ml of tetrahydrofuran. The reaction temperature was held at -60°C or less during the addition. The reaction mixture was stirred at -70°C for one hour, warmed to room temperature, and then transferred under nitrogen to a dropping funnel attached to a flask containing 8.1 g (0.04 mole) of P-(N,N-dimethylamino)-P-phenylphosphonic chloride (XI) dissolved in 50 ml of tetrahydrofuran. During the transfer, a white solid formed in the tetrahydrofuran containing the dilithiobenzene.

After the addition of the dilithiobenzene to the phosphonic chloride which was only mildly exothermic at -50°C , the reaction mixture was allowed to stir at ambient temperature. The addition of 10 ml of methanol, to react with any unreacted lithium compounds, resulted in the separation of two phases. The solvents were removed at reduced pressure and the resulting clear, yellow oil was dissolved in a mixture of 100 ml of isopropyl alcohol, 25 ml of water, and 10 ml of concentrated hydrochloric acid. After 18 hours at the reflux temperature, the volatile products were removed at reduced pressure, the residue dissolved in dilute sodium hydroxide, treated with charcoal and filtered, and subsequently acidified with concentrated hydrochloric acid. The resulting white powder weighed 4.0 g. Digestion of the powder with methanol or ethanol resulted in the recovery of a white powder, melting point above 315°C , which was identified as the desired p-phenylenebis(phenylphosphinic acid). Anal. calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_4\text{P}_2$: C, 60.34; H, 4.50; P, 17.29; Neut. Eq., 358.2. Found: C, 60.19; H, 4.82; P, 17.3; Neut. Eq., 365.6.

In a similar experiment but with the order of the addition reversed, there was added to 15 g (0.064 mole) of p-dibromobenzene in 100 ml of tetrahydrofuran under a dry blanket of nitrogen and in a flask fitted with a bottom take-off, 80 ml (0.128 mole) of n-butyllithium in hexane. The addition, carried out at -60 to -68°C , required 45 minutes. After stirring at -68°C for 15 minutes, the cooling bath was removed to allow a second flask to be attached to the bottom take-off by means of a rubber stopper. During the 15 minutes required for this attachment and purging with nitrogen, the temperature of the dilithio solution rose to $+32^{\circ}\text{C}$ and the solution became yellow in color. The dilithio solution was added over 24 minutes to 26.1 g (0.128 mole) of P-(N,N-dimethylamino)-P-phenylphosphonic chloride (XI) dissolved in 100 ml of tetrahydrofuran.

After stirring at ambient temperature for 2 hours, the reaction mixture was refluxed for 1 hour before being cooled. Removal of solvent at reduced pressure yielded a yellow-colored residual syrup. The syrup was dissolved in a mixture of 150 ml of methanol, 40 ml of water, and

15 ml of concentrated hydrochloric acid. The mixture was refluxed for 2.5 hours, cooled, and stirred overnight at room temperature. Forty ml of water and 10 ml of hydrochloric acid were added before resumption of the reflux. After 7 hours, the mixture was cooled and the solvents were removed at reduced pressure to yield a tacky, yellow-colored residual material and a clear aqueous phase.

The colored residual layer was separated, dissolved in methanol and treated with charcoal. Addition of water then precipitated an oil. The methanol and water were decanted from the oil which turned green-brown and did not dissolve in aqueous sodium hydroxide. On standing, the methanol-water layer, which had been decanted from the above oil, precipitated 4.1 g of white solids (some crystalline rosettes noted) melting at 270-285°C which are impure bis(phosphinic acid).

On partial neutralization of the first aqueous phase to a pH of about 3, a white solid precipitated. The solids, 3 g, were filtered, washed well with water, and vacuum dried. The melting point was above 310°C as expected for the bis(phosphinic acid). The yield of crude p-phenylenebis(phenylphosphinic acid) was about one-third of theory.

(2) In Ether (1945-118 and 178)

To a 66-ml (0.106 mole) quantity of an n-hexane solution of n-butyllithium at 20°C was slowly added 11.8 g (0.05 mole) of p-dibromobenzene dissolved in 100 ml of diethyl ether. The reaction mixture was allowed to stir for 1-1/2 hours at ambient temperature before being slowly added to a solution of P-(N,N-dimethylamino)-P-phenylphosphonic chloride dissolved in 100 ml of ether and 50 ml of tetrahydrofuran, and held at -5°C by means of an ice-salt bath. The reaction mixture, now containing a brown-colored, tacky substance was first stirred at -5°C for 2 hours and then at 40°C for an additional hour.

The clear liquid phase was then decanted and concentrated at reduced pressure to yield a colorless oil (A). The colorless oil (A) and brown residue (B) were dissolved in isopropyl alcohol and hydrolyzed by refluxing with dilute hydrochloric acid for 8 hours. On cooling, both hydrolyzates precipitated white solids. These mixtures were subsequently concentrated and the resulting solids washed well with water and partially dissolved in sodium hydroxide solution. The base insoluble materials were washed with water and vacuum dried to give a material which did not melt to 300°C. An infrared spectrum suggested that this unknown was a phosphorus acid or amide. However, analysis for bromine, nitrogen, and phosphorus were not definitive except for the lack of nitrogen; i.e., this unknown is not a phosphonamide.

Anal. Found: Br, 11.5; N, < 0.1; P, 11.3. P/Br = 2.54.

The base soluble material obtained from the hydrolysis of the colorless oil (A) precipitated a yellow oil on acidification with hydrochloric acid. On standing, the oil solidified to yield 4.6 g of impure

p-bromophenyl-phenylphosphinic acid, melting at 160-168°C.

From the base soluble fraction obtained from the hydrolysis of B was recovered a white solid after acidification and digestion with ethanol. This material melted above 300°C and had an infrared similar to that obtained for the p-phenylenebis(phenylphosphinic acid) prepared previously. Approximately 9.4 g of crude bis(phenylphosphinic acid) was recovered.

A second run in ether was carried out in exactly the manner as the preceding experiment, except there was no stirring period after the p-dibromobenzene had been added to the n-butyllithium. The ether solution thought to contain the dilithiobenzene was immediately added to the solution of P-(N,N-dimethylamino)-P-phenylphosphonic chloride.

After hydrolysis in isopropyl alcohol with hydrochloric acid, only about 0.5 g of the bis(phenylphosphinic acid), 2.3 g of p-bromophenyl-phenylphosphinic acid melting at 175-176°C (see also below) and 1.5 g of mixed acids were isolated.

d. 4-Bromophenyl-phenylphosphinic Acid (XIII) (1945-102)

A tetrahydrofuran solution expected to contain 1,4-dilithiobenzene was formed by slowly adding 15.1 g (0.064 mole) of p-dibromobenzene dissolved in 125 ml of tetrahydrofuran to a solution of 80 ml of 1.6M n-butyllithium in hexane and 50 ml of tetrahydrofuran at -64°C. The reaction mixture was allowed to warm to 10°C over a 25-minute period before being recooled to -70°C.

The addition of 26.1 g (0.128 mole) of P-(N,N-dimethylamino)-P-phenylphosphonic chloride in 50 ml of tetrahydrofuran to the dilithiobenzene at -54 to -70°C required 22 minutes. A black gum formed which made it impossible to stir the reaction mixture. When the temperature of the black reaction mixture had increased to -30°C, 15 ml of water and 10 ml of concentrated hydrochloric acid was added to the mixture. This addition caused the black color to dissipate and an orange layer to separate to the bottom of the reaction flask. After 2 hours at reflux, the mixture was cooled to ambient temperature and three phases were noted in the mixture.

