

STUDIES IN THE SYNTHESIS OF PRECURSORS FOR CYCLIC PHOSPHORUS COMPOUNDS

By

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FOR CYCLIC PHOSPHORUS COMPOUNDS

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INTRODUCTION

Phosphine oxides have long been prepared by means of Michaelis-Arbuzov rearrangements and by nucleophilic displacements on phosphorus by Grignard reagents. These methods proved valuable in the preparation of several unsymmetrical phosphine oxides selected as potential precursors for ring closure to form carbon-phosphorus heterocycles. Several attempts to promote ring closure of these compounds using usual ring closure reagents resulted in mixtures. In one attempt a solid tentatively designated a phosphorus heterocycle was isolated and partially characterized.

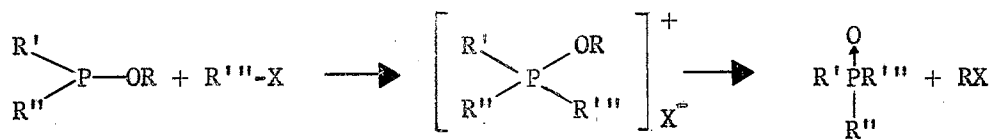
CHAPTER I

HISTORICAL

The Michaelis-Arbuzov Rearrangement

The Michaelis-Arbuzov rearrangement, discovered in 1898 by Michaelis and Kahne (67), has long been the best classical method of forming a carbon-phosphorus bond. Recently, an excellent review on this rearrangement was written (36).

Generally the mechanism can be envisioned as being a nucleophilic displacement of halogen by a trivalent phosphorus atom to form a quasiphosphonium intermediate. Decomposition of the intermediate eliminates alkyl halide and results in formation of a tetrasubstituted



phosphorus compound with a new carbon-phosphorus bond. This is in essence a valence shell expansion making use of low energy vacant 3d orbitals on phosphorus.

Since its inception, this rearrangement has been extended to phosphites, phosphonites and phosphinites with the ester group being either aryl or alkyl (2). The halide capable of effecting the

conversion can be primary or secondary (1), acyl (46), or aroyl (13). Tertiary alkyl esters (55) are not as effective as primary esters, and aryl esters with other than electro-withdrawing groups, are less reactive (4).

Although the relative ease of dealkylation of various groups has not been adequately examined so that conclusions may be drawn, studies conducted with methyl iodide to determine the relative ease of displacement of different alkyl groups has indicated that the methyl group is displaced more easily than ethyl and ethyl more easily than isopropyl (55). The usual halide reactivity is in the order iodide > bromide > chloride. Aryl halides, aliphatic vinyl halides, and fluorides do not react under normal conditions (36).

While the reaction has been studied with numerous variations in groups attached to phosphorus, much more careful kinetic studies are needed to make a more definitive statement on the mechanism. From the data available it is apparent that reactivity increases with increasing number of alkyl or aryl groups on phosphorus. Thus the order of reactivity, $C_2H_5OP(C_2H_5)_2 > (C_2H_5O)_2PC_2H_5 > (C_2H_5O)_3P$ and $C_2H_5OP(C_6H_5)_2 > (C_2H_5O)_2PC_6H_5 > (C_2H_5O)_3P$ has been established.

An ester exchange process has been shown (56) to occur with alkylating agents reacting with organophosphorus esters. The oxygen atom of the phosphoryl group acts as the nucleophilic center with subsequent displacement of alkyl group.



Nucleophilic Displacement on Phosphorus

It has long been known that phosphoryl chloride reacts with excess Grignard reagents in a nucleophilic displacement reaction to give phosphine oxides (49). Nucleophilic displacements on phosphorus halides and esters have recently been reviewed (14). Good yields of tertiary phosphine oxides are achieved by adding the phosphorus compound to an excess of the Grignard reagent. Some variation is observed, however, with aliphatic and aryl Grignard reagents.

Considerable data is available concerning the reactions of phosphoryl dihalides and trihalides with aryl and aliphatic Grignard reagents. By using a 1:2 ratio of phosphoryl chloride to Grignard reagent both a phosphinic acid and a tertiary phosphine oxide were

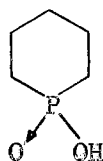


formed. By keeping the temperature low, Kosolapoff (48) found only phosphinic acids and phosphine oxides and no phosphonic acids. Moreover, the optimum conditions for maximum production of phosphinic acid included high dilution and the inverse addition technique.

The reaction of alkyl and arylphosphonic halides with Grignard reagents often gives inconsistent results. By reaction of equimolar quantities of phosphoryl halide and phenyl Grignard reagent, a good yield of diphenylphosphinic acid and a low yield of triphenylphosphine oxide can be realized (26). Using essentially these conditions, Berlin (12) attempted to synthesize diallylphenylphosphine oxide but obtained only

undistillable oils and tars.

Steric factors apparently are operative when phosphorus trichloride is allowed to react with t-butyl Grignard reagent since t-butylphosphonous dichloride was produced (24). A heterocycle, pentamethylenephosphinic acid (I), was isolated when pentamethylene



I

dibromide was converted to a Grignard reagent and reacted with N,N -diethylamidophosphoryl dichloride and then hydrolyzed.

Several unsymmetrical phosphine oxides have been synthesized in very good yields by Morrison (68). Diarylphosphinic halide was condensed at room temperature with the Grignard reagent. The acid was



shown not to be an intermediate in a control reaction. Similarly, unsymmetrical trialkyl phosphine oxides have been prepared by treatment of the appropriate dialkylphosphinic halide with Grignard reagents (52). Di-n-butylmethylphosphine oxide was so synthesized.



A thorough survey of the reaction of Grignard reagents on tetra-substituted esters has not appeared in the formal literature; however, Austin (7) has recently written a summary of this type of nucleophilic displacement. By proper selection of the appropriate phosphoro-chloridate or phosphorofluoridate and Grignard reagent, good yields

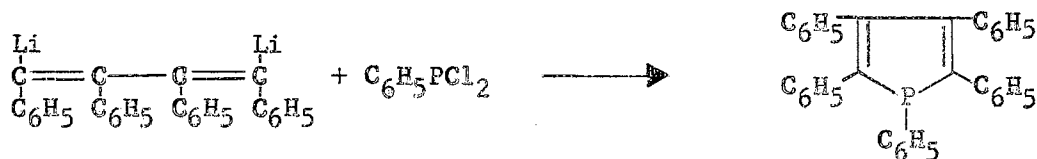


of the corresponding phosphonate can be obtained. The temperature is a controlling factor in many of these reactions and must be carefully regulated.

Ring Closure Leading to Cyclic Phosphorus Compounds

The belated synthesis and characterization of carbon-phosphorus heterocycles have been due largely to the difficulty in preparing these compounds. The increased interest in the last ten to fifteen years can be, at least in part, attributed to the interest to prepare phosphorus analogs of arsenic heterocycles.

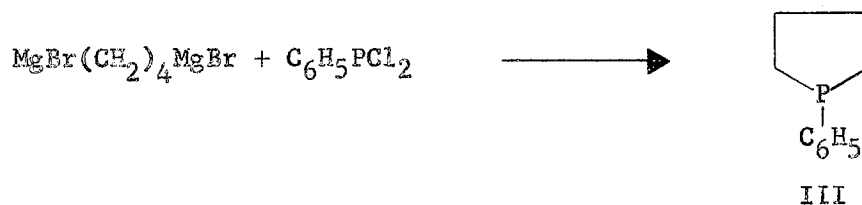
One of the most common methods of forming these heterocycles has been to use reactive dihalides, difunctional Grignard or dilithio reagents. Leavitt and coworkers (57) synthesized 1,2,3,4,5-



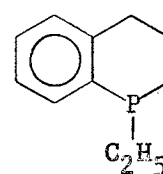
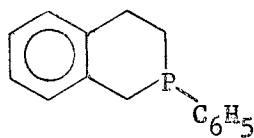
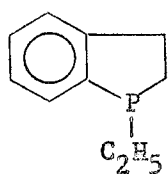
II

pentaphenylphosphole (II) by reacting 1,4-dilithio-1,2,3,4-tetraphenylbutadiene with phenylphosphonous dichloride. In an analogous manner, 9-phenyl-9-phosphafluorene (XV) was obtained by forming the dilithio derivative of 2,2'-dibromobiphenyl (from lithium foil) and then treating it with phenylphosphonous dichloride (9). Heats of formation and bond energy studies were made on these two compounds. Molecular orbital calculations indicate a considerable amount of conjugative energy for the phosphole and phosphine oxide when based on the assumption that the molecule is planar. However, from the chemical evidence available, it was concluded that the phosphole behaves as a conjugated diene and possesses little or no aromatic character. This conclusion was based on the ability of these molecules to complex with iron tetracarbonyl and to undergo Diels-Alder type reactions (17, 57). The participation of the unshared electrons on the phosphorus atom in the resonance system is not likely in view of the fact that the ring will form as readily when the phosphorus is in the pentavalent state. For example, when phenylphosphonous dichloride is reacted with an appropriate dilithio reagent, good yields of the phosphole oxide are obtained. Braye (15) was also able to isolate 1-methyl-2,3,4,5-tetraphenylphosphole-1-oxide by reacting 1,4-dilithio-1,2,3,4-tetraphenylbutadiene with methylphosphonous diiodide.

The use of di-Grignard and dihalide reagents have been one of the most fruitful areas for generation of a carbon-phosphorus heterocycle. The first five-membered carbon-phosphorus heterocycle III was synthesized by treating a di-Grignard reagent with phenylphosphonous dichloride (34). Dihalide reagents were also used in the

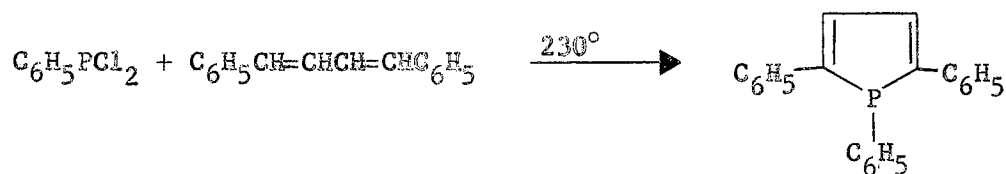


preparation of 1-ethylphosphindoline (IV), 2-phenyl-1,2,3,4-tetrahydroisophosphinoline (V) and 1-ethyl-1,2,3,4-tetrahydrophosphinoline (VI)



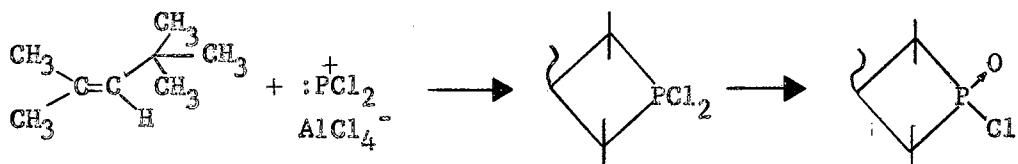
(10, 41, 61). Other dihalides have been used with varying degrees of success (32, 38, 41, 57).

Olefins are another class of starting materials that have been commonly employed for preparing four, five and six-membered heterocyclic rings (5, 6, 40, 44). One typical representative is the reaction of

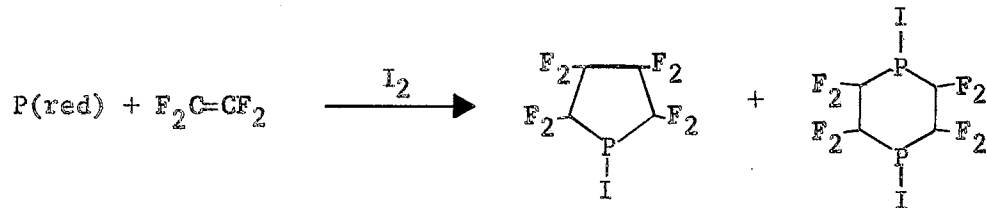


phenylphosphonous dichloride with 1,4-diphenylbutadiene (21). The phosphorylation reaction of olefins with phosphorus trichloride proved to be a very novel method of preparing four-membered rings (60).

Krespan (53, 54) has prepared several unusual fluorinated compounds

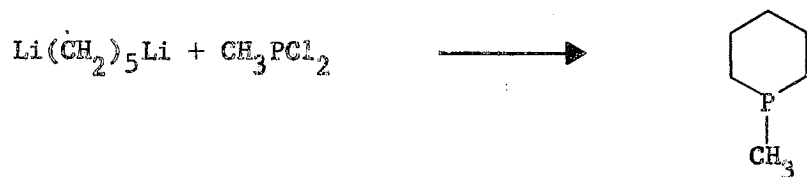


by reacting red phosphorus with polyfluoro-olefins. One phosphole (3-methyl-1-ethyl-3-phospholene-1-oxide) has been particularly

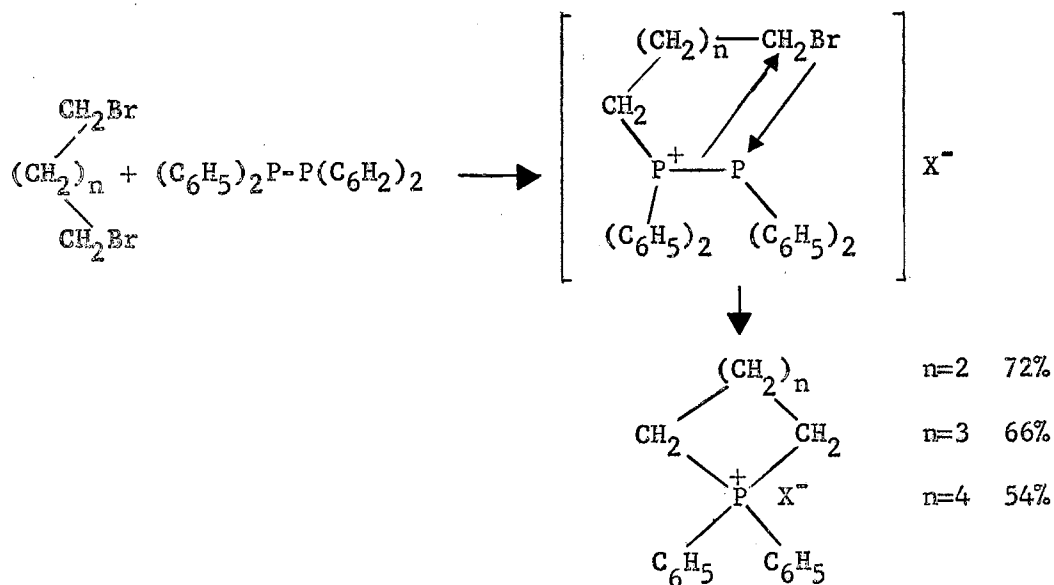


effective as a catalyst in the conversion of isocyanates to carbo-diimides (23).

