

- I. A STUDY OF THE NUCLEOPHILIC DISPLACEMENT REACTION ON TRIMETHYL
PHOSPHITE BY PHENYL GRIGNARD REAGENT
- II. THE PYROLYTIC DECOMPOSITION OF ALKYL DIPHENYLPHOSPHINATES --
AN OLEFIN FORMING ELIMINATION REACTION

By

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INTRODUCTION

The difference in the nature of these two investigations has required a division of the thesis into two sections. Each part is complete with its own historical introduction, discussion of results, experimental section, and bibliography.

The first section deals with the reactions of trimethyl phosphite with phenyl Grignard reagent. The results and conclusions which are discussed provide the only definitive study of this subject which has been recorded.

The second section of this thesis, which considers the pyrolytic decomposition of some alkyl diphenylphosphinates, was made possible by a novel observation during the routine preparation of several esters of diphenylphosphinic acid, a relatively rare class of compounds. Although the pyrolysis of acetates is well documented, this report represents the only attempt recorded to promote this same type of decomposition in a structurally similar phosphorus ester.

PART I

A STUDY OF THE NUCLEOPHILIC DISPLACEMENT REACTION ON TRIMETHYL
PHOSPHITE BY PHENYL GRIGNARD REAGENT

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CHAPTER I

HISTORICAL

The Reactions of Trivalent Esters of Phosphorus

Acids with Grignard Reagents

Those nucleophilic displacement reactions involving attack on a trivalent phosphorus atom which have been reported deal primarily with reactions of phosphorus halides (17). Prior to 1950, very little work had been recorded on the condensations of esters of trivalent phosphorus acids with organometallic reagents (59).

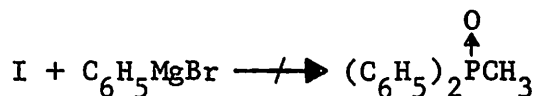
In 1926, Gilman and Vernon (34) stated that the reaction of triphenyl phosphite with an excess of the phenyl Grignard reagent gave triphenylphosphine (60 per cent) and phenol (68 per cent). Although



the experimental details are somewhat sketchy, the results are not unreasonable. Since a rigorous analysis of the reaction mixture was not made, other products could understandably be lost during crystallization. With an excess of the Grignard reagent, nearly quantitative yields of the products shown would necessarily have been expected.

Shortly thereafter, in 1929, Gilman and Robinson (33) showed that when trimethyl phosphite (I) was condensed with phenyl Grignard reagent (a slight excess; ca. 0.9 mole vs. 0.3 mole of ester), diphenylmethyl-

phosphine oxide was produced (42 per cent). Although this seems very unusual since it would involve a rearrangement or isomerization during



the reaction sequence, the authors accepted the result with a reminder that one of the reaction intermediates, namely methyl diphenylphosphinite, had been shown to give this same oxide (4). In the same article, it

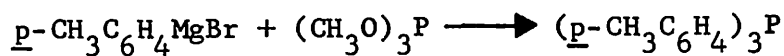


was reported that when triethyl phosphite (0.2 mole) reacted with 0.57 mole of the phenyl Grignard reagent, triphenylphosphine oxide was obtained after hydrolysis although in low yield (10 per cent).



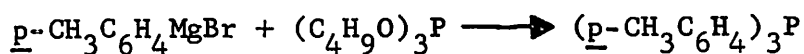
These two reactions of similar reagents under similar reaction conditions seem to give very different products. No data concerning this apparent discrepancy has appeared for several years.

Because of a need for compounds similar to those reported as a result of the condensation of trimethyl phosphite and the phenyl Grignard reagent, Morgan and Herr (72) repeated some of the reactions described above. They were unable to obtain diphenylmethylphosphine oxide under the conditions used. When trimethyl phosphite was added to p-tolyl Grignard reagent, tri-p-tolylphosphine (37.4 per cent) was isolated. With a reverse addition process (Grignard reagent added to



the phosphite), tri-p-tolylphosphine (41 per cent) was also isolated. In both cases the molar ratio of Grignard reagent to trimethyl phosphite was 3:1.

When a 4:1 ratio of p-tolyl Grignard reagent to tributyl phosphite was used, tri-p-tolylphosphine (16 per cent) resulted. Under conditions



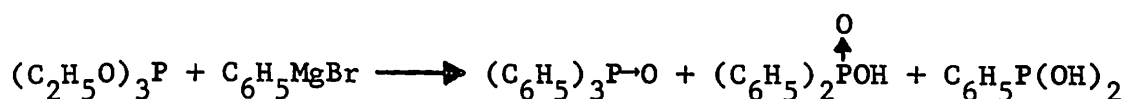
similar to those reported by Gilman and Robinson, Morgan and Herr were able to isolate only triphenylphosphine. Even when variations of concentration and mode of addition were examined, the authors (72) were still unable to obtain the reported diphenylmethylphosphine oxide. They concluded (72) that a reasonable interpretation of the early work (33) was possible only if dimethyl methylphosphonate (3) (product of isomerization of trimethyl phosphite) was a contaminant of the starting material trimethyl phosphite (I). The phosphonate is readily converted to diphenylmethylphosphine oxide (18) by the action of phenyl Grignard reagent.



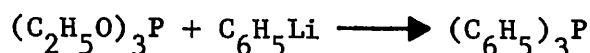
Similarly, when p-tolyl Grignard reagent is condensed with dimethyl methylphosphonate, di-p-tolylmethylphosphine oxide is produced (72).