After standing overnight, an additional 50 ml of water and 10 ml of concentrated hydrochloric acid were added and the mixture was further heated at the reflux temperature for 3 hours. After cooling and removing the volatiles at reduced pressure, the residual oil was dissolved in methanol. After standing for several hours, crystals were observed. The addition of water precipitated an oil which slowly solidified to an off-white solid melting at about 168-170°C. The solid was dissolved in methanolic sodium hydroxide, treated with charcoal and carefully filtered. Acidification of the filtrate with concentrated hydrochloric acid precipitated white solids. Recrystallization of the solids from methanol and water yielded rosettes of short needles melting at 174-176°C.

The above solubility of the acid in methanol and the low melting point are to be contrasted with the insolubility of the p-phenylene-bis(phenylphosphinic acid) in methanol and with the high melting point, above 315°C, of the bis-acid. Furthermore, an infrared spectrum of the new acid was very sharp and detailed in contrast to the very poor spectrum obtained for the bis-acid. Thus, it was clear that the desired bis-acid had not been obtained. The new acid was found to have a neutralization equivalent of 289 which was very close (97.3% of theory) to the value for p-bromophenyl-phenylphosphinic acid. The melting point was essentially the same as that previously obtained for this acid by Davies and Mann³⁵ using an alternate route. The identity was further confirmed by analysis. The 2.9 g (0.00976 mole) of p-bromophenyl-phenylphosphinic acid (XIII) recovered represents only a 15.3% yield.

Anal. calcd. for $C_{12}H_{10}BrO_2P$: C, 48.51; H, 3.39; Br, 26.90; P, 10.42; and M.W., 297. Found: C, 48.75; H, 3.45; Br, 26.6; and M.W., 289.

e. 4,4'-Biphenylenebis(phenylphosphinic acid) (XIV) (1945-109)

The addition of 100 ml of 1.6M butyllithium in hexane to 25 g (0.08 mole) of 4,4'-dibromobiphenyl dissolved in 200 ml of tetrahydrofuran at -62 to -64°C required 25 minutes. The gelatinous reaction, which could not be stirred too well, was then allowed to warm to +17° (50 min) before being recooled to -68°C for 1 hour. The mixture again was allowed to warm to 16°C during the attachment of the second reaction flask to the bottom take-off of the first reaction flask.

Addition of the 4,4'-dilithiobiphenyl solution to 45.5 g (0.223 mole) of P-N,N-(dimethylamino)-P-phenylphosphonic chloride dissolved in 75 ml of tetrahydrofuran was over a 45-minute period. Some dark spots appeared during this addition and stirring again became difficult. After completion of the addition and stirring at -68°C for 1 hour, the reaction mixture was warmed to room temperature.

The clear, pale, yellow-colored top layer was decanted from a tacky residue and concentrated at reduced pressure to yield additional oil. The two oils were dissolved in 150 ml of isopropyl alcohol, 35 ml of water, and 15 ml of HCl and then refluxed for 6 hours. At the end of this point, white precipitates were noted in both mixtures. The solids were filtered off, washed with water, and partially dissolved in dilute sodium hydroxide. Acidification yielded 10.5 g (32.1% yield) of crude bis(phosphinic acid) melting at 175-178°C. A sample of this material was used without further purification for the determination of the neutralization equivalent. The experimental value of 449.8 was very close to the theoretical value of 434.4. This neutralized sample was acidified with concentrated hydrochloric acid to yield a white gum which soon solidified. After a thorough washing with water and vacuum drying, the melting point was 192-195°C.

Anal. calcd. for $C_{24}H_{20}O_4P_2$: C, 66.36; H, 4.64; and P, 14.26. Found: C, 66.68; H, 5.39; and P, 13.85.

A second sample of the crude acid was dissolved in ammonium hydroxide solution, treated with charcoal, filtered, and vacuum dried to provide a second additional analytical sample.

Found: C, 65.84; H, 5.29.

The infrared spectra of these samples were identical and contained the expected absorptions: 2750-2000, 1600, 1438, 1224, 1130, 956, 813, 728-725, and 694-692 cm^{-1} .

f. Attempted Synthesis of 4,4'-Biphenylene-
bis(phenylphosphinic Acid (XIV)) (1945-75 and 76)

A slurry of 4,4'-dilithiobiphenyl (Lithium Corporation of America) thought to contain 0.12 mole of reagent was slowly added, under nitrogen to 49.6 g (0.24 mole) of N,N-dimethylamino-phenylphosphonamidic chloride dissolved in 150 ml of toluene. The reaction was only mildly exothermic, the reaction temperature increasing to 40° during the half-hour addition period. After an additional hour at reflux the mixture was cooled to ambient temperature and stirred overnight.

The liquid phase was decanted from the brown-colored solids and concentrated at reduced pressure. The residual liquid, 20.7 g, was treated with 100 ml of water and 50 ml of concentrated ammonium hydroxide which caused a tacky, green residue to form. After stirring overnight, the basic aqueous phase was decanted from the solids and acidified with concentrated hydrochloric acid. Only a small quantity of a brown, tacky substance precipitated.

The reaction solids were further extracted with 125 ml each of benzene and ether. Concentration of these extracts also yielded only a trace of yellow, tacky residue.

Then 7.5-g samples of the brown reaction solids were partially dissolved in isopropyl alcohol and dilute sodium hydroxide or hydrochloric acid and then heated at reflux for 8 hours. While the alcohol was being distilled from the basic hydrolysate, a white solid was noted in the Whitmore-Lux distillation head. This solid was subsequently identified by odor, infrared spectrum, and melting point as biphenyl. The residual solid-liquid mixture was filtered and the filtrate was acidified to give no phosphinic acid.

An acidic hydrolysis of the brown solids was similarly carried out. However, during the distillation of the isopropyl alcohol no biphenyl was observed. The residual solid-liquid mixture was first basified and filtered before reacidification with hydrochloric acid precipitated a voluminous off-white material. Attempts to crystallize this material were unsuccessful. Infrared examination of these solids, melting range 150-225°, not all melted, showed only the gross spectrum expected for this type of compound.

The major fraction of the brown-colored reaction solids were subsequently hydrolyzed under the acidic conditions to yield 17.8 g of off-white colored solids. Again considerable base insoluble fractions had to be removed before the acidification of the hydrolysate. The further work-up of these phosphinic acid fractions is underway.

A second similar run was carried out using benzene as the reaction solvent. The addition of the dilithiobiphenyl at 20-40°C resulted in the formation of an extremely viscous, black reaction product. Similar work-up gave 18.9 g crude bis-phosphinic acid XIV.

g. 4-(Diphenylphosphino)phenyl-
phenylphosphinic Acid (XXVII) (1945-124)

A solution of 17 g (0.05 mole) of 4-bromophenyldiphenylphosphine (II) in 100 ml of tetrahydrofuran was cooled, under dry nitrogen, to -60°C before 31 ml (0.05 mole) of n-butyllithium in hexane was slowly introduced. The cooling bath was removed and a second flask was attached to a bottom take-off of the first reaction flask. In the second flask, a solution of 22.8 g (0.112 mole, 124% excess) of P-(N,N-dimethylamino)-P-phenylphosphonic chloride (XI) and 75 ml of tetrahydrofuran was cooled to -45°C before beginning the addition of the aryl lithium solution. The resulting dark-colored reaction mixture became light-yellow in color on warming to room temperature.

After standing overnight, the solvents were removed at reduced pressure to yield a viscous, pale, yellow-green oil. The oil was first dissolved in 100 ml of isopropyl alcohol and then 20 ml of water and 10 ml of concentrated hydrochloric acid were introduced. The mixture was then vigorously refluxed for 6 hours. On cooling, a significant amount of white solids was noted. A small quantity of these solids was removed, filtered, and washed with water. After vacuum drying, these solids melted at 168-173°C and had all of the infrared absorptions expected for the half-tertiary phosphine-phosphinic acid XXVII. However, quite surprisingly these solids were not soluble in aqueous sodium hydroxide. Analyses of crude XXVII without further purification are in fair agreement with the calculated values.