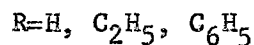
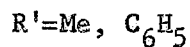
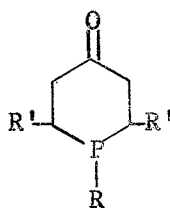
Saturated six-membered heterocycles have become accessible via reaction of 1,5-dilithiopentane with methylphosphonous dichloride (15).



Markl (65) was able to effect ring closure in preparing several methylene phosphonium salts by the use of a dibromide and tetraphenyl-biphosphine.

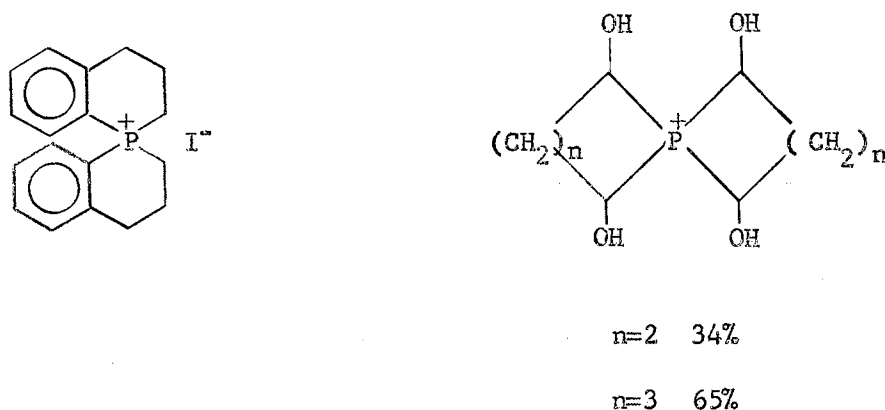


In 1960 a new type of phosphorus heterocycle was reported by Welch and coworkers (74). The compounds (4-phosphorinanones) were synthesized by the intramolecular condensation of bis-(2-cyanoethyl)-phosphines, followed by hydrolysis and decarboxylation, steps which



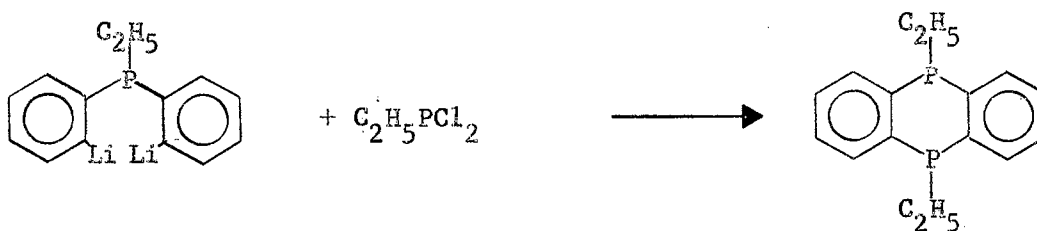
resulted in formation of a six-membered ring compound. It was later reported (75) that a more general approach involved primary phosphines and a conjugated dienone in a classic Michael addition process. The compounds give semicarbazone derivatives and are converted to alcohols with lithium aluminium hydride. This class of compounds has the potential of being a valuable intermediate in the preparation of other phosphorus heterocycles.

The first preparation of a spirocyclic phosphonium salt was reported in 1955 (35). The synthesis, which involved several steps, resulted in a spirocyclic salt which was resolved into its (+) and (-)



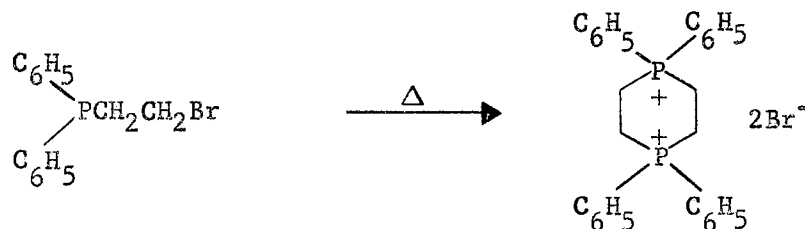
isomers of high optical stability. Later Buchler and Wystrach (17) were able to isolate a spirocyclic phosphonium salt by reacting a dialdehyde with phosphine.

An interesting diphosphorus heterocycle, isolated in two isomeric forms, was prepared from reaction of a dilithio reagent with



ethylphosphonous dichloride (25). Another diphosphorus heterocycle, 1,4-diphenyldiethylenediphosphine (VII), was synthesized by using a dihalide reagent (40). Intermolecular quaternization of

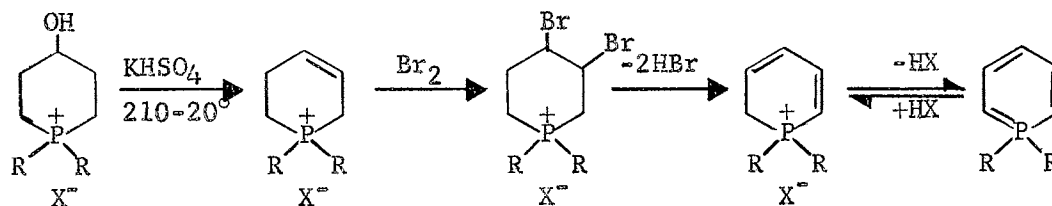
2-bromoethylethylphenylphosphine gave the best yields of this



VII

heterocycle.

There has long been an interest, mostly for theoretical purposes, to prepare a carbon-phosphorus heterocycle with aromatic properties. Isolation of such a compound has recently been reported (66). Precipitation of 1,1-diphenyl-1-phosphabenzene (VIII) (R=C₆H₅) as an



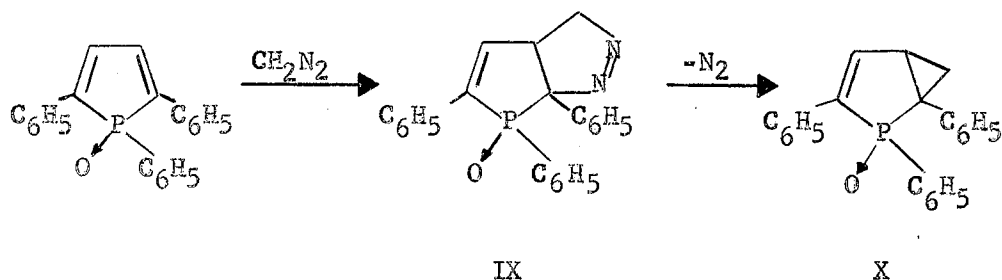
VIII

amorphous yellow powder was possible from an aqueous solution by addition of dilute sodium hydroxide. The evidence for this structure is not completely convincing and a more complete characterization should be forthcoming. Markl also has reported the preparation of 1,1-diphenyl-1-phosphanaphthalene (64).

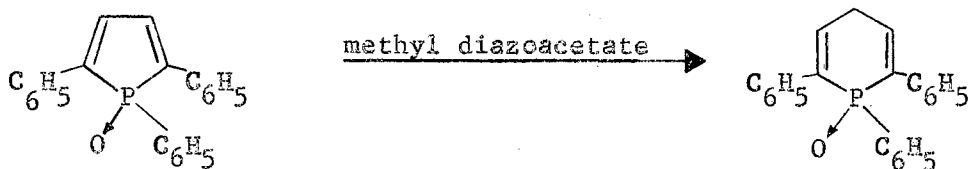
Several phospholes have recently been obtained and characterized by nuclear magnetic resonance, infrared and ultraviolet spectra (22). Dehydrogenation of saturated heterocyclic phosphorus compounds to give phospholes proved successful in several cases. Studies to determine

the degree of aromaticity of the phosphole system were conducted by treating the phospholes with diazomethane and methyl diazoacetate.

When 1,2,5-triphenylphosphole was treated with diazomethane, a

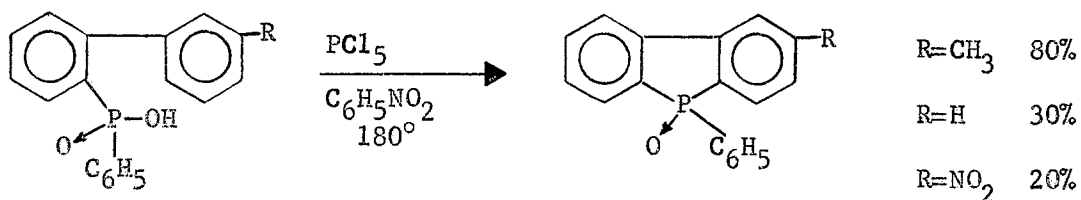


pyrazoline IX was produced which readily lost nitrogen to form the cyclopropane derivative X. Reaction of 1,2,5-triphenylphosphole with methyl diazoacetate is believed to yield a ring-expanded compound



which was characterized by instrumental methods.

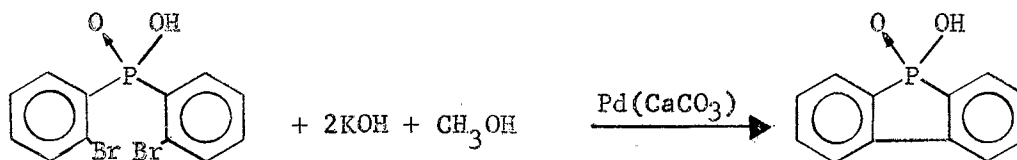
Perhaps more work has been done on the phosphafluorenes than any other group of carbon-phosphorus heterocycles. Indicative of the difficulty in effecting ring closure of some of these compounds is the work of Campbell and Way (20, 21). After several attempts failed to promote closure of the ring, success was finally realized in the preparation of 9-phenyl-9-phosphafluorene-1-oxide (XI) (in 30 per cent yield) by using phosphorus pentachloride in nitrobenzene. Optimum yields were obtained with a 3:1 excess of phosphorus pentachloride.



XI

It was suggested that the phosphinyl chloride, $\text{Ar}_2\text{P}(\text{O})\text{Cl}$, is formed initially and is converted at high temperatures into the trichloride, Ar_2PCl_3 . This compound, in the presence of phosphorus pentachloride, is ionized to $[\text{Ar}_2\text{PCl}_2]^+$, $[\text{PCl}_6]^-$. Cyclization by attachment of positive phosphorus on the adjacent ring would then follow. This appears to be a classic pattern of electrophilic substitution since a methyl group facilitates cyclization and a nitro group impedes it.

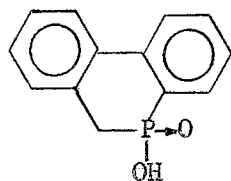
Ring closure of bis(o-bromophenyl) phosphinic acid was effected in 41 per cent yield to give the cyclic acid XII. The method was



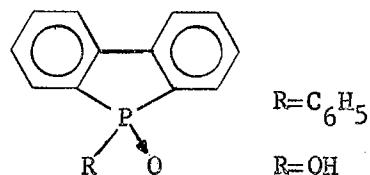
XII

that developed for catalytic reduction of halobenzene derivatives to biphenyl derivatives (30). Thermal cyclodehydration (59) proved to be an effective means of preparing 9,10-dihydro-9-

phosphaphenanthrene-9-oxide (XIII). By heating 2-phenylbenzylphos-



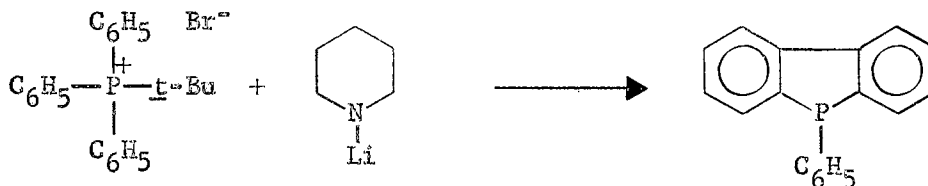
XIII



XIV

phinic acid in vacuum (350° , 0.2 mm.), the cyclic phosphinic acid was obtained in 50 per cent yield along with the anhydride. This same procedure was followed in an attempt to prepare 9-phenyl-9-phosphafluorene-9-oxide (XIV) ($R=C_6H_5$) but the yields were very low.