In a note in 1955, Maguire and Shaw (65) found no diphenylethylphosphine oxide among the products when triethyl phosphite was condensed with phenyl Grignard reagent. Under the conditions which they used,

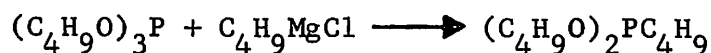
none of the actual intermediate esters were isolated and only the corresponding hydrolysis products (acids) were obtained. Oxidation of the reaction products was also evident as only tetrasubstituted phosphorus compounds were detected. With a 1:1 molar ratio of triethyl phosphite to phenyl Grignard reagent, the final reaction mixture contained triphenylphosphine oxide (14 per cent), diphenylphosphinic acid (7.2 per cent), and phenylphosphonous acid (15.3 per cent) (65). When a 2:1 molar ratio



was employed, triphenylphosphine oxide (10 per cent), diphenylphosphinic acid (20.1 per cent), and phenylphosphonous acid (5.8 per cent) resulted. In a lone report, triethyl phosphite was observed to condense with phenyllithium to give triphenylphosphine in 80 per cent yield (98).

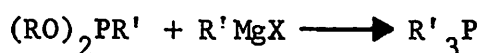


In a more recent study, Sander (86) found that when triethyl phosphite was condensed with several different Grignard reagents, using a 1:1 molar ratio, phosphonites of the type $(\text{C}_2\text{H}_5\text{O})_2\text{PR}$, were the only major products (31-55 per cent). Tributyl phosphite and n-butyl Grignard reagent gave dibutyl butylphosphonite (69 per cent).

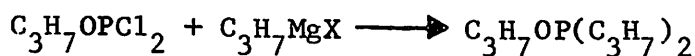


An unsuccessful attempt was made to convert trialkyl phosphites to the corresponding phosphinites by the action of 2 moles of Grignard

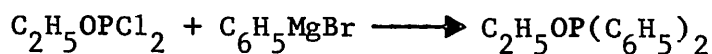
reagent on 1 mole of trialkyl phosphite. If a 2:1 molar ratio of Grignard reagent (ethyl, butyl, phenyl, benzyl) to triethyl phosphite was used in the condensation, tertiary phosphines and diethyl phosphonites were obtained. No double displacement reaction products, namely phosphinite esters, could be found. The author attributed this fact to the high reactivity of the phosphinite ester. As additional evidence for this postulate, one equivalent of Grignard reagent reacted with one equivalent of dialkyl phosphonite (86) to give a 50:50 mixture of tertiary phosphine and dialkyl phosphonite.



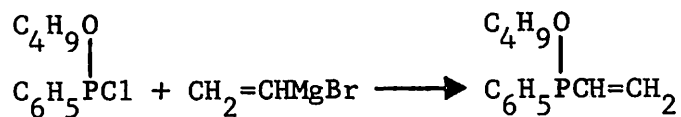
In cases where it is desirable to obtain phosphinite esters via displacement reactions, the use of phosphorodichloridites is usually employed (59). At low temperatures (ca. -60°) moderate yields of phosphinite esters have been obtained by this process. The reaction of n-propyl Grignard reagent with n-propyl phosphorodichloridite produced n-propyl di-n-propylphosphinite (46 per cent) (77).



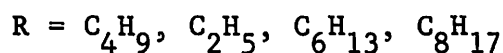
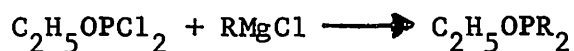
Similar results have been reported in the preparation of ethyl diphenyl-



phosphinite (77) and butyl phenylvinylphosphinite (52).

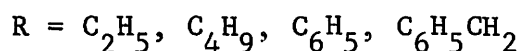
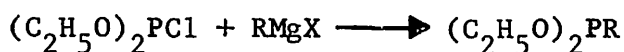


Sander (86) has made a fairly thorough study of the displacement process with certain compounds. Using a 2:1 ratio of Grignard reagent to ethyl phosphorodichloridite, yields ranging from 31-59 per cent of ethyl dialkylphosphinites were obtained. Similar condensations using



aryl Grignard reagents were not as easily controlled and mixtures were obtained with the corresponding tertiary phosphine as the major product (86). The use of phenyl phosphorodichloridite led to the formation of tertiary phosphines regardless of the Grignard reagent employed (86).

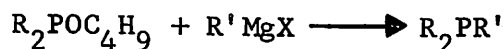
The preparation of phosphonite esters by the action of Grignard reagents is best accomplished using dialkyl phosphorochloridites. Using a 1:1 molar ratio of several Grignard reagents with diethyl phosphorochloridites, Sander (86) synthesized both diethyl alkyl- and aryl-phosphonites in moderate yields (47-63 per cent). These results have



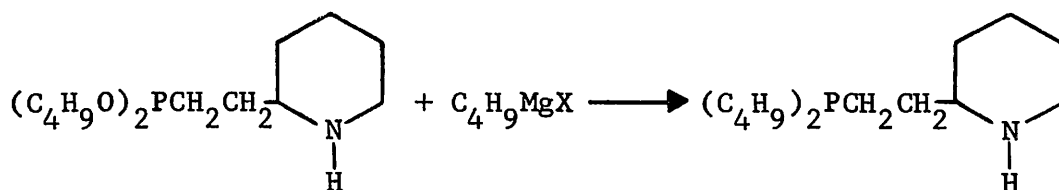
been verified in other reports (83, 95). Diphenyl phosphorochloridite has been used to produce diphenyl phosphonites (49).

Low temperatures have been reported to improve the results of the condensation of Grignard reagents with phosphorochloridites (55). Especially when the Grignard reagent is very reactive, low temperatures are necessary. For example, dibutyl phosphorochloridite was condensed with vinyl Grignard reagent at -60° in tetrahydrofuran to give, in moderate yield, dibutyl vinylphosphonite (51). The yield in this particular reaction was improved by 20 per cent when a reverse addition technique was employed. Other similar condensations have been reported (36, 55).

Condensation reactions of Grignard reagents with phosphinite esters have not received much attention in the literature. In one report several butyl phosphinites (50), (dipropyl, dibutyl, diamyl, and methylphenyl) were condensed with vinyl Grignard reagent to give unsymmetrical tertiary phosphines in high yield (59-82 per cent).