Anal. calcd. for $C_{24}H_{20}O_2P_2$: C, 71.64; H, 5.01; P, 15.4;
M.W., 402.4. Found: C, 70.35; H, 5.81.

Investigation of this material is continuing.

5. Preparation of Dialkyl Alkylphosphonates

a. Dimethyl-Methylphosphonate (XXX)

(1) Via Methyl Iodide (1945-130)

A solution of 124 g (1 mole) of trimethylphosphite and 14.2 g (0.1 mole) of methyl iodide were quickly heated to reflux. The

resulting exothermic reaction caused the reaction flask to separate from the attached Vigreux column and resulted in some loss of materials. Distillation of the residue through the Vigreux column yielded 100.7 g (0.811 mole, 81.1% yield) of dimethyl methylphosphonate boiling at 72-73°C/18 mm and n_D^{20} 1.4128-1.4135.

(2) Via Methyl p-Toluenesulfonate (1945-129)

Under a nitrogen blanket 124 g (1 mole) of trimethylphosphite and 18.6 g (0.1 mole) of methyl p-toluenesulfonate were mixed and sampled for an infrared spectrum. The absence of any absorption at 8μ made the following of the reaction easy since the product phosphonate would contain a P-O absorption at or close to 8μ . The mixture was then slowly heated and at about 100-110°C a vigorous reaction occurred, and the temperature in the Whitmore-Lux distillation head reached 100°C. The temperature dropped after 15 minutes and no further reflux was observed. The reaction mixture was allowed to heat for an additional hour, then cooled, and sampled for an infrared spectrum. A strong -PO absorption was readily noted which was indicative of reaction to the desired phosphonate.

Distillation at 18 mm yielded four fractions of dimethyl methylphosphonate (XXX) boiling at 70-73°C (n_D^{20} 1.4128-1.4132) which weighed 122.7 g (0.988 mole, 98.8% yield). Distillation of the residual methyl p-toluene-sulfonate yielded 16.9 g (0.0907 mole, 90.7% yield) of slightly impure material having an index of refraction at 20°C of 1.5100 (starting methyl p-toluene-sulfonate, n_D^{20} 1.5172).

(3) Via Methyl Benzenesulfonate (1945-135)

In a similar experiment, 62 g (0.5 mole) of trimethylphosphite and 8.6 g (0.05 mole) of methyl benzenesulfonate (n_D^{20} 1.5151) yielded 62 g (0.5 mole, 100% yield) of dimethyl methylphosphonate boiling at 75-77°C at 19 mm and n_D^{20} 1.4136. The distillation residue was slightly impure methyl benzenesulfonate n_D^{20} 1.5088.

The infrared spectra of these three preparations were superimposable. Vapor phase chromatography showed that these products were 98-99% pure and had the same retention times.

b. Diethyl Methylphosphonate (XXIX) (1945-125)

Diethylphosphite, 110.4 g (0.8 mole) was slowly added to 18.4 g (0.8 mole) of sodium, which had been cut into small pieces, in 100 ml of benzene. The reaction was vigorous with the temperature of the benzene increasing to 60° during the 1.5 hours' addition period. After 1.5 hours at reflux, all the sodium had reacted and the addition of the methyl iodide, 113.4 g (0.8 mole), was attempted at 30°C. However, the reaction was too vigorous at this temperature and the addition was completed at 10°C.

The salts were removed by filtration and the benzene was volatilized at reduced pressure. The resulting brown-colored liquid was distilled at 18 mm to give only 42.2 g (0.278 mole, 34.8% yield) of diethyl methylphosphonate, n_D^{20} 1.4154-1.4150. The distillation residue was a white solid.

c. Diethyl Ethylphosphonate (XXXI) (1945-134)

Following the same general tosylate procedure, 83 g (0.5 mole) of triethylphosphite and 10 g (0.05 mole) of ethyl p-toluenesulfonate were heated together under nitrogen until an exothermic reaction took place. Fractional distillation of the reaction mixture yielded 76.1 g (0.458 mole, 91.6% yield) of XII boiling at 90-92°C/18 mm and n_D^{20} 1.4156-1.4160. Ten grams (100% recovery) of ethyl p-toluenesulfonate, b.p. 108-110°C/0.75 mm and n_D^{20} 1.5100, were also recovered.

d. Mixed Tosylate-Trialkylphosphite Reactions

In these reactions, equal molar quantities of triethylphosphite were reacted with methyl tosylate and trimethylphosphite was reacted with ethyl tosylate in the same manner as described above. The reaction products were distilled at about 18 mm and samples were submitted for vapor phase chromatography. The results of these analyses are shown in Table III.

That the mixed dialkyl alkylphosphonates obtained were not artifacts formed in the VPC columns was shown by analyzing a known mixture of dimethyl methylphosphonate and diethyl ethylphosphonate in the same column. There was not any evidence for mixed esters in the chromatogram obtained and the percentage of the components were not changed. Diethylphosphite, an impurity in the triethylphosphite, was also readily analyzed and identified on the same column used for the phosphonates.

e. Attempted Reaction of Trimethylphosphite and Methyl p-Toluate (1945-142)

A mixture of 7.5 g (0.05 mole) of methyl p-toluate and trimethylphosphite was mixed together under nitrogen and sampled for infrared examination. The mixture was slowly heated over two hours to a pot temperature of 114°C at which time there was a gentle reflux in the attached Vigreux column. After 30 minutes, the reaction mixture was cooled and again sampled for infrared examination. Comparison of the two spectra showed that no P-O had formed in view of the absence of the expected strong absorption at 8.1 μ . Both reactants were subsequently recovered in nearly a quantitative amount.

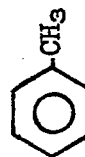
f. Attempted Reaction of Triethylphosphite and Ethyl Diphenylphosphinate (1945-139)

In a similar manner, 41.5 g (0.25 mole) of technical grade triethylphosphite and 6.6 g (0.027 mole) of ethyl diphenylphosphinate were

TABLE III

PRODUCTS OF TOSYLATE-PHOSPHITE REACTIONS

Tosylate ^a	Phosphite	% Content by VPC Analysis			
		CH ₃ P(OCH ₃) ₂	CH ₃ P(OC ₂ H ₅) ₂	C ₂ H ₅ P(O)(OCH ₃) ₂	C ₂ H ₅ P(O)(OC ₂ H ₅) ₂
C ₂ H ₅ Tos	(CH ₃ O) ₃ P	42.1	-	43.5 ^b	-
CH ₃ Tos	(C ₂ H ₅ O) ₃ P	-	74.0	21.5	2.7
CH ₃ Tos	(CH ₃ O) ₃ P	98.9	-	-	-
C ₂ H ₅ Tos	(C ₂ H ₅ O) ₃ P	-	94.7 ^c	-	-



- a. Where Tos = -OSO₂-CH₃
- b. Also may include some diethylphosphite impurity for the starting material
- c. Impurity from starting phosphite amounted to 4.8%

mixed, sampled for infrared examination, and heated to gentle reflux over an eight and one-half hour period. Distillation of the reaction mixture resulted in a 92% recovery of triethylphosphite. The distillation residue was impure ethyl diphenylphosphinate, n_D^{20} 1.5302.

g. Attempted Reaction of Triethylphosphite and Phenyl Tosylate (1972-197)

Two-tenth mole quantities of triethylphosphite (33.2 g) and phenyl tosylate were heated to 173°C over a 5-hour period, cooled, and distilled to yield 30.7 g of triethylphosphite, boiling point, 27°C at 0.75 mm, which is a 92.5% recovery of the starting material. Recrystallization of the distillation residue yielded 45 g of white, crystalline phenyl tosylate (90% recovery).

h. Tetramethyl p-Phenylenebisphosphonite (XXIV) (1945-144 and 149)

A quantity of crude, black-colored p-phenylenebis(phosphonous dichloride) thought to contain about 0.3 moles of the tetrachloro compound and 122 g (1.2 moles) of triethylamine was dissolved in a mixture of ether and tetrahydrofuran and cooled to 10° prior to the slow addition of 38.7 g (1.2 moles) of methanol. During the exothermic reaction, a thick, white precipitate formed which was very difficult to stir.