Recently (72), a unique synthesis of 9-phenyl-9-phosphafluorene (XV) (42 per cent yield) was reported. The process involved the use of triphenyl-*t*-butylphosphonium bromide and lithium piperidide. An ortho metalation process resulted to give an intermediate which

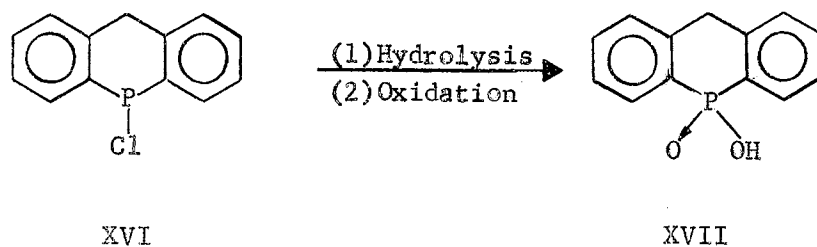


XV

underwent cyclization.

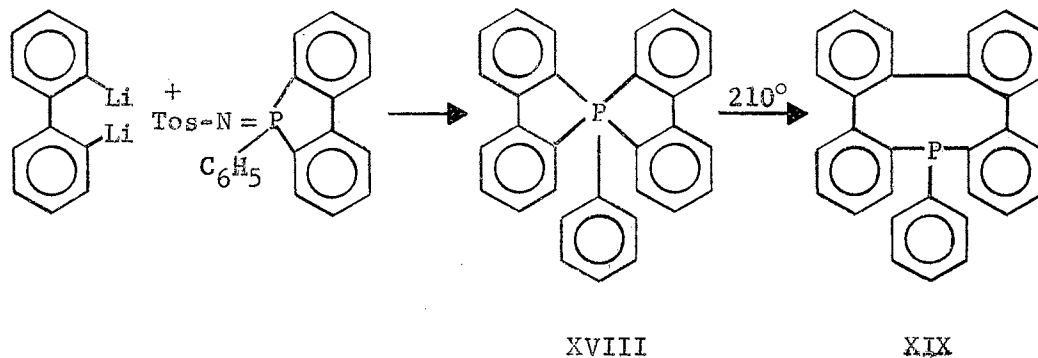
Cyclodehydrohalogenation was used by Doak and coworkers (28) in effecting ring closure of *o*-phenylbenzenediazonium fluoroborate. The resulting 5-chlorodibenzophosphole was hydrolyzed and oxidized to 9-phosphafluoric acid (5 per cent yield). This appeared to be a

suitable means of synthesizing carbon-phosphorus heterocycles since a number of similar arsenic and antimony compounds have been similarly prepared. By using a slightly modified procedure the 5-chloro intermediate XVI of the six-membered heterocycle obtained (25 per cent



yield) was hydrolyzed and oxidized with 30 per cent hydrogen peroxide. The ultraviolet spectrum of 5-hydroxy-5,10-dihydrodibenz[b,e]-phosphorin-5-oxide (XVII) is very similar to the noncyclic analog (*o*-benzylbenzenediazonium fluoroborate). This similarity is very likely associated with the absence of appreciable resonance interaction between two benzene rings joined by a methylene or a phosphinic acid group. Also the close similarity between the phosphinic and the arsenic analogs is remarkable.

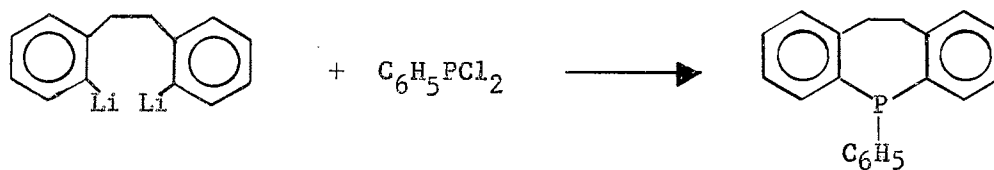
Perhaps one of the most unusual compounds of this type was recently reported by Wittig and Kochendoerfer (76). They prepared



phenyl-bis-biphenylenephosphan (XVIII) by means of a dilithio

reagent. When heated to 210° , XVIII rearranges to form a nine-membered ring XIX which then forms a phosphonium salt with methyl halide indicative of the presence of a trivalent phosphorus atom in the molecule. Additional work on this and related compounds is expected.

Isolation of a seven-membered cyclic phosphorus compound XX in moderate yield was effected by treating 2,2'-dilithiodibenzyl with phenylphosphonous dichloride (62). The ultraviolet spectrum of the



XX

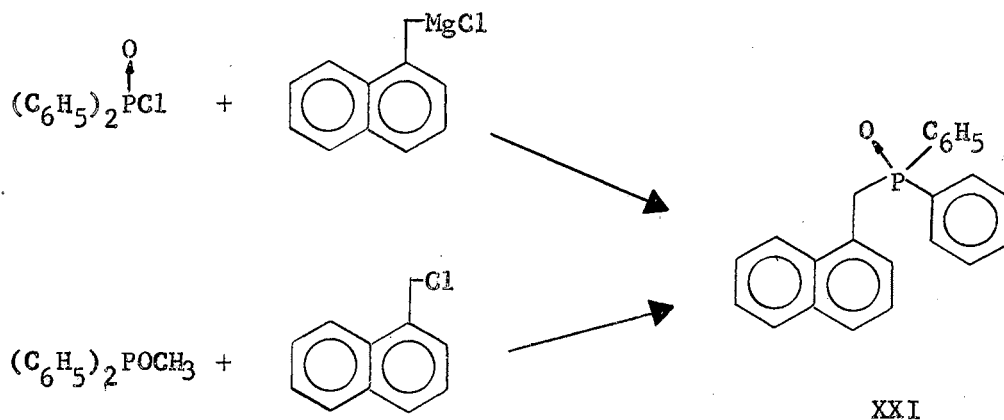
heterocyclic compound consists of one band (λ_{\max} 256-7 μ , ϵ_{\max} 11,200) indicating considerable resonance. If the molecule possessed three independent absorbing rings, several bands would be expected.

CHAPTER II

DISCUSSION OF RESULTS AND CONCLUSIONS

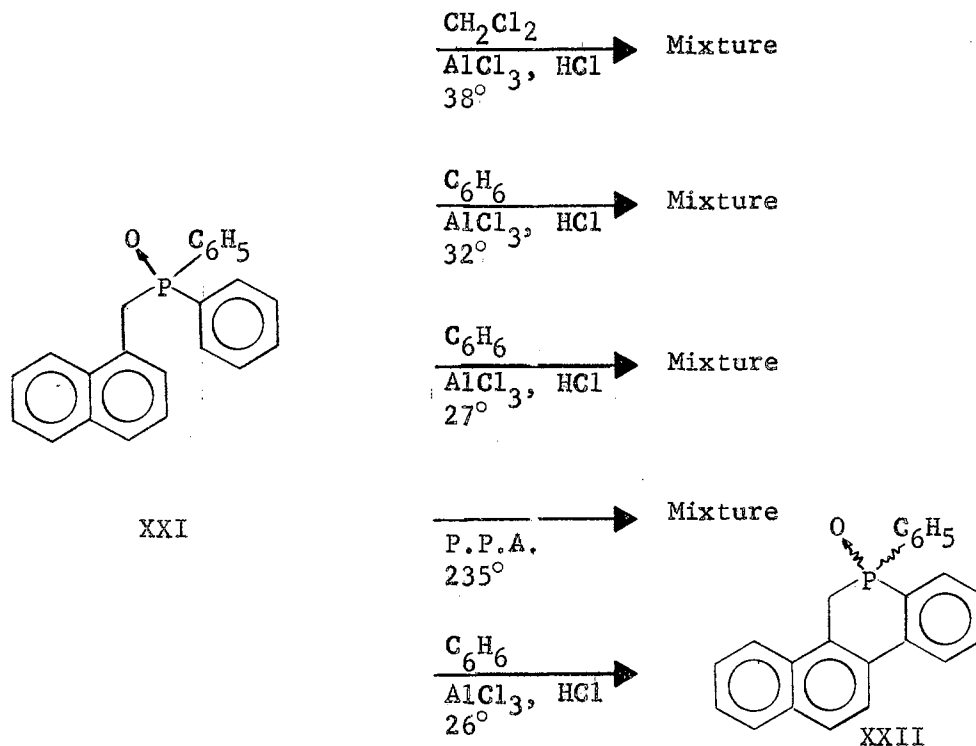
The object of this research was to synthesize potential precursors for the preparation of polynuclear aromatic hydrocarbons containing phosphorus. Several tertiary phosphine oxides have been obtained and the structures have been confirmed. Attempts were made to cyclize these compounds to high molecular weight polynuclear molecules containing phosphorus.

Diphenyl-(4-naphthylmethyl)phosphine oxide (XXI) was prepared by



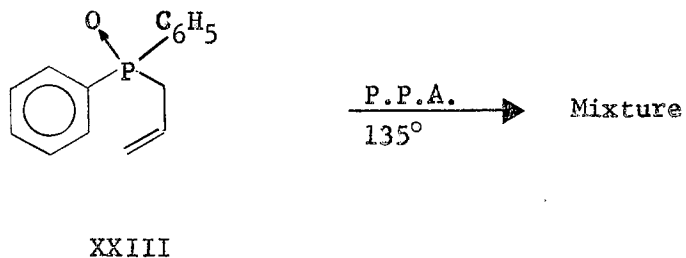
two alternate routes shown. Attempted ring closure with a variety of reagents gave complex mixtures except in one case. When a solution of the phosphine oxide in benzene was treated with anhydrous hydrogen chloride followed by periodic addition of aluminum chloride, a solid could be isolated in low yields (6-10 per cent). The compound isolated is

believed to have the structure XXII. This is supported by instrumental



data (infrared, nuclear magnetic resonance, ultraviolet). The cyclic phosphine oxide is the first example of a compound in this series.

Allyldiphenylphosphine oxide (XXIII) behaved in an analogous fashion as complex mixtures were obtained in addition to diphenyl-1-

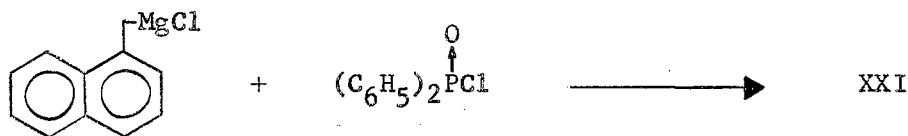


propenylphosphine oxide (XXVI). The latter compound simply resulted from isomerization of the double bond. Confirmation of the allyl and

1-propenyl derivative was achieved by reduction of both compounds to the known diphenylpropylphosphine oxide (XXIV).

Preparation of diphenyl-(1-naphthylmethyl)phosphine oxide (XXI) was achieved by reacting 1-naphthylmethyl chloride with methyl diphenylphosphonite in a classical Michaelis-Arbuzov rearrangement. An exothermic reaction occurred at 100°. After purification by crystallization, the compound was characterized by its infrared, nuclear magnetic resonance and ultraviolet spectra. The infrared spectrum possessed bands characteristic for P=O (1181 cm^{-1}) and PC_6H_5 (1436 cm^{-1}) (11). The nuclear magnetic resonance spectrum presented an excellent example of methylene splitting by phosphorus, showing a doublet at δ 4.08 ($J=14$ c.p.s.) and a multiplet at δ 7.5 (aromatic hydrogens). The elemental analysis also supports this structure. This method of preparation proved to be the most facile (54 per cent) and is the method of choice.

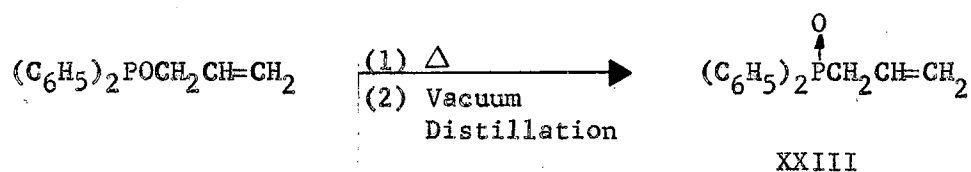
Preparation by an alternative method by condensing 1-naphthylmethylmagnesium chloride with diphenylphosphinic chloride proved to be a good method for structure confirmation. The product was found to be identical



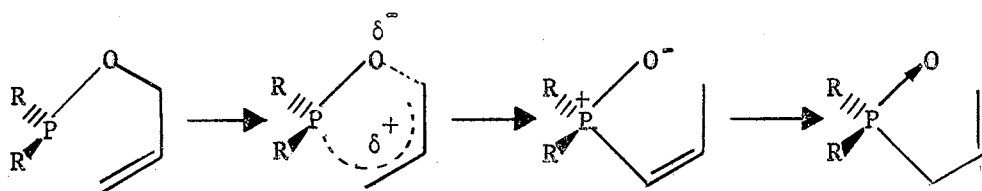
to the previously prepared phosphine oxide XXI. Although the yield was low (avg. 21.3 per cent), by very careful use of a larger excess of

Grignard reagent and high dilution, better yields could possibly be obtained. One reason for the low yield is the coupling of the 1-naphthylmethyl Grignard. The coupling process has been found to be extensive in the reaction of this Grignard reagent with several ketones (47).