Similar products result from the condensation of Grignard reagents with phosphonite esters. Condensation of n-butyl Grignard reagent with dibutyl 2-(2-piperidyl)ethylphosphonite resulted in formation of di-n-butyl-2-(2-piperidyl)ethylphosphine (53). Dibutyl vinylphosphonite



yielded dibutylvinylphosphine when condensed with butyl Grignard reagent (50).



The use of bifunctional Grignard (87) reagents to produce bis-dialkyl phosphinites results in moderate yields (18-47 per cent) when dialkyl phosphorochlorodites are utilized, but when trialkyl phosphites are employed, the returns are very low (less than 12 per cent). As an example, the bifunctional Grignard reagent of 1,4-dibromobutane was condensed with trimethyl phosphite. The product was isolated in low



I

yield (10 per cent). However, with diethyl phosphorochloridite in the condensation, the yields were improved (maximum of 47 per cent when the



Grignard of 1,6-dibromohexane was employed).

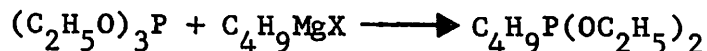
From the results quoted it is quite evident that many parameters control the course of the condensation reactions studied. The concentration of reagents is quite significant. By controlling this single parameter, one can obtain the phosphonite in moderate yield (86) or force the reaction to produce as a major product the tertiary phosphine.

Changes in temperature alter the process remarkably. Sander (86)

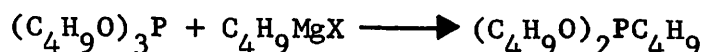
reported that reactions which normally proceed with monodisplacement, can be forced to give higher percentages of the tertiary phosphine by increasing the temperature of reaction alone.

The manner in which the reagents are brought together acutely influences the course of reaction. With active Grignard reagents, e.g. the benzyl reagent, and triethyl phosphite an inverse addition is required to limit the process to produce only the diethyl benzylphosphonite.

Likewise, the nature of the organic halide used to prepare the Grignard reagent markedly affects the yields in some cases. Triethyl phosphite with the butyl Grignard reagent from butyl chloride gives a 31 per cent yield of diethyl butylphosphonite when a 1:1 ratio is used (86). Similarly with the butyl Grignard made from butyl bromide, a 54 per cent yield is obtained (86).



Large differences in yields also result from changes in the nature of the phosphite. When triethyl phosphite is condensed with the butyl Grignard from butyl chloride using a 1:1 ratio, diethyl butylphosphonite is obtained (31 per cent). Tributyl phosphite gives dibutyl butylphosphonite (69 per cent) when treated similarly (86).

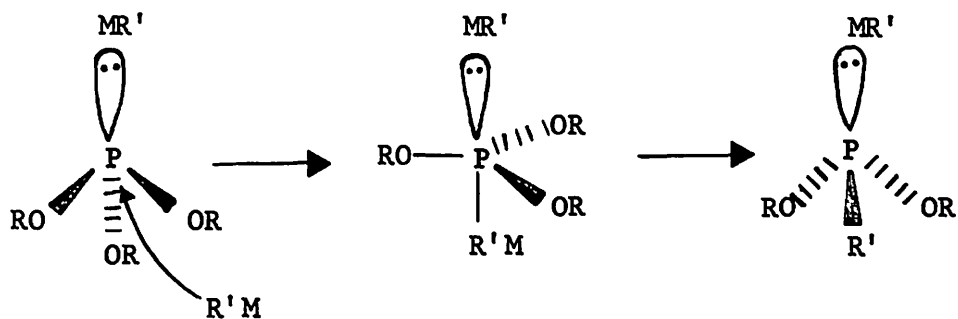


Since only meager data is available, more work must necessarily be done before some of these factors can be evaluated fully. A study of

the condensation reactions of mixed phosphites containing both alkoxy and aryloxy groups would be very rewarding in this respect. The effect of the leaving group (alkoxy vs. aryloxy) might possibly give information concerning the change in reactivity in a particular series of phosphites. As yet, little information is available to check the actual reactivity of the different trivalent esters in a particular series. A lone report (86) indicates that the phosphinites are the most reactive species in the series of phosphorus esters.

That complex formation is possible has been implied, but this area is especially in need of further study. Certainly the Grignard reagent in most of these reactions is not completely free to react. Stoichiometric quantities lead to only moderate conversions even under drastic conditions (33, 34, 72). Sander (86) stated that with alkyl compounds the order of stability of complexes with magnesium bromide is $R_3P > R_2POR' > RP(OR')_2 > P(OR')_3$. But whether this series holds for all types of phosphites, phosphonites, phosphinites, and phosphines is a moot question.

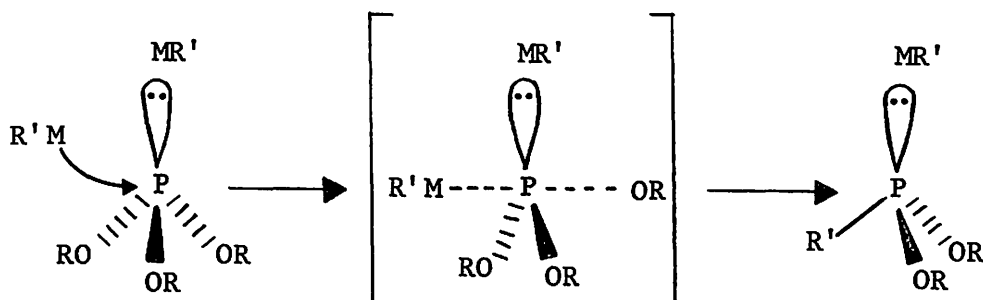
The actual mechanism of the reaction of phosphites and other trivalent esters with Grignard reagents has also not been investigated extensively. It seems plausible that initial complexing of the phosphite should activate the ester toward displacement since the bond angle is increased from trigonal to near tetrahedral (18). At any rate, the anionic nature of the Grignard reagent would seem to prohibit anything other than a backside attack on a trivalent phosphorus atom. It is possible that as the Grignard species attacks, it forms a transient intermediate involving a bipyramidal structure which collapses with expulsion of an OR anion.