The triethylamine hydrochloride was filtered from the reaction mixture in an enclosed fine glass-sintered funnel under nitrogen pressure. The filter cake was thoroughly washed with ether prior to the concentration of the solvents. The black residual liquid was fractionally distilled to give the following fractions:

	<u>Boiling Point</u>	<u>Weight, g</u>	<u>n_D^{20}</u>
1.	to 97°/0.1 mm	5.8	1.5507
2.	94-97°/0.2-0.3 mm	11.0	1.5479
3.	97-129°/0.2-0.3 mm	0.4	-
4.	130-133°/0.2 mm	1.7	1.5751

Fractions 1 and 2 had similar infrared spectra with fraction 2 appearing to be more pure. Absorptions associated with the phosphonite ester at 9.7 and 9.9 μ as well as para substitution at 12.2 μ were noted. Only very weak absorptions associated with P-O were present. Fractions 1 and 2 represent a 21.2% yield of XXIV.

Anal. calcd. for $C_{10}H_{16}O_4P_2$: C, 45.81; H, 6.15; P, 23.63.
Found: C, 45.90; H, 6.00; P, 22.6.

Fraction 4 contained extremely strong infrared absorptions due to P-O at 8.2 and 8.9 μ .

A second preparation yielded about 31.8 g (~22.1% yield) of XXIV. In addition, 15.3 g of higher boiling material containing strong P-O infrared absorptions was also recovered. Redistillation at 0.075 mm gave 12.7 g of pale, yellow-colored oil boiling at 115-130°C, $n_D^{19.8}$ 1.5820.

Anal. calcd. for $C_{10}H_{16}O_6P_2[(CH_3O)_2P(O)-\text{C}_6\text{H}_4-P(O)(OCH_3)_2]$:
P, 21.06. Found: P, 14.2.

i. Dimethyl p-Phenylenebis-methylphosphinate (XXV) (1945-148)

To 15.1 g (~0.576 mole) of tetramethyl p-phenylenebisphosphonite (XXIV) was added 1 ml of methyl iodide. The reaction mixture quickly exothermed and blew out the thermometer and a stopper in the condenser. It was, however, possible to obtain a small amount of a white solid from the reaction flask. After several washings with ether, the sample melted largely at 104-106°C. The infrared spectrum was similar to that of the starting material except that strong P-O absorptions were now present at 8.15 and 8.85 μ .

Anal. calcd. for $C_{10}H_{16}O_4P_2$: C, 45.81; H, 6.15; P, 23.63.
Found: C, 45.61; H, 6.44; P, 22.4.

A second experiment was carried out initially in ether. However, infrared monitoring indicated that the reaction was very slow at the reflux temperature. Benzene was added and ether was distilled from the reaction flask. After 4 hours at the reflux temperature in benzene, a small amount of white solids was removed by filtration prior to concentration of the filtered reaction mixture. The semisolid was washed with ether to yield 6.0 g (~58% yield) of slightly impure XXV.

j. Methylphosphonic Dichloride (XXXII) (1935-111)

A slurry of 229 g (1.1 mole) of phosphorus pentachloride and about 160 ml of carbon tetrachloride was warmed to a gentle reflux before slowly introducing 68.5 g (0.55 mole) of dimethyl methylphosphonate. After refluxing overnight, the carbon tetrachloride and by-product phosphorus oxychloride were removed via distillation through an 18-inch Vigreux column. Subsequent distillation of the residual liquid at 18 mm yielded 57.5 g (0.433 mole, 78.7% yield) of colorless crystals. On standing only a short time, most of the distillate had crystallized into beautiful hexagonal plates.

6. Preparation of Tris Phosphines

a. 4,4'-Bis(diphenylphosphino)-triphenylphosphine Oxide (XXXIXb) (1997-1)

A 500-ml, 4-neck Morton flask fitted with a condenser, rubber septum, mechanical stirrer, and addition funnel was flushed with

nitrogen gas for 5 minutes. n-Butyllithium, 4.8 g (0.074 mole) in 50 ml n-hexane, was introduced into the flask through the septum and was cooled to -70°C by means of a Dry Ice-acetone bath. To this cold solution 4-bromo-diphenylphenylphosphine (II) was slowly added 25.2 g (0.074 mole) in 150 ml tetrahydrofuran (THF). The reaction temperature was held at below -62°C . Immediately after the addition was completed, phenylphosphonic dichloride, 7.2 g (0.037 mole) in 150 ml tetrahydrofuran, was slowly added and the temperature was held at -64°C . The mixture was then slowly warmed to room temperature, 20 ml of methanol was added, and then concentrated at reduced pressure to yield 30.0 g of a light-yellow solid. Washing with diethyl ether gave a white solid melting at $90-120^{\circ}\text{C}$. The infrared spectrum showed strong $\text{P} \rightarrow \text{O}$ absorptions at 8.45 and 8.95μ as well as para-substitution at 12.25μ .

b. 4,4'-Bis(diphenylphosphino)tri-phenylphosphine (XXXIXa) (1997-8)

In a similar experiment, 4-bromophenyldiphenylphosphine (II) was first reacted with n-butyllithium at -66°C in tetrahydrofuran and then half an equivalent of phenyldichlorophosphine was added. Workup as above yielded a yellow-green oil which did not solidify. The infrared spectrum had the expected absorptions and did not have the $\text{P}-\text{O}$ absorption of XXXIXb.

The investigation of these two novel tris phosphines is continuing.

7. Preparation of Organometalloid Azides

a. Methylphenylphosphinic Azide (XXXV) (W-1893-136 and 145)

A solution of 16.5 g (0.094 mole) of methylphenylphosphinic chloride dissolved in 40 ml of pyridine was added to a slurry of 7.7 g (0.118 mole, 24.8% excess) of sodium azide in 200 ml of pyridine. The reaction mixture was stirred at ambient temperature overnight and turned slightly pink. By infrared analysis, the presence of the azide group was confirmed.

Exactly one-fifth of the pyridine solution was transferred to a distilling flask and the pyridine was removed under reduced pressure. A drop of the residue was subjected to a shock sensitivity test (2 Kg at 50 cm); no detonation occurred. Distillation of the residue resulted in the isolation of 1.881 g (0.010 mole, quantitative) of methylphenylphosphinyl azide, b.p. $65^{\circ}\text{C}/0.3$ micron. An infrared spectrum revealed the absorption bands expected, azide asymmetric absorption at 4.68μ and no absorptions due to impurities.

The distilled, neat azide was also submitted to a shock sensitivity test (50 cm with 2 Kg) and again no sensitivity was found. Additionally, it burned slowly in open air.

As a quantitative test for the presence of azide, a mixture of 104.5 mg (0.577 mmole) of methylphenylphosphinic azide, 265.4 mg (1.052 mmoles, 82.3% excess) and 3 ml of pyridine was sealed at -78°C under vacuum in a tube and heated at 112°C for two days. The evolved nitrogen gas was measured in a Sprengel pump as 13.1 cc (0.587 mmole, 101.7%). (See also below).

The remainder of the reaction mixture has now been freed of the pyridine by vacuum distillation at 0.2 micron and a bath temperature of $70-80^{\circ}\text{C}$. The azide XXXV 9.3 g (0.05 mole, 68%), was collected in a U-trap at -3°C and the pyridine at -78°C . Its infrared spectrum showed the expected azide absorption band at 2165 cm^{-1} .