Allyldiphenylphosphine oxide (XXIII) was prepared by heating allyl diphenylphosphinite in vacuum. Crystallization of the dis-

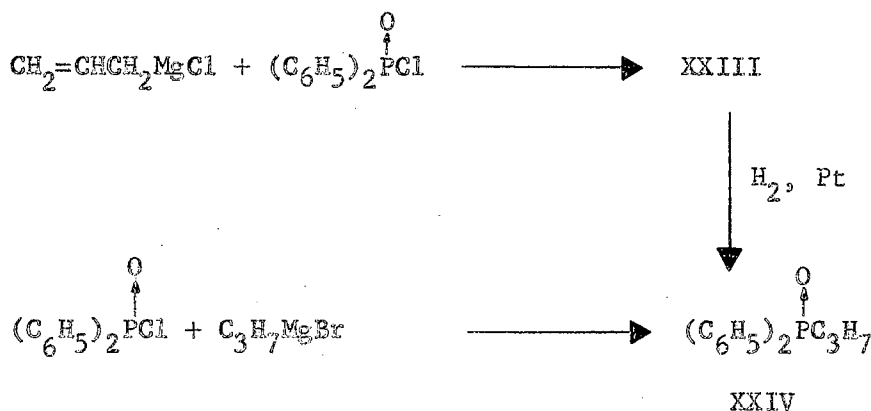


tillate which solidified was an effective means of purification giving XXIII in moderate yield (30.4 per cent). This skeletal rearrangement is similar to the thermal isomerization of α -methylallyl and crotyl phosphites described by Lemper (58) and of acetylenic phosphorus compounds reported by Mark (63). A cyclic transition state is very



possibly involved with formation of a carbon-phosphorus bond and breakage of an oxygen-carbon bond. It is conceivable that a vinyl compound might result, however, no such compound was detected. Complete characterization of XXIII was made by infrared and nuclear

magnetic resonance spectroscopy. The infrared spectrum had bands assigned to P=O (1178 cm.^{-1}), PC_6H_5 (1441 cm.^{-1}), C=C (1640 cm.^{-1}), C=CH₂ (921 cm.^{-1}). The nuclear magnetic resonance spectrum was also consistent with the assigned structure showing a quartet centered at δ 3.18 (CH₂ adjacent to phosphoryl group), and a complex multiplet at δ 5.28, apparently due to the terminal methylene hydrogen and internal vinyl protons. Elemental analysis also supports this structure. Arbuzov (3) reported this rearrangement but the solid he obtained melted at 94°. In view of this wide difference in melting point, synthesis by an alternate route seemed advisable. By condensing allyl Grignard with diphenylphosphinic chloride, XXIII was obtained in good yield (80.9 per cent) and is the method of choice. More conclusive



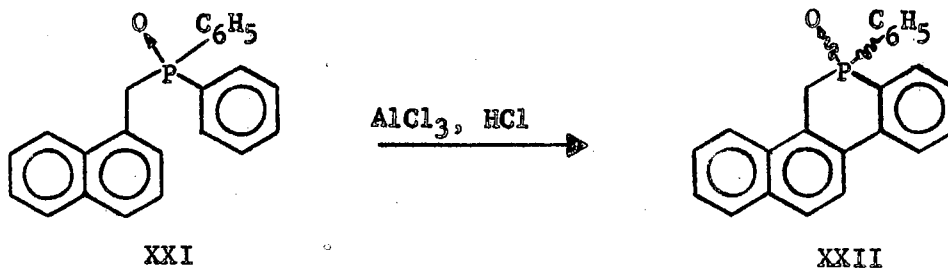
proof of structure for XXIII was afforded by hydrogenation using a platinum catalyst under pressure. Diphenylpropylphosphine oxide (XXIV) was prepared by condensing propylmagnesium bromide with diphenylphosphinic chloride.

An attempt to prepare allyldiphenylphosphine oxide via a Michaelis-Arbuzov rearrangement with allyl chloride and methyl diphenylphosphinite resulted in a mixture which could not be separated by

distillation or crystallization. The nuclear magnetic resonance of the mixture indicated the presence of diphenylmethylphosphine oxide showing a doublet at δ 2 ($J=14$ c.p.s.) which is identical to that of an authentic sample of diphenylmethylphosphine oxide.

Attention was next turned to attempting ring closure of XXI by selective reagents and controlled conditions. A survey of the literature failed to disclose a practical method of cyclization to give phosphorus heterocycles. The Scholl reaction is similar in that it involves formation of a bond between two aromatic nuclei. Dehydrogenation condensation of aryl nuclei has long been known to occur under the action of a strong Friedel-Crafts catalyst. This type of reaction can be either inter- or intramolecular and is usually conducted at high temperatures. Owing to the severity of the conditions, the yields are normally low because of side reactions. An extensive review of this reaction and related uses of aluminum chloride has recently been published (69). Johnson (45) in his synthesis of estrone and related steroids was successful in effecting closure of the A and B rings by using aluminum chloride. After analyzing and evaluating related reactions, aluminum chloride seemed to be a logical choice for ring closure of XXI.

Generally, the cyclization attempts were made by dissolving XXI



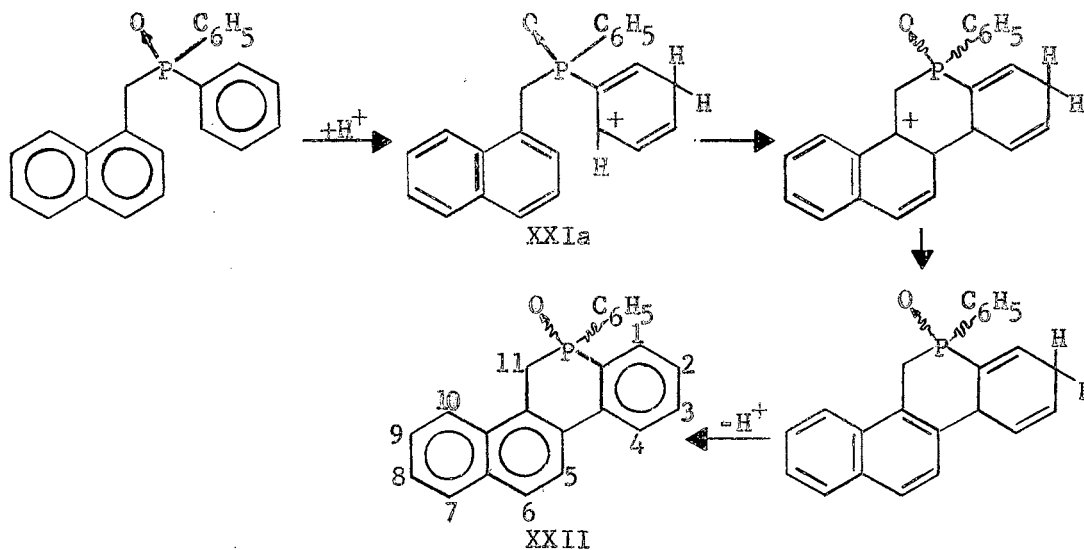
in benzene and saturating the cold solution with anhydrous hydrogen chloride for one hour. Addition of excess aluminum chloride (2.3:1 ratio) resulted in the evolution of a gas and a rapid change of color to a dark brown. In the several attempts made, the temperature was varied from 26° to 38° with a reaction time of from fourteen to twenty-seven hours. Workup of the reaction mixture consisted of pouring the mixture over ice and concentrated hydrochloric acid, extracting, washing, drying and concentration. Numerous attempts to crystallize the resultant orange solid were futile. Since the expected heterocyclic product would very possibly be a high-melting solid, column chromatography offered a suitable means of purification. To a chromatographic column, packed with acid-washed alumina (appx. 18 inches long), was added the solid which was dissolved in 15 ml. of benzene. When eluted with benzene, a yellowish oil was released. The infrared spectrum of this oil resembled that of a hydrocarbon. No additional separation was effected with either benzene, ether or methylene chloride as the eluent. Ethanol was used to strip the column giving a brownish-orange solid. Numerous attempts to crystallize this solid also failed. The wide melting range indicated that it was impure.

In the last cyclization attempt, a slightly modified method was used in an attempt to minimize the apparent cleavage of the molecule. Anhydrous hydrogen chloride was bubbled through the solution throughout the reaction period (26° for fourteen hours). In the purification step, a thirty-six inch column was used. Elution of the mixture with benzene yielded the same yellowish oil. When the eluent was changed to

5 per cent ethanol-ether, a reddish-yellow solid was removed. During the process, several orange and yellow bands were observed moving down the column and several viscous fractions were collected. A solid was obtained from cuts 67 and 68. After several recrystallizations from benzene-ether (in dry-ice bath) crystals were obtained (m.p. 188-90°).

Four factors can account for the isolation of crystals in this attempt. The temperature was reduced to 26°; however, this is a matter of only a few degrees and would not be expected to affect the reaction appreciably. Second, hydrogen chloride being bubbled through the solution continuously could very well be an important factor. Baddeley (8) has shown that in cyclization reactions using aluminum chloride, the presence of hydrogen chloride is essential to the reaction. Third, the column was increased twofold in length. This factor is most assuredly important for better separation. Last, the use of 5 per cent ethanol-ether proved to be a suitable combination to cause slow movement down the column and thus better separation.

Mechanistically the ring closure can be envisioned as taking place by first forming the conjugate acid XXIa with subsequent

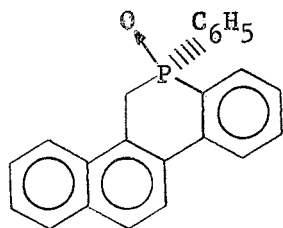


electrophilic attack on the adjacent naphthalene ring. Aromatization of the dihydro products would be expected to occur readily to give XXII. This structure is only one possibility, however, as fragmentation by carbon-phosphorus bond severance must also occur to give several products.

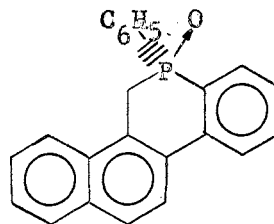
Spectroscopic data (infrared, nuclear magnetic resonance and ultraviolet) of the crystalline solid support the cyclic structure. The infrared spectrum is very similar to that of XXI, however, there are noticeable differences. Bands assigned to P=O (1182 cm.^{-1}) and PC_6H_5 (1440 cm.^{-1}) are present. The nuclear magnetic resonance spectrum shows a pronounced diamagnetic shift of the doublet assigned to the methylene protons (from δ 4.08 to δ 3.59) with the coupling constant relatively unchanged ($J=13.7 \text{ c.p.s.}$) from starting material ($J=14 \text{ c.p.s.}$). Examination of the ultraviolet spectrum discloses an interesting example of the strain that must be present in the molecule. By forming the expected bond, conjugation could be expected to increase. According to the established patterns (31, 43), this should cause a bathochromic shift and an increase in intensity. However, the opposite situation may occur in this case. The bands are decreased in intensity and shifted to a shorter wave length. Steric factors, known to cause such absorption patterns, may be important in causing the naphthalene ring to be twisted. Construction of molecular models of this heterocyclic molecule shows that the benzene bonded to the naphthalene ring is twisted out of coplanarity as a result of hydrogen-hydrogen interaction of the 3-hydrogen of naphthalene and the ortho hydrogen of the benzene ring. This model also shows twisting to

relieve the interaction of the 8-hydrogen of naphthalene and the methylene hydrogen. The bonds in XXII shown with a wavy line (phosphoryl and C_6H_5) are so represented to indicate that they may project above or below the rest of the molecule, depending upon the configuration.

Ring closure of XXI should result in two nonsuperimposable isomers. All of the spectroscopic evidence (infrared, nuclear



XXIIa



XXIIb

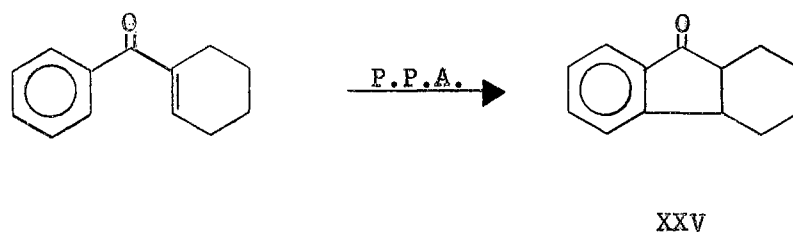
magnetic resonance, ultraviolet) favors the structure shown for the compound, although elemental analysis indicates it to be impure. It is quite possible that a product resulting from carbon-phosphorus bond breaking is a contaminate, as the phosphorus analysis on XXII is high.

In addition to being a new carbon-phosphorus heterocyclic compound, this synthesis is the first reported method of this type resulting in formation of a carbon-carbon bond between two aromatic nuclei with phosphorus in the ring. The most closely related work was the synthesis by Freedman and Doak using the Birch reduction method (30). Even though the yields were low, this type of ring closure opens an entirely new area for preparing heterocyclic phosphorus compounds and should be applicable to other appropriate aromatic systems. By selecting a milder Lewis acid (possibly stannic chloride), the apparent cleavage

may be reduced and the yield increased.

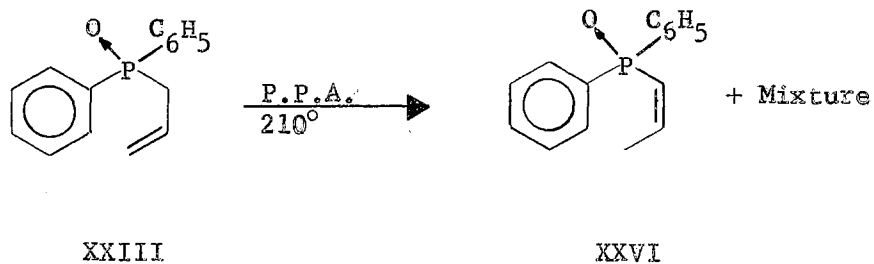
Plans have been made to hydrogenate the aromatic rings of XXII to form a steroid-like molecule with phosphorus in the 11-position. Much more work in this area is planned and should prove interesting.