R'M = Grignard Reagent

If this is the case, the angle of the attacking species and the leaving group would be 90° . This would involve a phosphorus atom with five bonds but 3d orbitals are available and this would be permissible (37).

It is also plausible that the reaction is a classical S_N2 process in which bond formation and bond cleavage is a concerted process. The angle of the attacking group and the leaving group in this case would be 180° . Work in this area should clear up these problems as well as



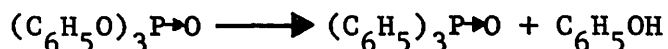
R'M = Grignard Reagent

other more subtle questions.

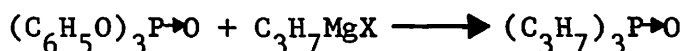
The Reaction of Tetrasubstituted Esters of Phosphorus

Acids with Grignard Reagents

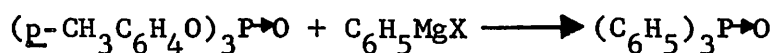
The literature records no definitive study on the condensation reaction of Grignard reagents and trialkyl or triaryl phosphates. Gilman and Vernon (34) reported triphenylphosphine oxide (17 per cent) and phenol (42 per cent) to be products when triphenyl phosphate was condensed with phenyl Grignard reagent (4:1 molar ratio).



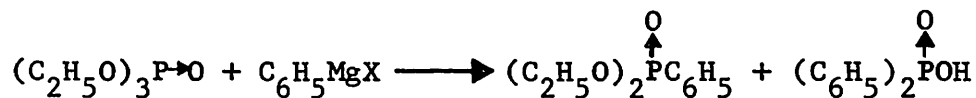
No reaction occurred when n-propyl Grignard reagent was boiled six hours in ether with triphenyl phosphate, although tri-n-propylphosphine oxide was obtained upon heating the propyl Grignard reagent with triphenyl phosphate at 95° in ether-toluene (34). Tri-p-tolyl phosphate gave an



uncharacterizable compound when treated with benzyl Grignard reagent while with phenyl Grignard reagent, triphenylphosphine oxide (50 per cent) resulted (34).

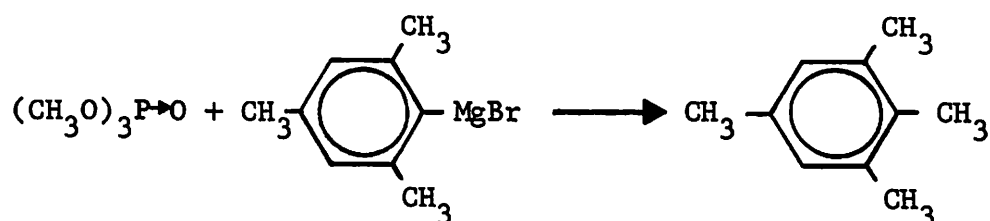


Triethyl phosphate, when condensed with phenyl Grignard reagent (33), was converted to diethyl phenylphosphonate (16 per cent) and diphenyl phosphinic acid (17 per cent). Trimethyl phosphate and an



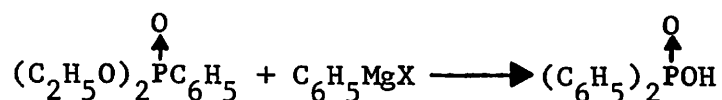
excess of phenyl Grignard reagent produced a complex mixture with triphenylphosphine oxide a minor product. When a 1:1 molar ratio was employed, no triphenylphosphine oxide was detected (19).

Trimethyl phosphate and mesityl Grignard reagent led mainly to alkylation of the mesityl radical producing 1,2,3,5-tetramethylbenzene

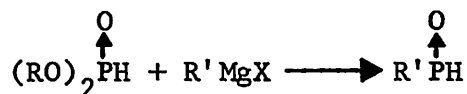


(35), evidently as a result of steric hindrance.

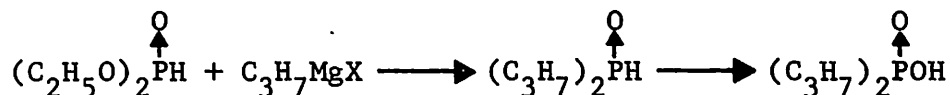
Reactions of Grignard reagents with substituted phosphonates are quite numerous but no systematic study has been published (59). Diethyl phenylphosphonate, in reaction with phenyl Grignard reagent, gave diphenylphosphinic acid (32 per cent) after hydrolysis, but no triphenyl-



phosphine oxide (58). This seems anomalous since the conditions of the reaction were quite strenuous. It is possible that insufficient Grignard reagent was present. Dawson and Burger (27) found that complexing of diethyl phenylphosphonate with magnesium bromide prior to the addition of phenyl Grignard reagent resulted in the formation of

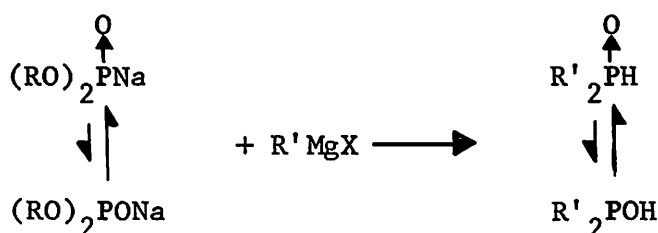


Diethyl hydrogenphosphonate with n-propyl Grignard reagent gave, after



oxidation, di-n-propylphosphinic acid (55 per cent) whereas with n-butyl Grignard reagent, di-n-butylphosphinic acid (72 per cent) was isolated (63). Di-n-butyl hydrogenphosphonate (99) similarly reacted with the appropriate Grignard reagent to give di-n-hexylphosphine oxide (29 per cent), di-n-octylphosphine oxide (70 per cent), and di-octadecylphosphine oxide (26 per cent).