Anal. calcd. for $\text{C}_7\text{H}_9\text{PON}_3$: M.W., 181.1; N, 23.20. Found: M.W., 185; N, 23.62.

b. Diphenylether-4,4'-di(sulfonyl azide) (1945-98 and 100)

A slurry of 1.3 g (0.02 mole) of sodium azide in 30 ml of tetrahydrofuran was stirred at ambient temperature with 3.7 g (0.01 mole) of diphenylether-4,4'-di(sulfonyl chloride) for 24 hours. The azide formation was followed by the increase in the absorption at about 2118 cm^{-1} . The addition of 5.2 g (0.02 mole) of triphenylphosphine in 8 ml of tetrahydrofuran resulted in the evolution of roughly half of the expected nitrogen, even after several hours at reflux. Infrared inspection of the reaction mixture revealed a strong azide absorption at 2118 cm^{-1} . The addition of 2.6 g (0.01 mole) more of triphenylphosphine dissolved in 5 ml of tetrahydrofuran caused the evolution of additional nitrogen. However, in spite of the use of a 50% excess of triphenylphosphine, the total uncorrected nitrogen evolution was less than theory.

In a second survey experiment, a similar slurry of sodium azide and di(sulfonyl chloride) was allowed to stir in tetrahydrofuran over the week end. The azide absorption then was almost twice as strong as in the first experiment. Again the addition of two equivalents of triphenylphosphine failed to liberate all of the expected nitrogen. A strong azide absorption was still present in the reaction mixture. The solvent was removed at reduced pressure and the solid residue was retained for further examination as time may permit.

c. Dimethyltin Diazide (XXXVIII) (1945-86)

To a mixture of 25 ml of pyridine and 1.3 g (0.02 mole) of sodium azide was added 2.2 g (0.01 mole) of dimethyltin dichloride. There was an immediate formation of the white pyridine-dimethyltin dichloride complex. A 20-ml quantity of benzene was then added to aid in the

stirring of the mixture. After 24 hours' stirring at ambient temperature, the azide absorption at 2085 cm^{-1} was very strong and the insoluble complex had dissolved to yield a clear solution.

The solution of the tin diazide was brought to the reflux temperature prior to the addition of 5.2 g (0.02 mole) of triphenylphosphine dissolved in 20 ml of pyridine and 5 ml of benzene. There was not any nitrogen evolved after 2 hours at reflux and then stirring overnight. An additional infrared spectrum of the reaction mixture showed that the azide absorption at 2085 cm^{-1} was unchanged. This investigation was discontinued.

8. Preparation of Azidophosphoranes

a. P-Phenyl-N-(triphenylphosphoranylidene)-phosphonamidic Azide (XLIV) (1874-67)

Following the previously described procedure,²³ phenylphosphonic diazide was reacted with one equivalent of triphenylphosphine to liberate nitrogen (89.7% of theory) and form the azidophosphorane XLIV. The reaction mixture was poured into ice-water, filtered, and washed with dilute ammonium hydroxide and with cold methanol to yield 12.7 g of a white, crystalline powder, m.p. $146-149^{\circ}\text{C}$. Further extraction with ether gave 12.0 g (76% yield) of XLIV melting at $148-149^{\circ}\text{C}$. This material was used to develop an analytical method for determining the azide content of the azidophosphoranes (see below).

b. N,N'-[4,4'-Diphenylene ether bis(diphenylphosphoranylidene)]bis-P-phenylphosphonamidic Azide (XLVc) (1972-104)

Into a 3-neck, 200-ml flask fitted with a rubber septum, condenser, and gas outlet were placed 3.38 g (0.052 mole) of sodium azide, 40 ml of benzene, and 3.55 ml of pyridine. After stirring the slurry for 10 minutes, 5.6 g (0.0287 mole) of phenylphosphonic dichloride was added and the resulting reaction mixture was allowed to stir at ambient temperature for 24 hours. Without removing the salts from the mixture, 5.38 g (0.01 mole) of 4,4'-bis(diphenylphosphino)diphenyl ether (Ic) in 50 ml of benzene was added at room temperature. In 3 hours, approximately 93% of the nitrogen had been evolved. The mixture was filtered to remove salts, and the solvents removed from the filtrate under reduced pressure to yield 9.0 g of a sticky, white residue. After washings with dilute ammonium hydroxide and with ether, 7.5 g (84% yield) of a white, flaky solid, melting over the range $120-125^{\circ}\text{C}$ was recovered.

c. Quantitative Analyses of Azidophosphoranes

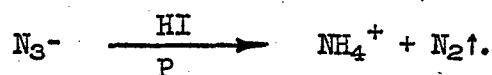
(1) Sealed Tube-Vacuum Line Analysis (1893-161)

Into a 90-ml tube were placed 0.8816 g (1.993 mmoles) of the azidophosphorane XLIV and a solution of 0.9805 g (3.738 mmoles, 87.6% excess) of triphenylphosphine dissolved in 5 ml of toluene. While held at -78°C , the tube containing the reactants was sealed under high vacuum. The tube was then heated at $110-120^{\circ}\text{C}$ for 27 hours. When the tube was opened on a vacuum line, 44.0 cc (1.965 mmoles, 98.6%) of the nitrogen gas was measured in a Sprengel pump.

(2) Wet Chemical Analysis (1835-23)

(a) Friedrich-Modified Kjeldahl (Nitrogen)

A nitrogen determination was made by the Friedrich modification of the Kjeldahl method, which uses a pretreatment with red phosphorus and hydroiodic acid to decompose the azido group. This determination yields all of the amino nitrogen and one-third of the azido nitrogen, since



(b) Azide Determination

The sample is treated with aqueous sodium hydroxide, and the solution is then transferred to a steam-distillation apparatus and acidified with sulfuric acid. The hydrazoic acid is steam-distilled into diluted sodium hydroxide. Upon completion of the distillation, the sample is made acidic to phenolphthalein with glacial acetic acid, and excess 0.1N ceric ammonium nitrate solution is added, followed by 5 ml of concentrated sulfuric acid. The excess ceric solution is back-titrated to the ferroin endpoint with 0.1N ferrous ammonium sulfate solution.

Calculation: The Friedrich-modified Kjeldahl result is corrected for the azide component by subtracting one-third of the latter to yield the amino nitrogen. To the amino nitrogen is added the azido nitrogen to yield the total nitrogen. This technique then gave the following data: for the azidophosphorane XLIV: calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_4\text{OP}_2$: N_3 , 9.50; N_{total} , 12.66; N_{amino} , 6.32; P, 14.00. Found: N_3 , 10.06; N_{total} , 12.8; N_{amino} , 6.08; P, 14.05. Thus, the two methods agree well.

d. Quantitative Analyses for Active Azide in Various Phosphoranes (1893-141)

(1) Determination of Azide in N,N'-
[p-phenylenebis(diphenylphosphoranylidene)-
bis-P-phenylphosphonamidic Azide](XLVa) (W-1972-2)

A 70 ml tube containing 2.2008 g (2.73 mmoles) of N,N'-[p-phenylenebis(diphenylphosphoranylidene)bis-P-phenylphosphonamidic

azide, 2.4573 g (9.73 mmols, 78.2% excess) of triphenylphosphine and 5 ml of pyridine was sealed at -78°C and placed in an oven at 110°C overnight.

The evolved nitrogen gas was measured in a Sprengl pump as 109 cc (4.88 mmole, 89.4%).

In a second experiment as a check on the amount of available azide in the phosphorane 2.1258 g (2.63 mmols) of the same compound was mixed with 5 ml of pyridine in a 70 ml tube. While the tube was held at -78°C a solution of 1.6751 g (6.63 mmols, 26.0% excess) of triphenylphosphine dissolved in 5 ml of pyridine was added. The tube then was sealed under high vacuum and heated at 110°C for four days.