Attention was next directed toward promoting ring closure of allyldiphenylphosphine oxide (XXIII). A thorough survey of the literature contains no close analogy to this proposed ring closure. Dev (27) in his cyclization reaction with polyphosphoric acid (P.P.A.)

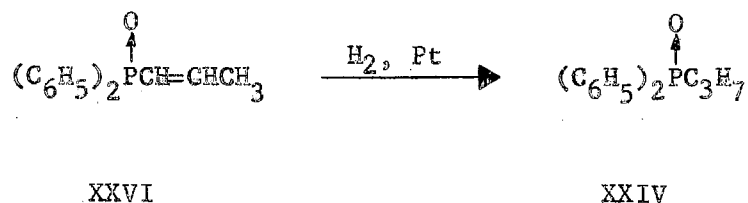


obtained the cyclic ketone shown, in 65 per cent yield. Although differences due to the hetero phosphorus atom were anticipated, this reagent seems to be a logical choice (70).

A mixture of XXIII and polyphosphoric acid was heated at 210° for one and a half hours. The mixture was poured into cool water, and the mixture was extracted and worked up as usual. An intractable yellowish



mass and a solid (m.p. 124.5-6°) were separable. The infrared spectrum of this solid confirmed a double bond, however, the band at 920 cm^{-1} ($\text{C}=\text{CH}_2$) was absent. The immediate assumption was that the double bond had shifted into the vinyl position, which is plausible under acidic conditions and at high temperature. The nuclear magnetic resonance spectrum also supports this vinyl structure showing multiplets at δ 7.5 (aromatic protons), δ 6.5 (vinyl protons) and a doublet at δ 1.69 ($J=6$ c.p.s., methyl protons). Thin layer and gas liquid chromatography (hydrogen flame unit) indicated only a trace of impurity. Elemental analysis also supports this structure. Hydrogenation of XXIII to give diphenylpropylphosphine oxide was readily achieved under mild



conditions. The product XXIV was identical to that prepared by the alternative route.

CHAPTER III

EXPERIMENTAL^{1, 2, 3, 4, 5, 6}

Preparation of Dimethyl Phenylphosphonite. The procedure was essentially that used by Harwood (37). Filtration of the amine hydrochloride was conducted under nitrogen (inverted funnel). After removal of excess ether in vacuo, the main product distilled at 80-81° (4 mm.); n_D^{29} 1.5258 [lit. (37) n_D^{25} 1.5261]. Three separate preparations were made of this compound with an average yield of 39.6 per cent. The infrared spectrum showed bands at 1440 (P-C₆H₅), 1180, 1105, 1040, 742, 720 and 700 cm.⁻¹.

¹All melting points and boiling points are uncorrected.

²The infrared spectra were determined on Beckman IR-5 and IR-5A spectrometers as films on sodium chloride or as potassium bromide pellets.

³The nuclear magnetic resonance spectra were determined on a Varian A-60 high resolution spectrometer with a field-sensing stabilizer ("Super Stabilizer"). Tetramethylsilane was used as the internal standard.

⁴The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

⁵The ultraviolet spectra were obtained from a Cary Model 14 recording spectrophotometer using quartz cells.

⁶Gas chromatographic analyses were performed using a Aerograph Hy-Fi Model A-550 with a hydrogen flame ionization detector from Wilkins Instrument and Research, Inc., Walnut Creek, California.

Attempted Preparation of Methyl 1-Naphthylmethylphenylphosphinate.

Freshly prepared dimethyl phenylphosphonite (10.0 g., 0.58 mole) was placed in a 200-ml., three-necked flask fitted with mechanical stirrer, reflux condenser (CaCl₂ tube) and a pressure-equalizing addition funnel. The system was flushed and maintained under deoxygenated nitrogen. Freshly distilled 1-naphthylmethyl chloride (10.24 g., 0.058 mole) was placed in the addition funnel and added dropwise to the phosphonite. An immediate reaction was not observable. After 2 ml. of the halide had been added the temperature was raised to 130° and the remaining halide added dropwise (1 hr.). Gas evolution accompanied the rise in temperature. The reaction mixture was heated at 140° for 15 hr. and at 155° for 2 hr.. When cooled, the mixture became very viscous and had a lavender color.

Several operations were performed in an effort to purify the phosphinate. A portion of the reaction mixture placed in a vacuum oven for 15 hr. became a clear yellow solid. Numerous attempts to crystallize the solid from several solvents and solvent pairs failed. After several unsuccessful attempts to purify the product by vacuum distillation, an ester identified as methyl methylphenylphosphinate was obtained using a short-path distillation apparatus. The infrared spectrum was identical to that of an authentic sample. It had bands at 3400, 1439 (P-C₆H₅), 1303 (P-C), 1220 (P-O), 1122, 1040, 892, 795, 740 and 695 cm.⁻¹. Approximately 20 per cent of the reaction mixture consisted of this side reaction product.

Attempts were made to determine the composition of the remaining reaction mixture by use of g.l.c. (hydrogen flame unit) with a 6' x 8'

silicone-rubber column at temperatures from 150° to 300°. At no time was any material detected on the column.

Attempts were made to separate the mixture using a chromatographic column packed with acid-washed alumina in cyclohexane. Three grams of material were placed on the column and eluted with cyclohexane, ether, benzene and methanol. Bottles number 18 - 20 yielded a few droplets of a clear oily material. Bottles number 40 - 50 gave a dark oily substance (removed with methanol). This oil was then rechromatographed using a small column (50-ml. pipette). Bottles number 30 - 40 left a large amount of dark oily material (removed with methanol). Attempts were made to crystallize the material without success.

Preparation of Methyl Diphenylphosphinite. The ester was prepared according to the method developed in this laboratory (7). Methanol (7.6 g., 0.240 mole), triethylamine (22.84 g., 0.226 mole), 150 ml. of dry ether, and diphenylphosphinous chloride (50 g., 0.226 mole) in 100 ml. of dry ether were employed. Methyl diphenylphosphinite distilled at 103-8° (1 mm.), 33.21 g. (67.9 per cent), n_D^{29} 1.6013 [lit. (3) n_D^{20} 1.6030]. Three preparations gave yields of 67.9, 68.2 and 76.5 per cent. The infrared spectrum showed bands at 3020, 2800, 1480, 1436 (P-C₆H₅), 1178, 1095, 1038 (P-O-C), 730 and 695 cm.⁻¹.

Preparation of Diphenyl-(1-naphthylmethyl)phosphine Oxide (XXI)
via a Michaelis-Arbuzov Rearrangement. Freshly prepared methyl diphenylphosphinite (45.0 g., 0.207 mole) was placed in a three-necked flask fitted with a reflux condenser, mechanical stirrer and pressure-equalizing addition funnel under a nitrogen atmosphere. 1-Naphthylmethyl chloride (37.16 g., 0.207 mole) was added to the addition

funnel and a dropwise addition was started. Since no apparent reaction occurred after approximately one-third of the halide had been added, the flask was heated slowly to 100-115°. A very exothermic reaction resulted and a gas was evolved, with a sharp rise in the temperature to approximately 180°. When the initial vigorous evolution of gas had subsided the remainder of the halide was added dropwise (1 hr.). When the addition was complete, the reaction mixture was heated at 140-5° for 1 hr.. When allowed to cool below 130°, the mixture solidified. Recrystallization of the solid from benzene-ether gave crystals, 42.4 g. (54.1 per cent), m.p. 162-3.5°. The infrared spectrum (plate I) showed bands at 3010, 1436 (P-C₆H₅), 1392, 1265, 1181 (P-O), 1114, 1100, 1010, 875, 855, 832, 794, 774, 740, 722 and 694 cm.⁻¹.

The nuclear magnetic resonance spectrum (plate V) shows a doublet centered at δ 4.08 (J=14 c.p.s.; methylene hydrogen) and a multiplet centered at approximately δ 7.5 (aromatic hydrogen).

The ultraviolet spectrum (CH₂Cl₂) shows bands at 228 m μ (ϵ_{\max} 81,000), 266.5 m μ (ϵ_{\max} 6,340), 277 m μ (ϵ_{\max} 8,500), 287.8 m μ (ϵ_{\max} 11,000), 298.2 m μ (ϵ_{\max} 6,920), 314.7 m μ (ϵ_{\max} 680).

Anal. Calcd. for C₂₃H₁₉OP: C, 80.59; H, 5.50; P, 9.04.

Found: C, 80.53; H, 5.45; P, 8.91.

Preparation of Diphenyl-(1-naphthylmethyl)phosphine Oxide (XXI) via a Grignard Reaction. 1-Naphthylmethylmagnesium chloride was prepared using essentially the method employed by Wolhuis (77). To the Grignard reagent (0.271 mole) was added dropwise (under nitrogen) diphenylphosphinic chloride (47.31 g., 0.20 mole) in 80 ml. of dry

ether. Moderate heat was generated and after the addition was complete, the mixture was boiled for 2 hr.. A gummy orange-colored solid formed. Decomposition was effected with 20 per cent aqueous ammonium chloride at room temperature. The resulting heterogeneous mixture was stirred for 14 hr. at room temperature during which time the mixture turned chalky white. The solid was filtered and the organic layer was separated. The aqueous layer was extracted three times with benzene-ether and combined with the original organic layer which was washed with 10 per cent sodium bicarbonate, dried (Na_2SO_4), and concentrated to give a dark oil from which crystals deposited, m.p. $162-3^\circ$ [lit. 161° (47)], identified by infrared analysis as 1,2-dinaphthylethane. The original solid was dissolved in hot benzene. The insoluble fraction was isolated by filtration. The soluble fraction upon concentration cooling gave white crystals which after three recrystallizations melted at $162-3^\circ$, 10.0 g. (14.6 per cent). The infrared spectrum was identical to that of the previously prepared phosphine oxide and a mixture melting point determination showed no depression. The yields in three separate runs averaged 21.3 per cent.

The benzene-insoluble fraction mentioned, when crystallized from ethanol, consisted of white needles (m.p. $191-3^\circ$) and was identified as diphenylphosphinic acid.

Attempted Ring Closure of Diphenyl-(1-naphthylmethyl)phosphine Oxide (XXI) with Aluminum Chloride. Diphenyl-(1-naphthylmethyl)phosphine oxide (3.0 g., 0.008 mole) was dissolved in 60 ml. of methylene chloride and placed in a three-necked flask fitted with mechanical stirrer, condenser and fritted-glass inlet tube. The solution was saturated at ice-bath

temperature (3-6°) with dry hydrogen chloride for 1 hr.. The inlet tube was then replaced with a piece of large-diameter tubing placed over a 50-ml. Erlenmeyer flask to which was added anhydrous aluminum chloride (2.53 g., 0.019 mole). The aluminum chloride was slowly added and, after approximately one-half had been introduced, the solution turned pink and gradually became a dark red. Within 2 hr. the color of the mixture was almost black. Stirring was continuous and, after all the aluminum chloride had been added, the mixture was allowed to attain room temperature (26°), after which time it was stirred for 14 hr.. The mixture was then heated to 37-8° and stirred for 12 hr., cooled to room temperature and poured over a mixture of ice and 25 ml. of concentrated hydrochloric acid. A brownish-colored mixture resulted and two layers formed. The layers were separated and the aqueous phase was extracted (benzene-ether). The combined organic extract and original phase were washed (NaHCO₃), and dried (Na₂SO₄). The organic solvents were removed and a benzene-soluble (1.1 g.) and benzene-insoluble (1.2 g.) fractions were obtained. When concentrated, the benzene-soluble fraction deposited an orange solid, m.p. 180-210°. The solid was chromatographed on an acid-washed alumina column but no separation was effected.

Essentially the same experiment was conducted with 3.0 g. (0.008 mole) of the phosphine oxide dissolved in 80 ml. of benzene. Stirring of the solution was continuous for 12 hr. at 26-7° and at 65-70° for 12 hr.. The work up was the same as in previous experiment, but no crystals could be obtained from the concentrated benzene solution. The residual oily material was chromatographed on an alumina column (acid-washed) from which was obtained a yellow oil (0.3 g.), having an infrared

spectrum like that of a hydrocarbon with bands at 3028, 2860, 1600, 1492, 1450, 1075, 1038, 749 and 698 cm.^{-1} . A second small fraction (0.02 g.) was obtained which, when recrystallized from benzene, gave white crystals. The infrared spectrum had bands at 3440, 3030, 1490, 1445, 1329, 1158, 1012, 890, 758 and 698 cm.^{-1} . A yellowish solid was obtained from the column in bottles number 47 - 64. When the solid was dissolved in benzene-ether, a sticky material was deposited. The infrared spectrum of this fraction had bands at 3440, 2850, 1596, 1487, 1439 ($\text{P-C}_6\text{H}_5$), 1192 (P-O), 1119, 1070, 1029, 998, 773, 746 and 693 cm.^{-1} . The fraction stripped from the column with ethanol was a dark-brown solid, m.p. 50-80°. Several attempts at recrystallization of this material were made using benzene, ether, acetone, ethanol, Skellysolve F, acetic acid and mixed solvents without success. The infrared spectrum had bands at 3030, 1595, 1490, 1439 ($\text{P-C}_6\text{H}_5$), 1191 (P-O), 1117, 1072, 1039, 999, 825, 775 and 694 cm.^{-1} .

Another cyclization attempt with aluminum chloride was made using essentially the same procedure as before except that the reaction mixture was heated to 32° for 15 hr.. The color changed from white to dark brown. The work-up was essentially the same as before. When chromatographed on alumina, the same mixture of products was obtained.