Sodium salts of the dialkyl hydrogenphosphonates behave as expected with Grignard reagents to give secondary phosphine oxides (76). Yields in this case are 60 to 70 per cent. The equilibrium shown in the equation

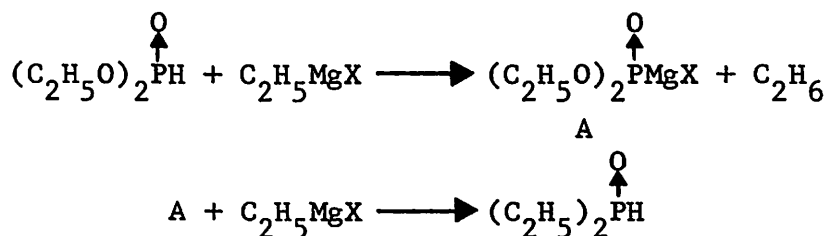


has been shown to exist; the equilibrium mixture is composed chiefly of the unsymmetrical phosphine oxide rather than the di-substituted phosphinous acid (45).

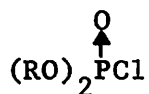
If ethyl Grignard reagent is added to diethyl hydrogenphosphonate, an equivalent amount of ethane is produced to form the salt of the phosphonate. A second and a third equivalent of the Grignard reagent

readily convert this material to the halomagnesium salt of the diethylphosphine oxide (78). Exclusive formation of the salt prior to condensation is facilitated by an inverse addition (Grignard reagent added to the phosphonate).

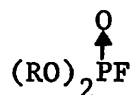
In instances where it is desirable to obtain products in which



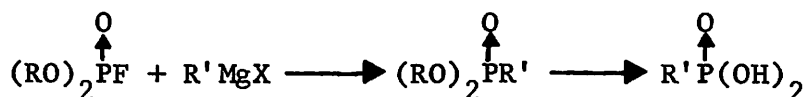
single displacement or double displacement have occurred, normal tetra-substituted esters give poor results. However, substituted phosphoro-



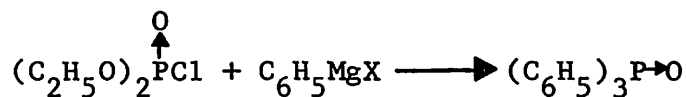
chloridates and dichloridates can be utilized to give the desired material. An even better method is the use of alkyl or aryl phosphoro-



fluoridates (90, 91). By using properly substituted phosphorofluoridates, and the appropriate Grignard reagent, yields as high as 61 per cent of the corresponding phosphonate have been realized. These esters can

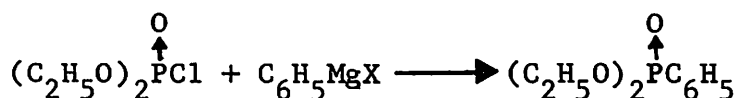


readily be hydrolyzed to the corresponding phosphonic acids. Although the reaction above is possible to accomplish in boiling ether, the corresponding process using diethyl phosphorocloridate and phenyl

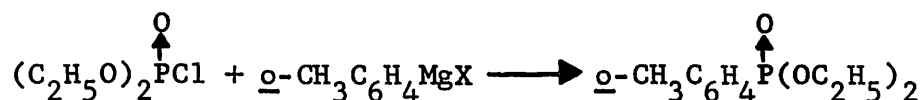


Grignard reagent yields triphenylphosphine oxide at temperatures above 0° (26). The reaction of the n-butyl Grignard reagent with n-amyl phosphorodichloridate yields n-amyl di-n-butylphosphinate (75).

At ice-bath temperatures the reaction of dialkyl phosphorochloridates with aryl Grignard reagents can be controlled and moderate yields



(26-55 per cent) of dialkyl phosphonates obtained. However, at room temperature or above, displacement of OR group also occurs unless the Grignard reagent is prepared from an aryl halide containing an ortho



substituent (26). Phenyl phosphorodichloridate has been reported to give triphenylphosphine oxide when treated with a sufficient quantity of phenyl Grignard reagent (70).

In the conversion of diethyl phosphorochloridate to triphenylphosphine oxide with phenyl Grignard reagent, it seems reasonable to assume that diethyl phenylphosphonate is an intermediate reactant (27). This ester, however, was not converted by phenyl Grignard reagent even under severe conditions (58). Nevertheless, the conversion of the phosphorochloridate to triphenylphosphine oxide is quite easily achieved (27). It is also important to note that diethyl phenylphosphonate is

converted to triphenylphosphine oxide if magnesium bromide is used to complex the reagent prior to the addition of the Grignard reagent (27). Work in progress in this laboratory should shortly result in elucidation of several questions concerning the actual displacement process.

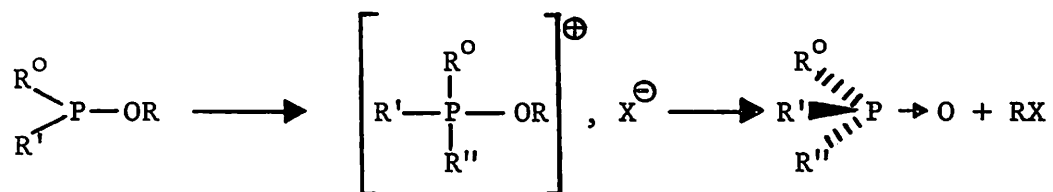
The Michaelis-Arbuzov Rearrangement

Because an early report on the reaction of trimethyl phosphite with phenyl Grignard reagent (33) implies that a Michaelis-Arbuzov type rearrangement might be operative, a short discussion of this rearrangement follows. This is a brief survey and is not complete but a recent review is available (41).