When opened the evolved nitrogen gas was measured in a Sprengl pump as 104 cc (4.64 mmole, 88.2%).

(2) Determination of Azide in $\text{N,N}'\text{-[p,p'-biphenylene-bis(diphenylphosphoranylidene)]bis-P-phenylphosphonamidic Azide (XLVb)}$ (1972-61)

Into a tube was placed 2.1583 g (2.44 mmols) of $\text{N,N}'\text{-[p,p'-biphenylene-bis(diphenylphosphoranylidene)]bis-P-phenylphosphonamidic azide}$ and a solution of 2.5130 g (9.96 mmols, 204% excess) of triphenylphosphine dissolved in 5 ml of pyridine. The tube was sealed under vacuum at -78°C and heated in an oven at 110°C for three days.

The nitrogen gas evolved was measured in a Sprengl pump as 111 cc (4.93 mmols, 101.0%).

e. Hydrolysis of $\text{N,N}'\text{-[p-phenylene-bis(diphenylphosphoranylidene)]bis(P-phenylphosphonamidic Azide)}$ (XLVa) to its Acid (1943-157)

When 5.0 g of crude bis-azidophosphorane XLVa was recrystallized from pyridine-ethanol-water solvents system, only 1.5 g (30%) of pure XLVa was recovered. The remainder was converted in part to the phosphinic acid. This crude acid was purified by treating it with dilute ammonium solution to form a soupy ammonium salt solution. This salt was filtered and the filtrate acidified to yield a white solid which was washed thoroughly with water and dried. The melting point was $240\text{-}243^{\circ}\text{C}$. The molecular weight determined by titration was found to be 756 as compared to the calculated value of 755.9.

Anal. calcd. for $\text{C}_{42}\text{H}_{36}\text{O}_4\text{N}_2\text{P}_4$: P, 16.3; N, 3.7. Found: P, 16.4; N, 3.4.

f. P-Methyl-P-phenyl-N-triphenyl-phosphorylidinephosphinic Amide (XL) (1893-163)

Into a 100 ml, 2-neck flask were dropped, from a syringe, 6.9436 g (0.0383 mole) of methylphenylphosphinic azide and 30 ml of toluene. A solution consisting of 10.0489 g (0.0383 mole, stoichiometric) of triphenylphosphine dissolved endothermically in 20 ml of toluene was added through a small addition funnel to the azide solution at 50°C over a period of 1.5 hours. The evolved nitrogen gas displaced the water from two 500-ml graduated cylinders. The reaction mixture was refluxed for 2 hours to insure complete evolution of the gas. After corrections were made for the presence of water vapor, system warm-up, barometric pressure, and ambient temperature, the nitrogen gas measured 846 cc (0.0378 mole, 98.7%).

The solvent, toluene, was removed under reduced pressure until a viscous yellow residue remained. The bound toluene then was removed under high vacuum with a bath at 63°C surrounding the flask holding the residue, which turned to a solid chunk. The solid was broken into smaller chunks and triturated. An infrared spectrum of the crude phosphorane, m.p. 111-117°C, displayed a few minor variations among the absorption bands as compared to the previously prepared sample.

The resultant powder was washed first with 40 ml of ether to remove unreacted triphenylphosphine. Then the white powder was slurried in 40 ml of dilute ammonium hydroxide and stirred for one hour to remove any methylphenylphosphinic acid that may have been produced from hydrolysis of unreacted azide. When a final ether wash was put upon the wet cake from filtration of the ammoniacal slurry, the solid partially dissolved to form a slimy semisolid on the Buchner funnel. All washes were combined and the solvents removed to isolate again the solid which was triturated a second time. An infrared spectrum showed that no hydrolysis of the phosphorane had occurred and that it was not appreciably different from the solid before washing. This time the triturated powder was washed with methylcyclohexane, and when dried gave a melting point of 116-119°C. The total yield of phosphorane melting at 110-118°C was only about 64%.

A small portion of the crude phosphorane weighing 0.7492 g was slurried in 50 ml of dilute ammonium hydroxide. At first, a globule formed but dispersed into a flocculent white powder during a stirring period of two days. The resultant powder weighed 0.6873 g, representing a loss of 0.0599 g which formed oil globules in the ammoniacal mother liquor. The dried white powder melted at 119-121°C, but the cloudiness of the melt remained to a high temperature, clearing at about 280°C. Its infrared spectrum showed typical absorption bands for a phosphorane.

Anal. calcd. for $C_{25}H_{23}NP_2O$: M.W. 415.389; C, 72.28; H, 5.58; N, 3.37; P, 14.91. Found: M.W. 395 (Neumeyer, chloroform, 0.03M); C, 72.35; H, 5.54; N, 3.22; P, 14.8.

g. Attempted Reaction of Diphenylphosphinic Azide (XLI) and Diphenylphosphine (XLII) (1945-84 and 85)

Diphenylphosphinic azide was formed in 25 ml of pyridine solution by stirring together 2.4 g (0.01 mole) of diphenylphosphinic chloride and 0.65 g (0.01 mole) of sodium azide for 4 hours at ambient temperature. The subsequent addition of 1.9 g (0.01 mole) of diphenylphosphine dissolved in 10 ml of pyridine failed to yield any appreciable quantity of nitrogen. A yellow solid was observed to have formed after stirring for 18 hours. Infrared examination of the supernatant pyridine failed to show absorptions due to the azide, P-H, or phosphorane groups.

A second similar experiment was carried out except that the phosphinic azide was refluxed for two hours prior to the addition of the diphenylphosphine. The nitrogen evolution was approximately two-thirds of theory. Infrared examination again was inconclusive as absorptions due to azide, and phosphorane were observed; again no P-H absorption was present.

9. Preparation of Phosphorane Polymers

a. Polymerization of N,N'-[p-phenylene-bis(diphenylphosphoranylidene)]-bis(P-phenylphosphonamidic Azide) (XLVa) and 1,4-bis(dimethylphosphino)benzene (VI) (1972-42)

Into a 300-ml, 3-neck flask, flushed well with nitrogen and fitted with a condenser, thermometer, and addition funnel was placed 50 ml of dimethylformamide. Under nitrogen atmosphere, 2.7 g (0.013 mole) of 1,4-bis(dimethylphosphino)benzene (VI) was added. The solution was heated to 70°C under static nitrogen pressure. As soon as the reaction temperature stayed steady, the bis-azidophosphorane XLVa, 10.48 g (0.013 mole) in 50 ml dimethylformamide was slowly added with vigorous stirring. The nitrogen gas evolved from the reaction was collected, measured and calculated to approach 89.3% conversion in four hours. The solvent was removed under vacuum to yield 15.0 g of light-brown-colored solid. The melting point range was only 60-65°C. No fibers could be drawn from this polyphosphorane when placed in warm (60-70°C) water.

Anal. calcd. for $C_{52}H_{50}O_2N_4P_6$: P, 19.58; N, 5.90. Found: P, 17.6; N, 5.44.

b. Reaction of 4,4'-Bis(diphenylphosphino)diphenyl Ether (Ic) and the Bis-azidophosphorane (XLVc) (1972-115)

Into a 3-neck, 500-ml flask fitted with a condenser, thermometer, and addition funnel was placed 2.5 g (0.0046 m) of 4,4'-bis(diphenylphosphino)-diphenyl ether (Ic) in 100 ml of dimethylformamide and then heated to the reflux temperature. To this hot solution was added, slowly with stirring, 4.16 g (0.0046 m) of the bis-azidophosphorane XLVc, suspended in 40 ml DMF. The nitrogen gas evolved from the reaction was collected and measured. After the reaction was considered to be completed, the reaction mixture was cooled

to room temperature and filtered under nitrogen pressure. The solvent was removed from the filtrate under reduced pressure to yield 6.3 g of a yellow-colored sticky residue. Long flexible fibers were drawn when the residue was treated with hot water. Other fibers were drawn directly from the residual polyphosphorane XLIX. An average molecular weight determined by the Neumeyer method in chloroform was found to be only 1185.