The last cyclization attempt followed essentially the same procedure described above with the following exceptions. A steady stream of dry hydrogen chloride was slowly bubbled through the solution throughout the reaction period (14 hr. at 26°). The usual work-up was followed resulting in a brownish-orange solid. This solid was dissolved in 15 ml. of benzene and placed on a thirty-six inch chromatographic

column (packed with acid-washed alumina). Elution with benzene removed the same yellowish oil (bottles numbers 8 thru 11). When a 5 per cent ethanol-ether solution eluted the mixture, several bands were observed moving down the column. A reddish-orange solid was collected in bottles number 64 thru 75. Crystallization of a solid (.38 g., 6.3 per cent) in bottles 67 and 68 was effected with benzene-ether (dry-ice bath). After five recrystallizations, a feathery yellowish solid was isolated (m.p. 188-90°). As the temperature rose past 160-5°, while taking the melting point, white needle-like crystals formed on top of the solid. This continued until the solid melted. The infrared spectrum (plate II) had bands at 3030, 2880, 1600, 1499, 1440 (P-C₆H₅), 1410, 1336, 1314, 1241, 1182 (P=O), 1140, 1121, 1070, 1032, 1001, 910, 850, 778, 754, 743, 721 and 694 cm.⁻¹. The nuclear magnetic resonance spectrum (plate VI) shows a doublet centered at δ 3.59 (J=13.7 c.p.s., methylene hydrogen) and a multiplet centered at δ 7.49 (aromatic hydrogen). The ultra-violet spectrum (CH₂Cl₂) shows bands at 226.5 m μ (ϵ_{\max} 12,600), 254.5 m μ (ϵ_{\max} 810), 260 m μ (ϵ_{\max} 980), 265.6 m μ (ϵ_{\max} 1,110) and 272.2 m μ (ϵ_{\max} 860). It is apparent from the elemental analyses that the compound is still impure.

Anal. Calcd. for C₂₃H₁₇OP: P, 9.38

Found: P, 14.95

Attempted Ring Closure of Diphenyl-(1-naphthylmethyl)phosphine Oxide (XXI with Polyphosphoric Acid. To a three-necked flask equipped with a thermometer and a magnetic stirrer was added diphenyl-(1-naphthylmethyl)phosphine oxide (5.0 g., 0.014 mole) and 50 g. of polyphosphoric acid (105 per cent). No visible reaction or color change occurred, so

the temperature was increased gradually to 230-5° for 3 hr. and a dark green color appeared. The reaction mixture was then poured into 200 ml. of ice and water and allowed to warm to room temperature. A yellowish solid was suspended in the water and an insoluble greenish mass remained in the bottom. Extraction with benzene dissolved only a small amount of the greenish mass. The extracts were washed (NaHCO₃), dried (Na₂SO₄) and evaporated to approximately 5 ml., and upon cooling, crystals were deposited, 3.5 g., m.p. 161-2.5°. Absorption bands in the infrared spectrum indicated it to be starting material. The loss of 1.5 g. can be attributed to the intractable greenish mass.

Attempted Preparation of Allyldiphenylphosphine Oxide (XXIII) via Michaelis-Arbuzov Rearrangement. Methyl diphenylphosphinite (20.0 g., 0.092 mole) was placed in a three-necked flask fitted with a condenser (CaCl₂ tube), magnetic stirrer and pressure-equalizing addition funnel (all under nitrogen). Allyl chloride (6.8 g., 0.92 mole) was added dropwise with no apparent reaction. When addition was complete, the mixture was heated to reflux for 4 hr.. Vacuum distillation produced a liquid (13.3 g.) boiling at 110-12° (0.7-0.8 mm.). The infrared spectrum indicated it to be methyl diphenylphosphinate.

This reaction was repeated using a 3:1 ratio of halide to phosphinite and a reflux time of 48 hr.. When cooled, the reaction mixture partially solidified. Attempts were made to crystallize the material using various solvents without success. Vacuum distillation using a short-path column resulted in separation of a material boiling at 173-8° (0.3 mm.). The compound solidified upon standing. A small sample of this solid became sticky and appeared to be hygroscopic. The

infrared spectrum had an absorption at 3380 cm.^{-1} . This sticky material melted completely at $90\text{-}92^\circ$ indicating a mixture. A doublet centered at $\delta\ 2.0$ ($J=14\text{ c.p.s.}$), which is identical to that of an authentic sample of diphenylmethylphosphine oxide is visible in the nuclear magnetic resonance spectrum.

Preparation of Allyldiphenylphosphine Oxide (XXIII) via Rearrangement. The procedure followed was similar to that of Arbuzov (3). Allyl alcohol (7.89 g., 0.136 mole), 10.75 g. of pyridine and 250 ml. of dry ether were placed in a three-necked flask fitted with a mechanical stirrer, pressure-equalizing addition funnel and condenser (CaCl_2 tube). The system was cooled to $3\text{-}6^\circ$ (ice bath) and maintained under nitrogen. Diphenylphosphinous chloride (30.0 g., 0.136 mole) was added dropwise (1 hr.). After the addition was complete, the reaction mixture was allowed to attain room temperature and was stirred an additional 1 hr.. The suspension was filtered under nitrogen and the solvent was flash-evaporated. The yellowish, oily residue was distilled to yield a fraction boiling at $98\text{-}110^\circ$ (0.15 mm.) which partially solidified (4.1 g.) after standing one day. The infrared spectrum had characteristic bands at 1436 ($\text{P-C}_6\text{H}_5$), 1175 (P-O) and 1020 (P-O-C), indicating that this fraction was allyl diphenylphosphinate. A second fraction was taken at $135\text{-}49^\circ$ (0.15 mm.) and solidified immediately. Recrystallization from benzene-Skellysolve F gave white crystals, m.p. $109\text{-}10.5^\circ$, 7.8 g. (30.4 per cent). The infrared spectrum (plate III) had bands at 3030, 2760, 1640 (C=C), 1480, 1441 ($\text{P-C}_6\text{H}_5$), 1178 (P-O), 1115, 983, 921 (C=CH_2), 826, 772, 716 and 698 cm.^{-1} .

Anal. Calcd. for $\text{C}_{15}\text{H}_{15}\text{OP}$: C, 74.40; H, 6.19; P, 12.79.

Found: C, 74.38; H, 6.28; P, 12.78

The nuclear magnetic resonance spectrum (plate VII) showed a quartet centered at δ 3.18 (CH_2 adjacent to phosphoryl group) with each signal of nearly equal area and $J=7$ c.p.s. The center of a complex multiplet is located at δ 5.28.

The presence of the double bond was verified with a bromine test which gave a yellowish cloudy solution which became clear after standing 2 hr..

Preparation of Allyldiphenylphosphine Oxide (XXIII) via a Grignard Reagent. To the allyl Grignard reagent (0.74 mole) prepared by the method of Grummitt (33) in a three-necked flask fitted with a condenser (CaCl_2 tube), mechanical stirrer and pressure-equalizing addition funnel was added dropwise at $0-5^\circ$ diphenylphosphinic chloride (23.64 g., 0.1 mole). After the addition was complete, the mixture was stirred for 2 hr. and allowed to attain room temperature. Decomposition was effected with 20 per cent aqueous ammonium chloride. A pasty mass formed which was filtered and two layers separated. The aqueous phase was extracted with benzene-ether and the organic layers were combined, washed (NaHCO_3), dried (Na_2SO_4) and concentrated. Upon cooling, the oily residue deposited crystals. Two recrystallizations from benzene-Skellysolve F gave crystals, 15.2 g. (80.9 per cent), m.p. $109-10.5^\circ$. The infrared spectrum was identical to that of the previously prepared phosphine oxide.

Hydrogenation of Allyldiphenylphosphine Oxide (XXIII). The allyldiphenylphosphine oxide (2.0 g., 0.01 mole) was dissolved in 70 ml. of benzene and placed in a taped coke bottle. Platinum oxide (25 mg.) catalyst was added to the bottle which was then fastened to a Parr

hydrogenation apparatus (12). After flushing the system four times with hydrogen, the pressure was increased to 3 atm. and the shaker started. The pressure decreased slowly and after 1 hr. was at 1.1 atm. The catalyst was filtered and the solution was concentrated. Skellysolve F was added until the solution turned cloudy and crystallization resulted (1.6 g.). Purification of the solid via two additional recrystallizations gave diphenylpropylphosphine oxide (XXIV) melting at 100-1.5°. The infrared spectrum was very similar to that of the allyl compound except that the bands at 1640 and 921 cm.^{-1} were absent.

The nuclear magnetic resonance spectrum (in CHCl_3) showed a multiplet centered at δ 7.62 (aromatic hydrogen), a triplet centered at δ 1.0 ($J=7$ c.p.s.; methyl protons) and multiplets centered at δ 2.26 and δ 1.67 ($-\text{CH}_2-\text{CH}_2-$).

Preparation of Diphenylpropylphosphine Oxide (XXIV). Propylmagnesium bromide was prepared by the usual method resulting in 90 per cent yield (0.06 mole). Diphenylphosphinic chloride (10.0 g., 0.042 mole) added dropwise to the Grignard reagent caused a slightly exothermic reaction. After the addition was complete, the mixture was boiled for 1 hr., decomposed with 20 per cent aqueous ammonium chloride and the resulting mixture was stirred for 4 hr.. The organic layer was separated and combined with the benzene-ether extracts. The resulting solution was washed (NaHCO_3), dried (Na_2SO_4) and evaporated to a volume of 75 ml.. The crystals formed, after purification from benzene-heptane, melted at 98.5-100° [lit. (73) 100-1°], 93.7 per cent. The infrared spectrum was identical to that of the product prepared by hydrogenation.

Attempted Ring Closure of Allyldiphenylphosphine Oxide (XXIII).

To a 100-ml. three-necked flask fitted with a condenser (CaCl₂ tube), magnetic stirrer and thermometer was added allyldiphenylphosphine oxide (5.0 g., 0.026 mole) and polyphosphoric acid (50.0 g., 105 per cent). The mixture was heated (with stirring) to 135° for 1.5 hr.. The mixture which had turned a brownish color, was poured into 300 ml. of ice and water. Benzene was used to extract the mixture. The organic solution was washed (NaHCO₃), dried (Na₂SO₄) and concentrated to give a solid which was recrystallized from benzene-Skellysolve F, 3.1 g., (62 per cent), m.p. 105-8°. The infrared spectrum was identical to that of starting material. An intractable yellowish material explains the 1.9 g. loss.

This same procedure was repeated in a second run except the temperature was raised to 210° for 1.5 hr.. The color changed to a brownish red. Essentially the same work up produced crystals, 0.9 g. (18 per cent), m.p. 120-3°. These crystals were chromatographed on alumina (acid-washed) with no apparent purification. After four recrystallizations from benzene-Skellysolve F, a product was obtained melting at 124.5-6°. The infrared spectrum (plate IV) was almost identical to that of starting material except the band at 920 cm.⁻¹ was absent. Thin layer chromatography and g.l.c. (H₂ flame unit) indicated that only a trace of impurity was present.

Anal. Calcd. for C₁₅H₁₅OP: C, 74.40; H, 6.19; P, 12.79.

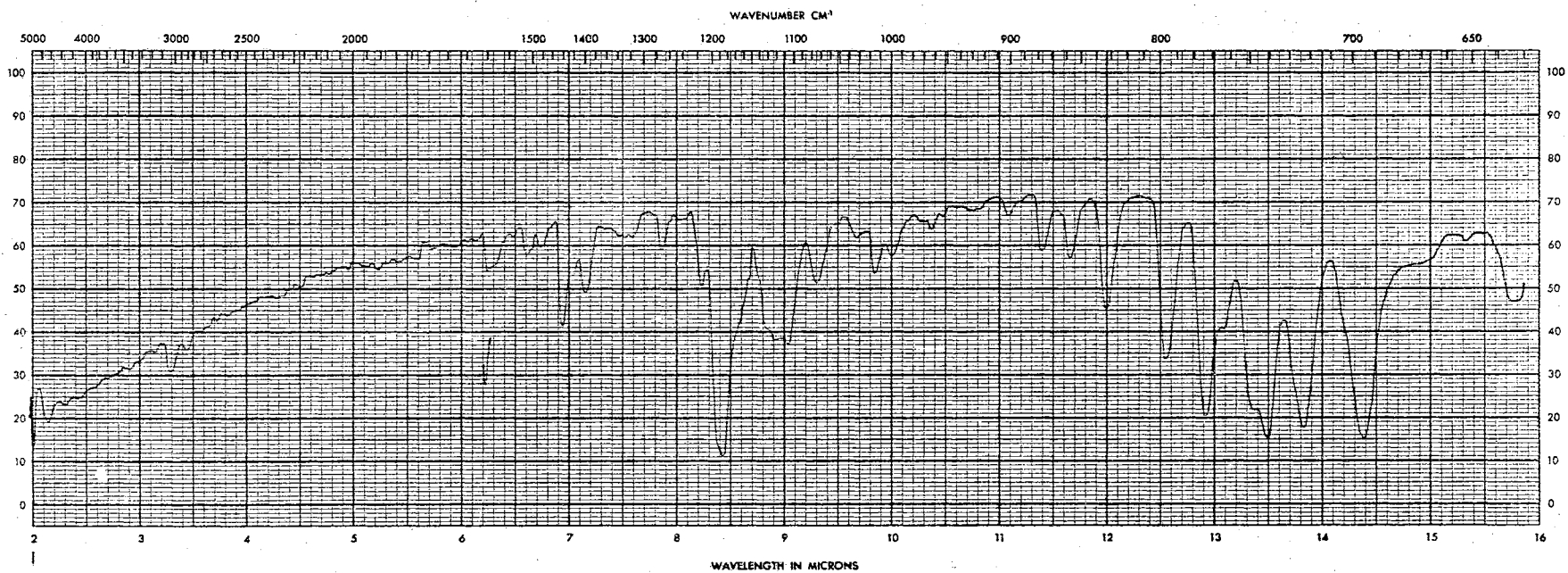
Found: C, 74.25; H, 6.14; P, 12.78.