The reaction under discussion was discovered by Michaelis and Kaehne in 1898 (68), further explored by Arbuzov (3), and has been studied extensively by numerous workers since the pioneering efforts. It has been reviewed on several occasions (24, 41, 59, 60, 89) and is probably the most well studied, highly documented, and best understood area of organophosphorus chemistry.

In general, the reaction involves the conversion of a trivalent phosphorus ester to a tetrasubstituted phosphorus compound with formation of a new carbon-phosphorus bond. The ester can be a phosphite (4), a phosphonite (4), or a phosphinite (4) and the ester moiety may be either aryl (5) or alkyl (4). The reaction is initiated by primary or secondary alkyl halides (3) and by acyl (54) and aroyl (21) halides. Aryl and vinyl halides are not effective in promoting the conversion (38). Difficulty is encountered when the ester is derived from a tertiary alcohol (41) or a phenol containing other than electron-withdrawing groups (5).

The reaction has been pictured as involving a nucleophilic attack by phosphorus on the halide giving a quasi-phosphonium salt as an



intermediate. Subsequent collapse of the salt with concomitant expulsion of one mole of organic halide gives the product.

When an examination was made of the reaction of methyl iodide with mixed phosphites, it was found that the ease with which the R group was displaced increased in the series isopropyl, ethyl, and methyl (64). In two series, the relative reactivity of the phosphorus esters have been studied. Ethyl diethylphosphinite is more reactive than diethyl ethylphosphonite, each in turn is more reactive than trimethyl phosphite (81, 82, 84). In another report (4) it was found that ethyl diphenylphosphinite was more reactive than diethyl phenylphosphonite. This latter ester was more reactive than triethyl phosphite in reactions with organic halides. The relative reactivity of the halides involved is generally considered to be iodide > bromide > chloride (41). Fluorides do not undergo the reaction under normal conditions (38).

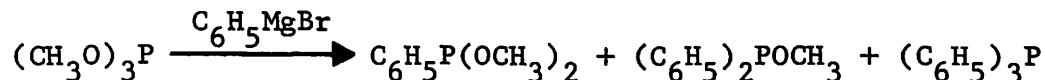
Although most of the literature concerning the mechanism of this reaction has been covered by the most recent review (41), one report published later should be mentioned (1). Kinetic data indicates that contrary to previous findings (22) the first step (formation of the phosphonium intermediate) is rate-determining in the reactions of ethyl diphenylphosphinite, diethyl phenylphosphonite, and triethyl phosphite with ethyl iodide. All of these reactions exhibited first-order kinetics

whereas second-order kinetics were observed for the formation of the stable phosphonium compound from triphenylphosphine and ethyl iodide (1). It was also found that the reaction was influenced by the dielectric constant of the reaction medium.

CHAPTER II

DISCUSSION OF RESULTS AND CONCLUSIONS

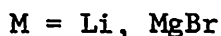
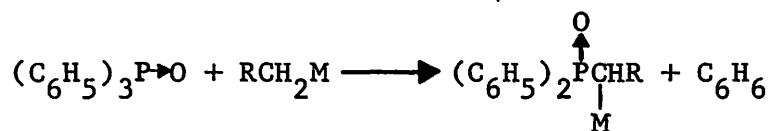
The condensations of trimethyl phosphite with phenyl Grignard reagent was studied in which the molar ratio of Grignard reagent to trimethyl phosphite was varied from 1:1 to 7:1. With an excess of Grignard reagent (4:1 or more), triphenylphosphine was obtained in quantitative yield. Triphenylphosphine, methyl diphenylphosphinite, and dimethyl phenylphosphonite were detected in relative molar ratios of 1:1.2:2.3 when a 1:1 ratio of the starting reagents was employed.



In Table VII it is evident from a large number of experiments that displacement of methoxy groups from trimethyl phosphite is stepwise in nature. Evaluation of the conversions of trimethyl phosphite to the corresponding phosphonite, phosphinite, and phosphine by phenyl Grignard reagent clearly shows the reaction has a marked dependence on: concentration of reactants, mode of combining the reactants, and the addition time. From this data the mechanism is postulated to involve initial formation of a soluble Grignard-phosphite complex. On the basis of the ultraviolet spectrum of triphenylphosphine (46, 47), and from chemical evidence, the stability of the complexes is postulated to increase in the order $(\text{C}_6\text{H}_5)_3\text{P} < (\text{C}_6\text{H}_5)_2\text{POCH}_3 < \text{C}_6\text{H}_5\text{P}(\text{OCH}_3)_2 < \text{P}(\text{OCH}_3)_3$.

It is assumed that competition between the intermediate esters for the Grignard reagent is operative and according to the above order of stability, the phosphonite and phosphite esters bind the Grignard reagent much more effectively. This is based on the fact that when trimethyl phosphite is added to the phenyl Grignard reagent (1:1) in a reverse addition, only dimethyl phenylphosphonite is obtained (41 per cent). It is also postulated that attack occurs on the complex, the geometry of which may include a phosphorus atom with groups attached in a near tetragonal arrangement.

Complexing is known to occur with phosphonates (27). Magnesium bromide, when added to an ethereal solution of diethyl phenylphosphonate prior to condensation with the phenyl Grignard reagent, greatly facilitated the reaction. In this laboratory triphenylphosphine oxide was found to complex with phenyl Grignard reagent in ether to give an insoluble species whereas triphenylphosphine under similar circumstances gave no precipitate. This is in agreement with the results of one experiment in which the solid residue (which forms when the reactants are mixed) was worked up separately. Triphenylphosphine oxide, methyl diphenylphosphinate, and dimethyl phenylphosphonate were found in the extract from hydrolysis of the solid. No trivalent species were present and it is postulated that oxidation occurred during workup and the compounds were precipitated as Grignard adducts. Seyferth (94) has shown that under certain conditions alkyl organometallic reagents attack triphenylphosphine oxide to give a phosphorus-containing organometallic reagent and benzene.