- c. Partial Polymerization of N,N'-[p-phenylene-bis(diphenylphosphoranylidene)]-bis-P-phenylphosphonamidic Azide (XLVa) and 1,4-bis-diphenylphosphino)benzene (Id) (1972-70)

Into a 200-ml, 3-neck flask fitted with a condenser, thermometer and addition funnel were placed 2.23 g (0.005 mole) of 1,4-bis-(diphenylphosphino)benzene, in 25 ml of benzene, and 2 ml of dimethylformamide. The system was first flushed with nitrogen gas and then heated to the reflux temperature at 74°C. To this hot solution bis-azido phosphorane, 4.03 (0.005 mole) in 25 ml of benzene and 2 ml of DMF, was slowly added. Nitrogen gas evolved from the reaction was collected and measured. After 24 hours the conversion was calculated to be 43.5%. Solvents were removed under reduced pressure to yield 6.5 g yellow, flaky solid which softened at 80°, foamed at 125° and melted at 140°C. Infrared spectrum showed medium strong azide absorption at 4.64μ. When it was treated with hot water fibers up to 2-3 feet long could be drawn. The hot water treated solid softened at 115°, foamed at 125° and melted at 250°C. When this water-treated solid was heated to 125°C under 520 psi, a yellow-colored, brittle disc was formed. Infrared examination showed considerable decrease in intensity of azide absorption at 4.64μ. It now softened at 125°, foamed at 165° and showed only sign of melting at 260°C.

- d. Fractionation of Phosphorane Polymers (1972-72,73 and 74)

Into a 250-ml, 3-neck flask fitted with a condenser, addition funnel and thermometer was added a weighed quantity of the phosphorane polymer and 20 ml monochlorobenzene. This mixture was heated to reflux and to this hot solution was added n-hexane until the solution became cloudy. After cooling to room temperature the solids were removed by filtration. The filtrate was again heated to reflux and n-hexane again added to the cloud point. The same procedure was repeated several times for each polymer system. The individual fractions of solid collected were dried over hot water in vacuum. The melting point range and infrared spectra were taken for comparison and are shown in Tables IV-VI. This investigation is being continued.

10. Miscellaneous

- a. Reaction of P-phenyl-N-(triphenylphosphoranylidene)-phosphonamidic Acid (I) and Cobalt (II) Acetate (1945-82)

A slurry of 2.1 g (0.005 mole) of the phosphonamidic acid I and 1.25 g (0.005 mole) of cobalt (II) diacetate tetrahydrate in 50 ml of

TABLE IV

FRACTIONATION OF PHOSPHORANE POLYMER*

(Prepared in DMSO)

Fract. No.	Reflux Temp °C	n- Hexane ml Added	Wt (g)	% Yield	m. p. Range °C		
					Soften	Foam	Melt
0	0	0	3.5	100	105	145	195
1	132	0	0.19	5.5	-	-	285
2	132	10	0.60	17.1	150	-	175
3	98	10	1.10	31.4	125	-	260

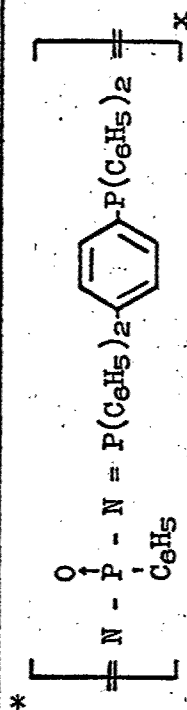


TABLE V

FRACTIONATION OF PHOSPHORANE POLYMER*

(Prepared in HPT)

Fract. No.	Reflux Temp °C	n- Hexane ml Added	Wt g	% Yield	m. p. Range		
					Soften	Foam	Melt
0	0	0	2.0	100	110	145	185
1	132	10	0.7	35	145	150	210
2	88	10	0.5	25	80	105	115

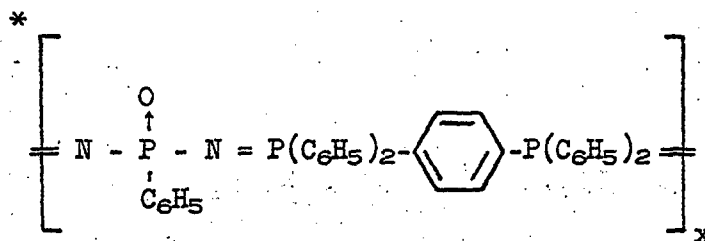
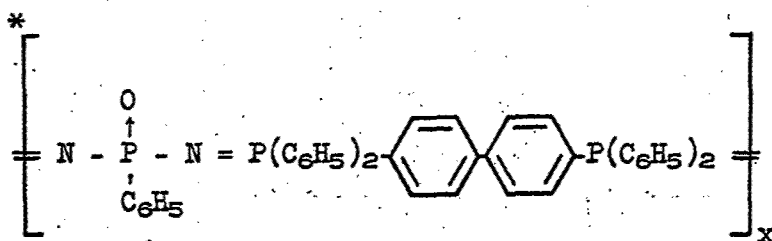


TABLE VI

FRACTIONATION OF PHOSPHORANE POLYMER*
(Prepared in DMF)

Fract. No.	Reflux Temp °C	n- Hexane ml Added	Wt g	% Yield	m. p. Range		
					Soften	Foam	Melt
0	0	0	4.0	100	105	130	185
1	132	10	2.1	52.5	130	145	185
2	85	20	0.5	12.5	95	115	140
3	80	25	0.6	15.0	75	115	140



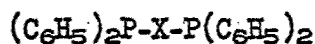
ethanol were warmed and swirled briefly on a steam bath with the formation of violet-colored solids. The violet-colored solution was decanted and concentrated at reduced pressure to yield a tacky violet-colored residue. The violet solids were washed with ether, air dried, and found to melt at 134-136°C. The melt became dark-blue in color and appeared to be stable to 300°C in the melting point capillary. Infrared examination of these solids revealed a complex spectrum which suggested a mixture.

A small amount of the violet solids were further digested with ethanol to yield a bright-blue ethanol phase above the violet-colored solids. The mixture was left to stand, exposed to the atmosphere, over the week end. Blue crystals were then observed and additional reflux resulted in the whole mixture becoming bright-blue in color. The solids were removed by filtration, washed with ether, and vacuum dried to give a fine, blue-colored powder melting at about 275-280°C. At almost 300°C the blue melt was observed to be giving off volatile material. The infrared spectrum of this fraction was notably changed from that of the violet-colored solids. There were no longer absorptions due to the phosphonamidic acid at 2500-2000 cm^{-1} and 950 cm^{-1} .

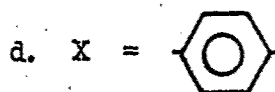
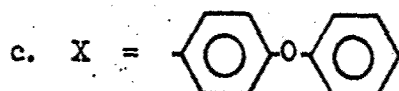
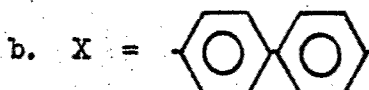
Anal. calcd. for 1:1 compound: Co, 12.7; N, 2.94; P, 13.3
(Co:N:P = 1:1:1). Found: Co, 20.6; N, 1.66; P, 7.71 (Co:N:P = 2:1:3).