The nuclear magnetic resonance spectrum (plate VIII) showed a multiplet at δ 7.5 (aromatic protons) and δ 6.5 (vinyl protons) and a

doublet at δ 1.69 (J=6 c.p.s.; methyl protons). The data support the structure as that of diphenyl-1-propenylphosphine oxide.

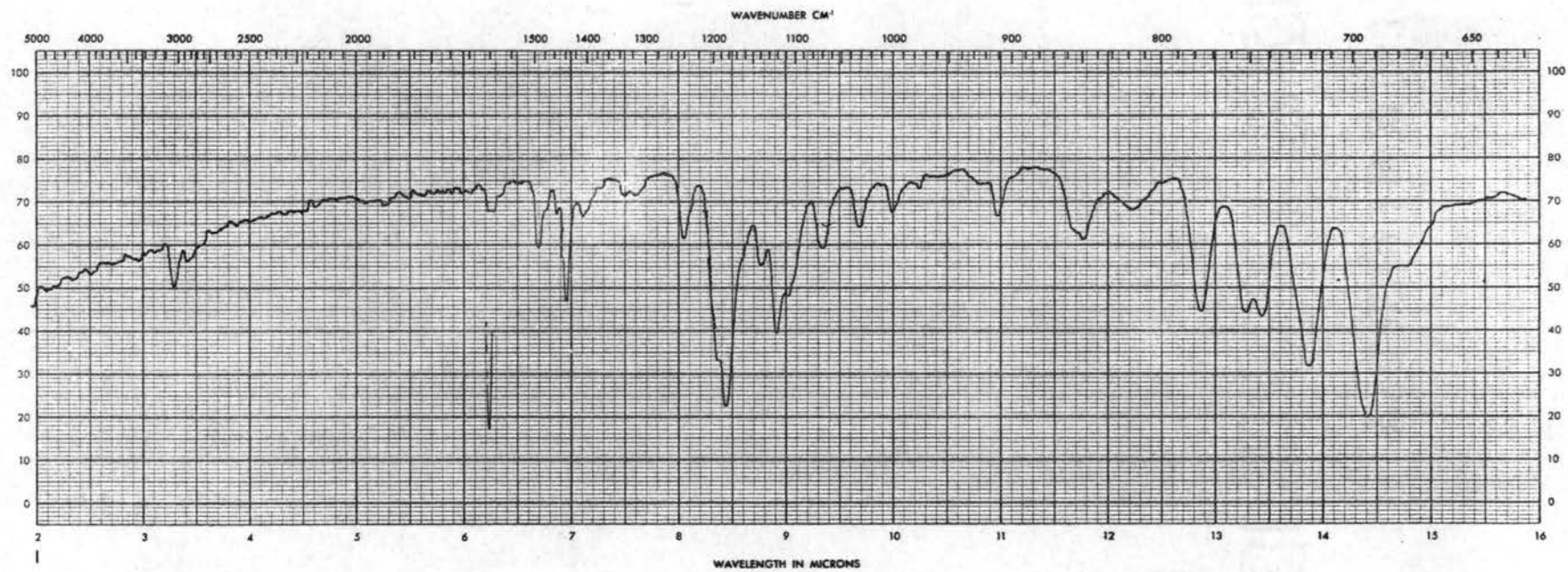
Hydrogenation of Diphenyl-1-propenylphosphine Oxide (XXVI). The same apparatus and procedure was used as in the hydrogenation of the allyl compound. White crystals were obtained, 70.4 per cent, m.p. 100-1° (from benzene-Skellysolve F). The mixture melting point with diphenylpropylphosphine oxide (XXIV) was undepressed and the infrared spectra of the two compounds were identical.

Plate I



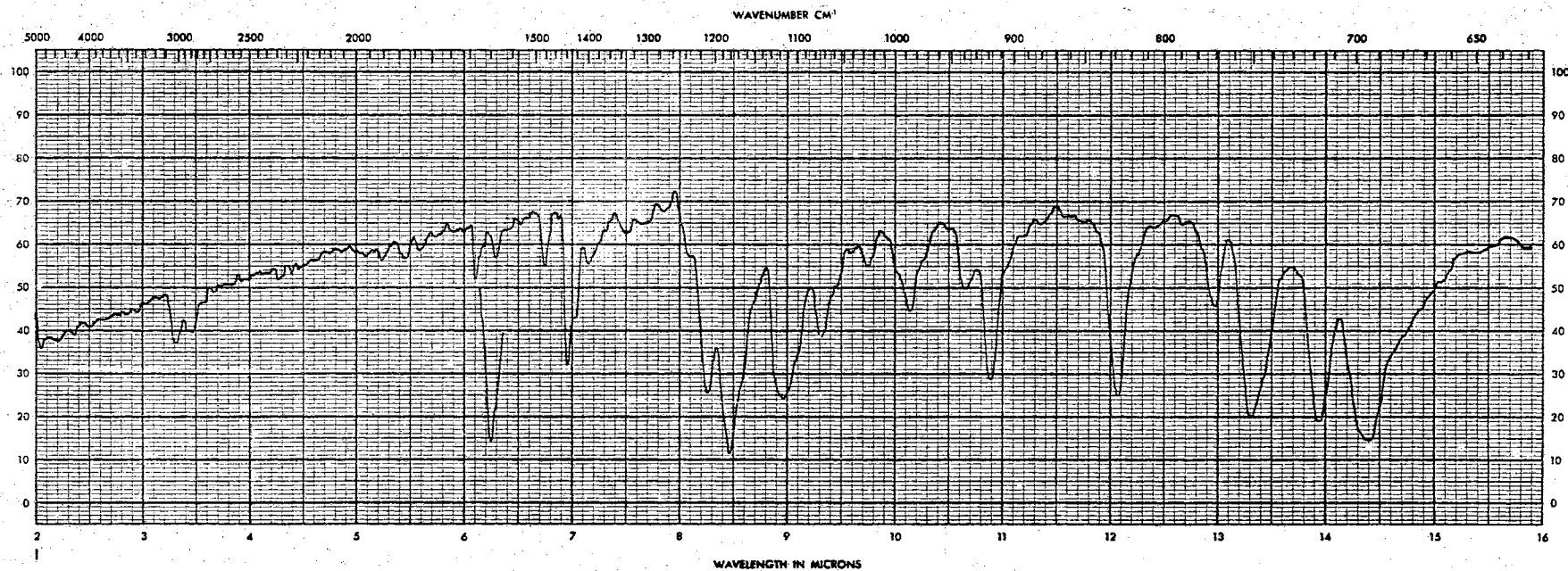
Diphenyl-(1-naphthylmethyl)phosphine Oxide (XXI), KBr Pellet

Plate II



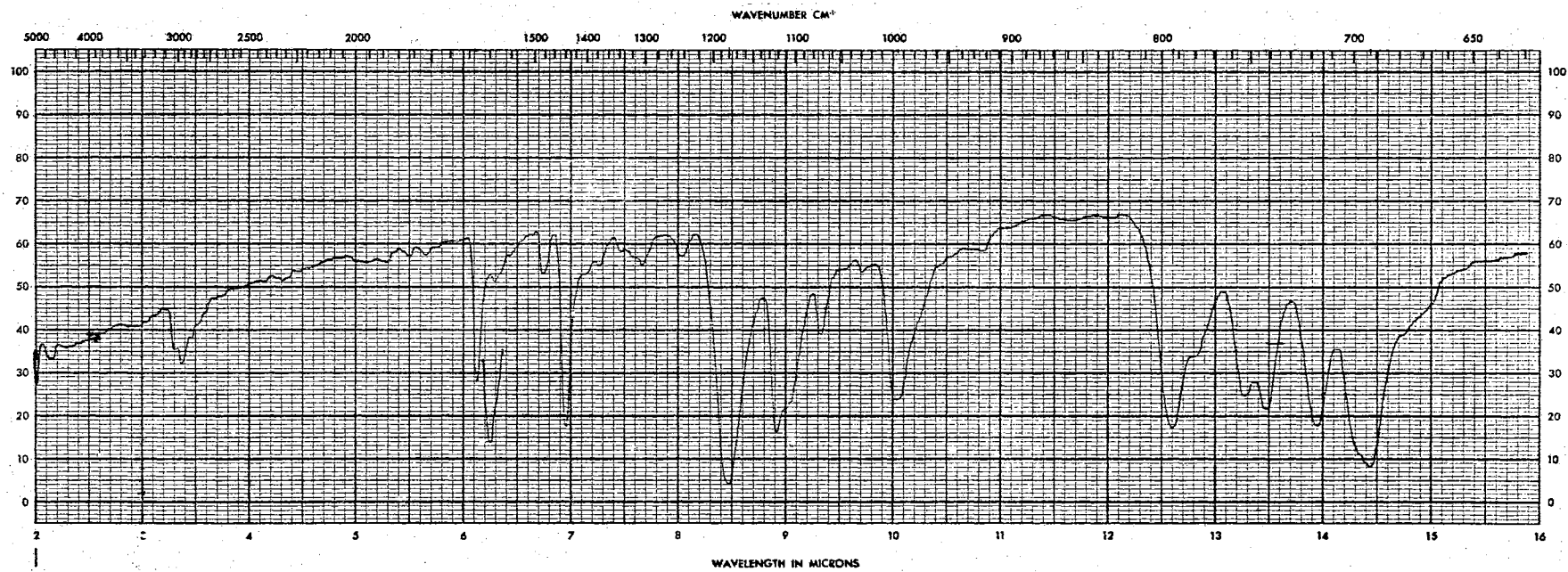
Product of Ring Closure Attempt on XXI, KBr Pellet

Plate III



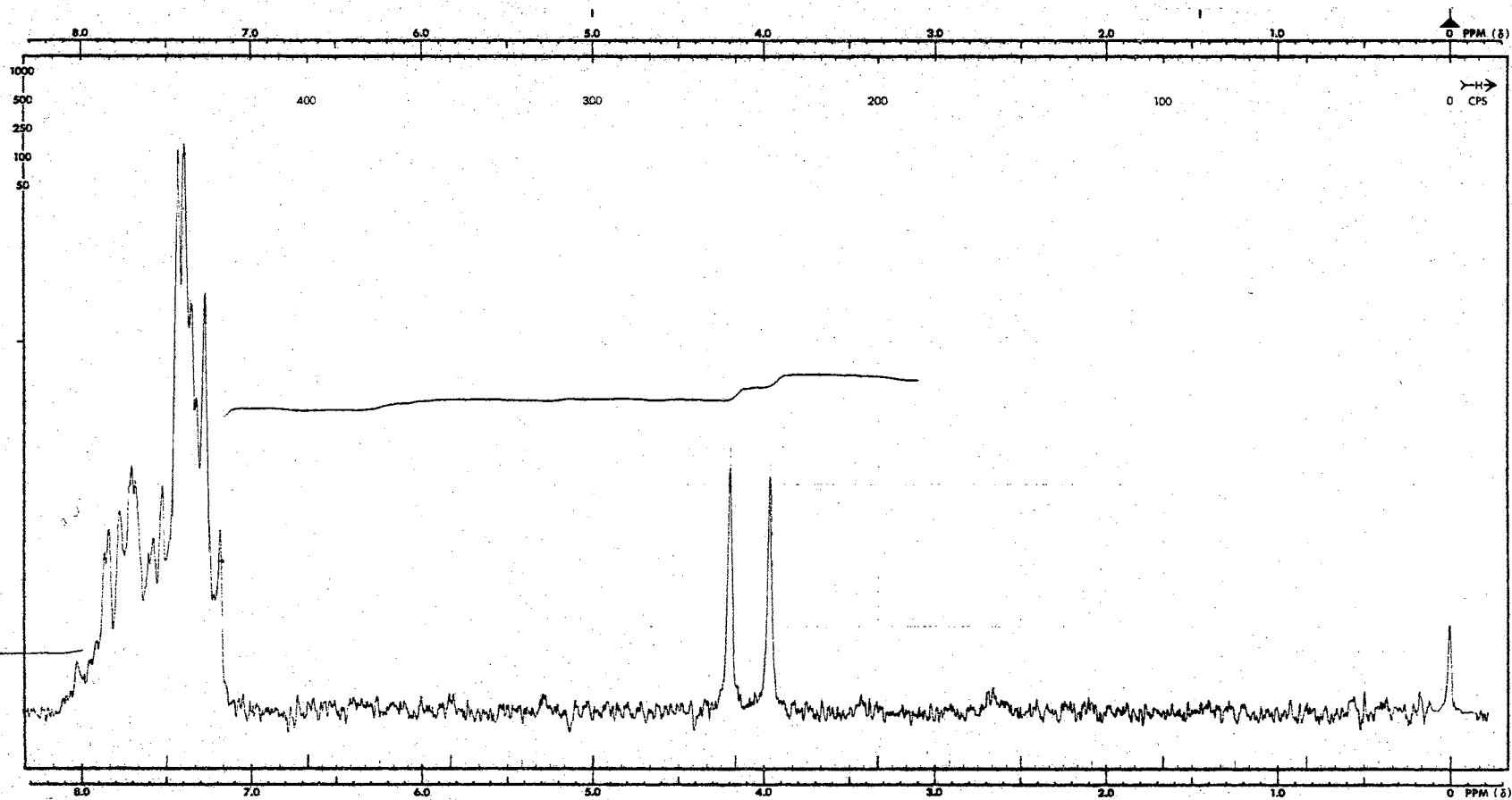
Allyldiphenylphosphine Oxide (XXIII), KBr Pellet