Formation of benzene occurred from the action of lithium reagents in ether solutions, but with Grignard reagents higher temperatures were required such as that produced with boiling tetrahydrofuran.

Hydrolysis of the solid residue from the condensation of trimethyl phosphite with phenyl Grignard reagent was extremely exothermic whereas hydrolysis of the supernatant liquid did not result in an appreciable rise in temperature. Under these circumstances, the extract of the solid hydrolyzate contained two compounds which were absent when normal work-up procedures were followed. Diphenylmethylphosphine oxide and methyl methylphenylphosphinate, which is formed by an as yet unknown pathway, were detected in trace quantities.

Several phosphorus compounds were required for this investigation. Some of these materials were obtained commercially while others were prepared by methods obtained from the literature. Most of the compounds were either distilled or recrystallized immediately prior to their use. Table I lists those compounds used, the physical characteristics, the methods used for purification, and references to sources of information. Methyl diphenylphosphinate (18) was apparent unknown and was synthesized by the following reaction sequence. Gas liquid chromatography (g.l.c.)

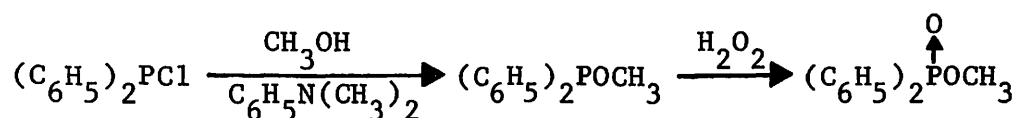


TABLE I
PHYSICAL CHARACTERISTICS OF COMPOUNDS

Compound	B.p. or m.p.:	Literature Value	Literature Reference	Method of Preparation
$(\text{CH}_3\text{O})_3\text{P}^1$	109°/741 mm.	111°/760 mm.	6	
$(\text{CH}_3\text{O})_3\text{P}\rightarrow\text{O}^2$	188°/741 mm.	192°/760 mm.	2	
$\text{CH}_3\text{O}(\text{O})(\text{OCH}_3)_2$	181°/739 mm.	67°/ 12 mm.	10	
$(\text{CH}_3\text{O})_2\text{PC}_6\text{H}_5$	38°/0.95 mm.			
$\text{C}_6\text{H}_5\text{P}(\text{O})(\text{OCH}_3)_2$	84°/2.0 mm.	247°/760 mm.	67	18
$\text{CH}_4\text{OP}(\text{C}_6\text{H}_5)_2$	113°/1.1 mm.	151°/ 10 mm.	7	
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{OCH}_3$	140°/0.35 mm.	140°/0.35 mm.	18	18
$\text{C}_6\text{H}_5(\text{CH}_3\text{P}(\text{O})\text{OCH}_3)$		137°/ 11 mm.	31	
$(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{CH}_3$	111 - 2°	111 - 2°	69	18
$(\text{C}_6\text{H}_5)_3\text{P}^4$	80 - 80.5°	79.5°	29	
$(\text{C}_6\text{H}_5)_3\text{P}\rightarrow\text{O}$	152 - 3°	152 - 3°	56	93
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{H}$		55°/ 10 mm.	11	

¹Appreciation is extended to Dr. W. D. Ebert of Victor Chemical Company and to Dr. E. L. Kubiak of the parent Stauffer Chemical Company for generous supplies of these materials.

²A generous supply of this material was obtained through the courtesy of Ethyl Corporation.

³Appreciation is expressed for a sample of this material obtained from Dr. H. J. Harwood. This compound was used without further purification (g.l.c. indicated one peak).

⁴Triphenylphosphine was obtained commercially.

⁵A sample of this material obtained through the courtesy of Victor Chemical Company was used without further purification (g.l.c. indicated the material to be quite pure).

was used to check the purity of all material immediately prior to their use.

Phenyl Grignard reagent for the condensation reactions was prepared from bromobenzene and magnesium turnings in anhydrous ether, in all cases. Aliquots of the Grignard reagent were withdrawn and titrated (35) immediately prior to its reaction with the phosphorus ester. Filtration of the Grignard reagent through glass wool appeared to remove nearly all excess magnesium.

Commercial nitrogen was dried and deoxygenated before use (96). An anaerobic condition was needed because of the extreme ease with which esters of trivalent phosphorus are oxidized to the tetravalent counterparts (48). In addition the use of anhydrous nitrogen prohibited any possible hydrolysis of the Grignard reagent and the phosphorus esters.

It must be emphasized that during the actual condensation and workup of the reaction, and while the concentrated reaction mixture was stored prior to g.l.c. analysis, a blanket of anhydrous, deoxygenated nitrogen was maintained at all times. Only when this was done was oxidation of the material completely prevented. Buckler (23) states that triphenylphosphine is difficultly oxidized even if oxygen is bubbled through a solution of the compound, but in these reaction mixtures, this oxidation occurs rapidly, especially at higher temperatures.

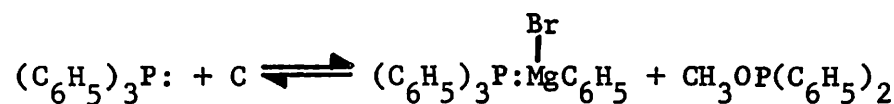
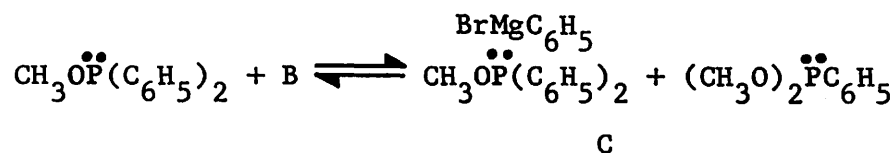
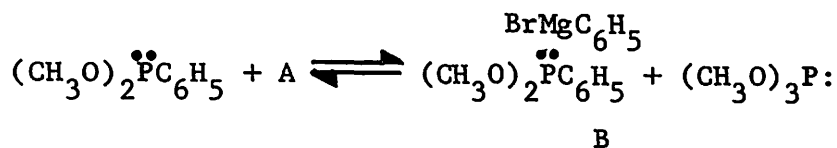
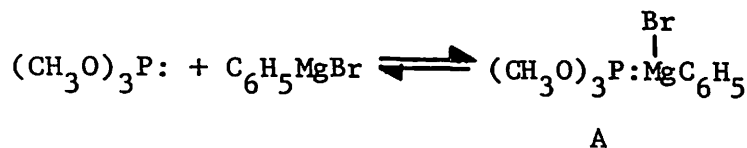
Displacement reactions by Grignard reagents on phosphorus esters have been known for many years (17) but a systematic study had not been

reported prior to this investigation. This problem was examined with emphasis on the molar ratios of products obtained from reactions in which several parameters were varied.