III. SUMMARY AND CONCLUSION

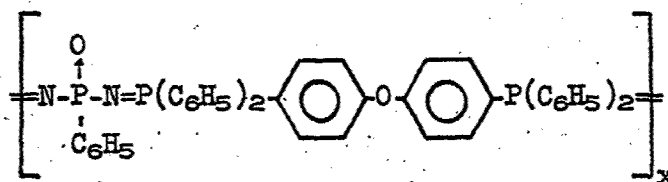
The transmetallation reaction between n-butyllithium and aryl halides has been extended to use with arylenedihalides to prepare arylenedilithium intermediates and has resulted in the ready syntheses of several bis tertiary phosphines Ib-d required for this program. The ether-linked bis tertiary phosphine Ic has been converted into its bis-azidophosphorane



I



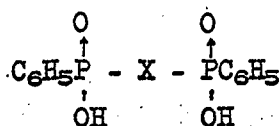
derivative XLVc which on further polymerization resulted in the first polyphosphorane (XLIX) from which long, flexible fibers could be drawn.



XLIX

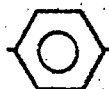
A polyphosphorane prepared from 1,4-bis(dimethylphosphino)benzene (VI) and phenylphosphonic diazide failed to yield fibers on attempted drawing from warm water. However, light scattering measurements have suggested that the p-phenylene and the biphenylene-linked polyphosphoranes have molecular weights of 20,000 and 12,000, respectively. These values correspond to approximate degrees of polymerization of 33 and 20, respectively. Additional polymerization studies under more rigorously controlled conditions are planned.

Further utilization of the arylenedilithium intermediates has resulted in the preparation and characterization of the bis phosphinic acids XII and XIV. These acids are expected to provide polyphosphoranes which will



XII

X =



XIV

X =



have increased thermal stabilities.

The synthesis of the first example of an alkyl-arylphosphinic azide, methylphenylphosphinic azide, was also carried out. This azide XXXV was found to be stable to shock and heat. The phosphorane XL prepared from this azide was found to be stable to hydrolysis and to oxidation and to be more soluble than the fully phenylated homolog. As a result of these promising results, a new and shortened route to p-phenylenebis(methylphosphinic acid) and related compounds was successfully developed. Investigation of these p-phenylene bis(methylphosphinic acid) derivatives will be continued and is expected to yield more soluble polyphosphoranes.

A further benefit derived from the use of n-butyllithium has been an improved synthesis of 4-bromophenyldiphenylphosphine (II). This compound as well as its 3-bromophenyl isomer will provide intermediates for conversion to a variety of tris tertiary phosphines and mixed tertiary phosphine-phosphinic acids. This promising area will be more fully exploited during the next year.

During the syntheses of dialkyl alkylphosphonates required as intermediates for the preparation of certain methylphosphinic compounds, it was found that alkyl p-toluenesulfonates could successfully replace alkyl halides in certain Michaelis-Arbusov reactions. Thus, high yields of pure dialkyl alkylphosphonates were obtained by this modified Michaelis-Arbusov reaction if the alkyl groups of the p-toluenesulfonate and the trialkylphosphite were the same. If a mixed reaction was undertaken, a complex mixture of reaction product was obtained.

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APPENDIX

Listed in Table VII are the new compounds prepared during the period 1 April 1965 and 1 April 1966 under Air Force Contract No. AF 33(657)-11129. References indicate page numbers of this report.

TABLE VII
NEW COMPOUNDS

Name (Text Number)	Structural Formula
4,4'-Bis(diphenylphosphino)diphenyl Ether (Ic)	$(\text{C}_6\text{H}_5)_2\text{P}-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{P}(\text{C}_6\text{H}_5)_2$
4,4'-Bis(diphenylphosphino)diphenyl ether Bisoxide	$(\text{C}_6\text{H}_5)_2\text{P}(=\text{O})-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{P}(=\text{O})(\text{C}_6\text{H}_5)_2$
4-Diphenylphosphinophenyl-phenylphosphinic Acid (XXVI)	$(\text{C}_6\text{H}_5)_2\text{P}-\text{C}_6\text{H}_4-\text{P}(=\text{O})(\text{OH})(\text{C}_6\text{H}_5)$
p-Phenylenebis(phenylphosphinic Acid) (XII)	$\text{C}_6\text{H}_5\text{P}(=\text{O})(\text{OH})-\text{C}_6\text{H}_4-\text{P}(=\text{O})(\text{OH})\text{C}_6\text{H}_5$
4,4'-Biphenylenebis(phenylphosphinic Acid) (XIV)	$\text{C}_6\text{H}_5\text{P}(=\text{O})(\text{OH})-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{P}(=\text{O})(\text{OH})\text{C}_6\text{H}_5$
Tetramethyl p-phenylenebisphosphonite (XXIV)	$(\text{CH}_3\text{O})_2\text{P}-\text{C}_6\text{H}_4-\text{P}(\text{OCH}_3)_2$
Dimethyl p-phenylenebismethylphosphinate (XXV)	$\text{CH}_3\text{P}(=\text{O})(\text{OCH}_3)-\text{C}_6\text{H}_4-\text{P}(=\text{O})(\text{OCH}_3)\text{CH}_3$
Methylphenylphosphinic Azide (XXXV)	$\text{C}_6\text{H}_5\text{P}(=\text{O})(\text{CH}_3)\text{N}_3$

Melting Point, °C	Boiling Point °C/mm	Remarks	Reference
114-116			3, 5, 39
			41
		Incompletely characterized	16, 52
> 300		Insoluble most organic solvents	11, 47
195			12, 50
	94-7°/0.2 mm	Viscous liquid; no P → O absorption	15, 56
104-106		Strong P → O absorption	15, 57
	65°/0.3 micron	Strong N ₃ absorption; stable to heat and shock	20, 58

TABLE VII (CONT)
NEW COMPOUNDS

Name (Text Number)	Structural Formula
Methylphenyl-N-triphenylphosphorylidene-phosphinic Amide (XL)	$\begin{array}{c} \text{O} \\ \uparrow \\ \text{C}_6\text{H}_5\text{P}-\text{N}=\text{P}(\text{C}_6\text{H}_5)_3 \\ \\ \text{CH}_3 \end{array}$
N,N'-[4,4'-Diphenylene ether bis(diphenylphosphoranylidyne)]bis(P-phenylphosphonamidic Azide) (XLVc)	$\left[\begin{array}{c} \text{O} \\ \uparrow \\ \text{C}_6\text{H}_5\text{P}-\text{N}=\text{P}(\text{C}_6\text{H}_5)_2 \\ \\ \text{N}_3 \end{array} \text{---} \text{C}_6\text{H}_4 \text{---} \right]_2 \text{O}$

Melting Point °C/mm	Boiling Point °C/mm	Remarks	Reference
119-121			22, 63
120-125			24, 60

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13. ABSTRACT A new route to bis tertiary phosphines, utilizing n-butyllithium, has been developed and has resulted in the improved syntheses of these vital intermediate compounds. As a result, the new bis-tertiary phosphine, 4,4'-bis(diphenylphosphino)diphenyl ether, has been successfully prepared and converted to the corresponding bis-azidophosphorane. The further polymerization of this bis-azidophosphorane has resulted in the first polyphosphorane from which long flexible fibers could be drawn. Other polyphosphoranes have been shown to have molecular weights of approximately 12,000 to 20,000. Two new bis phosphinic acids, p-phenylene- and 4,4'-biphenylenebis-(phenylphosphinic acids) have also been synthesized via this n-butyllithium route. These compounds will be used in preparing a new type of polyphosphorane. The new methylphenylphosphinic azide and its triphenylphosphine phosphorane were readily prepared and shown to be equally as stable to heat and to hydrolysis as were the fully phenylated homologues. Based on these results, a shortened route to the corresponding p-phenylenebis-(methylphosphinic acid) derivatives was successfully worked out. This series of compounds should result in more soluble polyphosphoranes.			

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