Plate IV



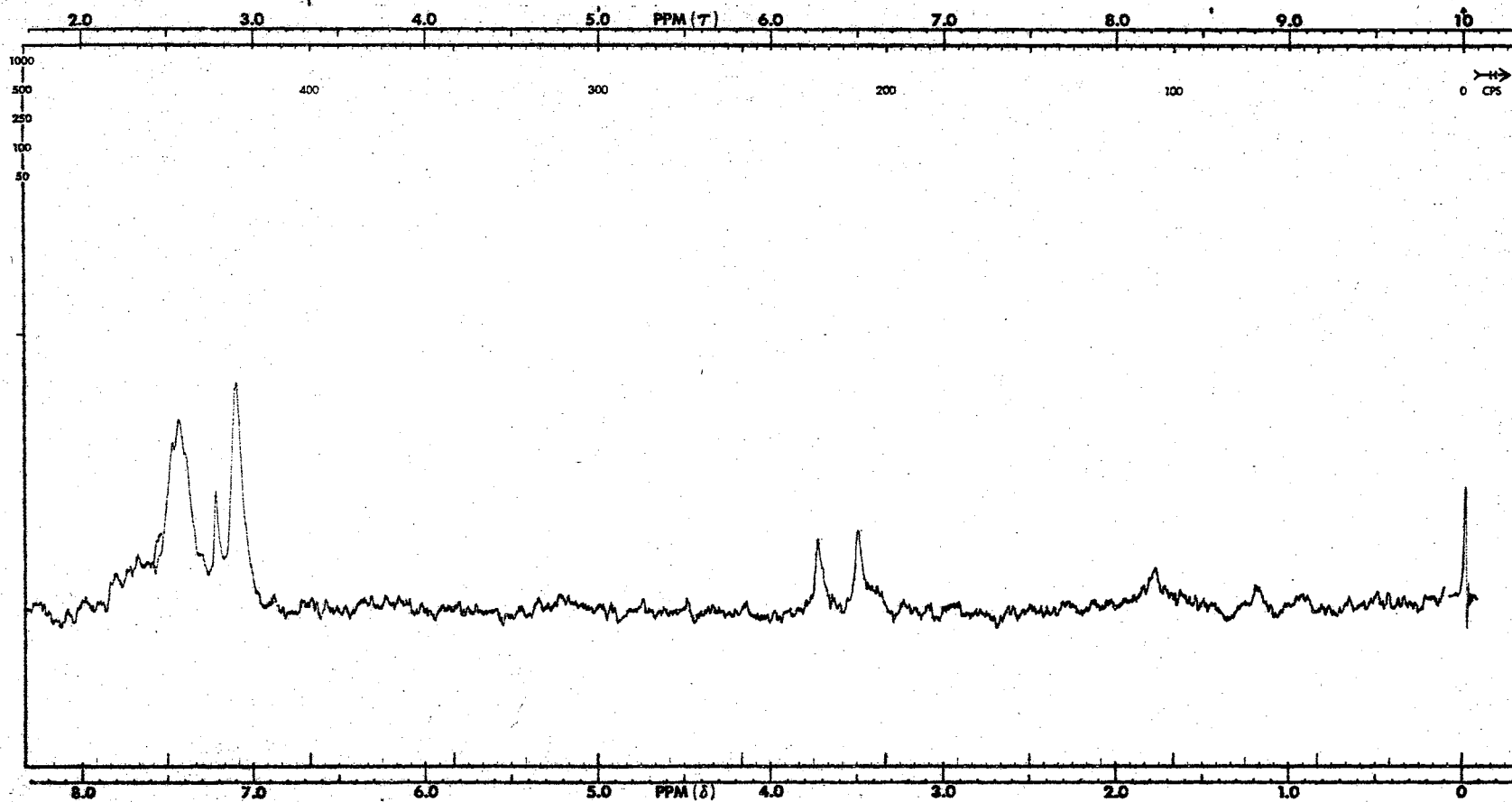
Diphenyl-1-propenylphosphine Oxide (XXVII), KBr Pellet

Plate V



| | | | | | | | | |
|-------------------|-----------------|--|---------------------|--------------|--------------|--------------|--------------|----|
| Solvent | CDCl_3 | Diphenyl-(1-naphthylmethyl)phosphine Oxide (XXI) | R.F.Field | 0.2 mG | S.W. | 500 cps | S.A. | 20 |
| F.B. | 1.0 cps | S.T. | 250 sec | S.O. | 000 cps | I.A. | 16 | |

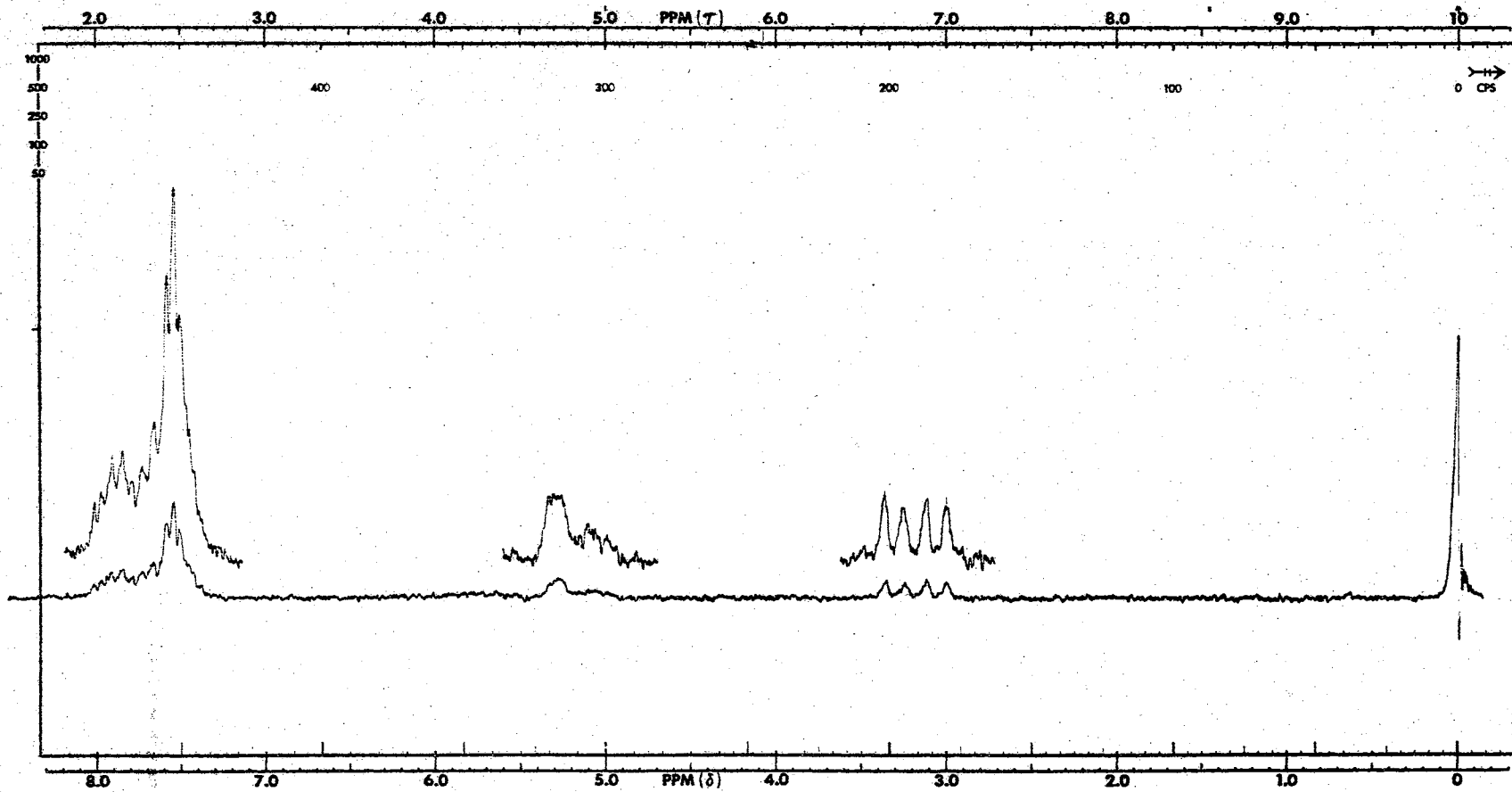
Plate VI



Product of Ring Closure Attempt on XXI

| | | | |
|------------------------------------|------------------------------|----------------------|------------------|
| Solvent CCl ₄ | R.F. Field 0.15 mG | S.W. 500 cps | S.A. 100 |
| F.B. 0.10 cps | S.T. 500 sec | S.O. 000 cps | I.A. off |

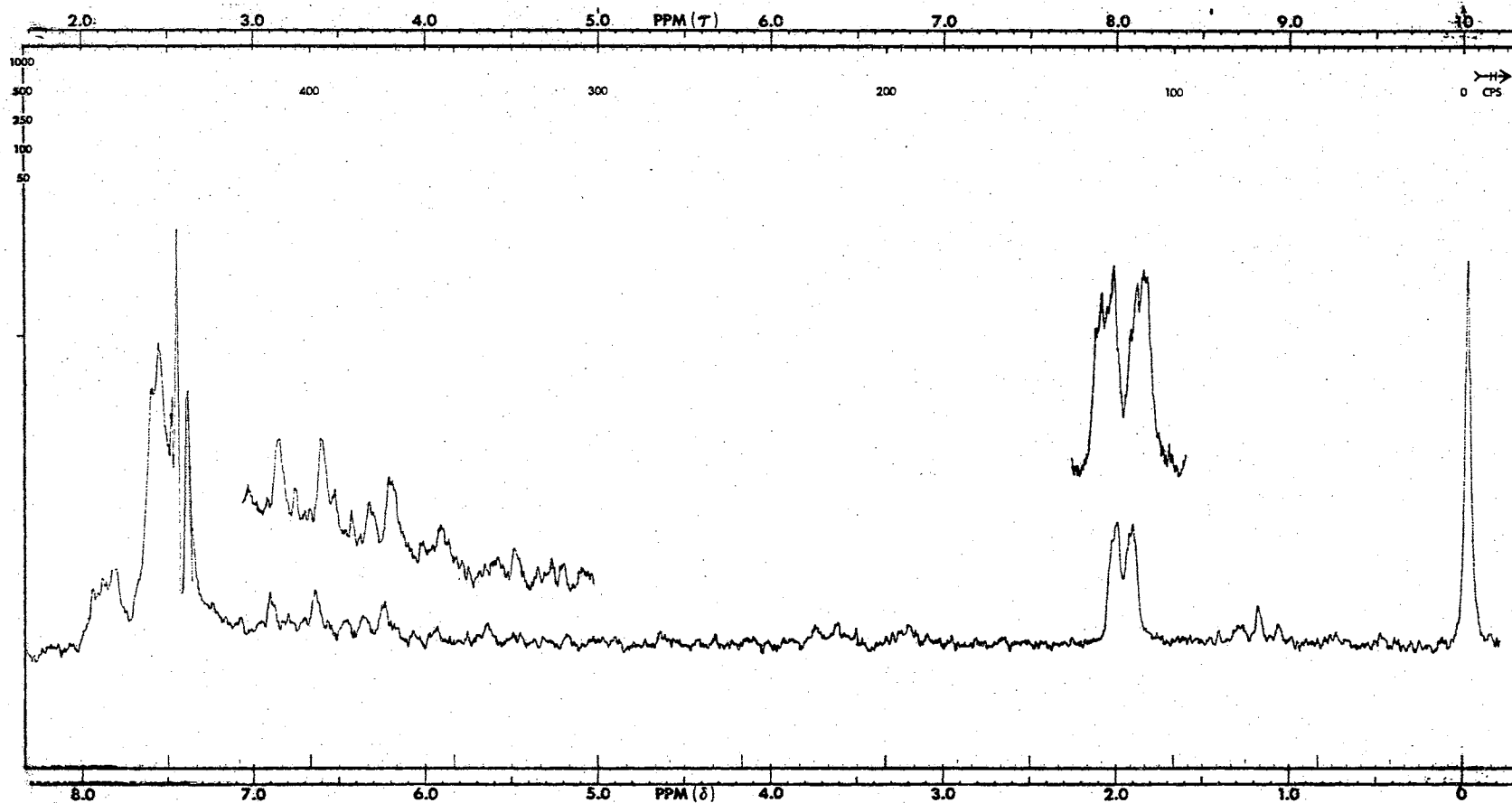
Plate VII



Allyldiphenylphosphine Oxide (XXIII)

| | | | | | | | |
|-------------------|-----------------|----------------------|---------|--------------|---------|--------------|-----|
| Solvent | CDCl_3 | R.F. Field | 0.2 mG | S.W. | 500 cps | S.A. | 3.2 |
| F.B. | 2.0 cps | S.T. | 250 sec | S.O. | 000 cps | I.A. | off |

Plate VIII



Diphenyl-1-propenylphosphine Oxide (XXVII)

| | | | | | | | |
|-------------------|-----------------|----------------------|---------|----------------|---------|----------------|-----|
| Solvent | CHCl_3 | R.F. Field | 0.2 mG | S.W. | 500 cps | S.A. | 16 |
| F.B. | 0.4 cps | S.T. | 250 sec | S.O. | 000 cps | I.A. | off |

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