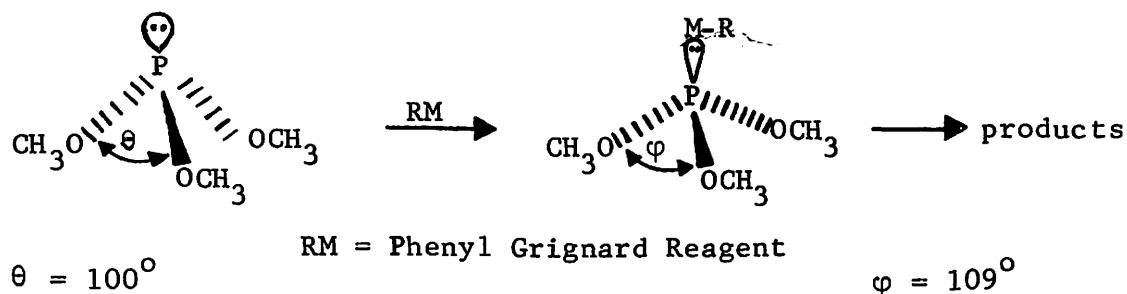
As stated previously, a ratio (1:1) of trimethyl phosphite to phenyl Grignard reagent produced all three displacement products (triphenylphosphine methyl diphenylphosphinite, and dimethyl phenylphosphonite) in relative molar ratios of 1:1.2:2.3 when trimethyl phosphite was added to the Grignard reagent using a 30-minute addition time. The amount of triphenylphosphine was more than doubled when the addition time was increased to 3.5 hours, while the amounts of methyl diphenylphosphinite and dimethyl phenylphosphonite were greatly reduced.

Under normal conditions, the reagent is normally added to the Grignard reagent. However, when the phenyl Grignard reagent was added to the trimethyl phosphite (reverse or inverse addition) while holding all other variables constant only dimethyl phenylphosphonite was obtained. Regardless of the mode of addition, the reaction is extremely exothermic and in the first few seconds of reaction, a white, finely divided material is formed and precipitates. Tests (infrared spectrum and ash content) indicate this material to be inorganic in nature and it is believed to be the magnesium salt (methoxymagnesium bromide). Thus the reaction appears to be driven rapidly to completion by the precipitation of the salt.

The displacement process is envisioned to occur by initial complex formation between trimethyl phosphite and the phenyl Grignard reagent. This is postulated to activate the ester toward nucleophilic attack. Molecular models of trimethyl phosphite indicate the backside of phosphorus to be sterically hindered. Frontal attack by a nucleophile would



be inherently discouraged by the nonbonded orbital on phosphorus. Normal bond angles for the O-P-O bonds are approximately 100° and if complex formation were to occur, the molecule would revert from trigonal to near tetrahedral, thereby increasing the O-P-O angle by approximately 9° . This would result in the activation (increase in positive charge on phosphorus by partial electron transfer) of the molecule and would reduce steric hindrance to backside attack by relief of compressional forces exerted by the nonbonded orbital on the P-O bonds.



The chemical evidence which supports complex formation is as follows. Stoichiometric quantities of reagents never result in products approaching

quantitative yields. On the contrary, a 3:1 ratio of Grignard reagent to trimethyl phosphite gave only 63 per cent of triphenylphosphine (18). This suggests that the Grignard reagent is not completely free to react.

Groups attached to phosphorus which could interfere with the availability of the electrons on phosphorus would be expected to decrease the extent of effective complexing and thereby result in higher yields of products. This has been observed (86). Tributyl phosphite when condensed with the Grignard reagent from butyl chloride gave dibutyl butylphosphonite (69 per cent). Under the same conditions, triethyl phosphite gave only 31 per cent of diethyl butylphosphonite.

Examination of the dipole moments of trialkyl phosphites (8) does not provide the expected information concerning the basic strengths of the different trialkyl esters. Table II shows that there is no marked change in the values as the length of the alkyl group is increased.

TABLE II
DIPOLE MOMENTS-TRIALKYL PHOSPHITES (8)

Compound	Dipole Moment (D)
$(\text{CH}_3\text{O})_3\text{P}$	1.83
$(\text{C}_2\text{H}_5\text{O})_3\text{P}$	1.96
$(\text{C}_3\text{H}_7\text{O})_3\text{P}$	1.99
$(i\text{-C}_3\text{H}_7\text{O})_3\text{P}$	1.98
$(\text{C}_4\text{H}_9\text{O})_3\text{P}$	1.92

Further information concerning the basic strength was provided by a study of the trialkylphosphite-borane adducts (85). These esters have

been shown to be approximately equal in basicity to the corresponding amine (85) in regard to borane as the Lewis acid.

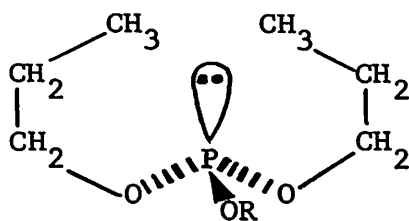


The reaction of the phosphite-borane adduct with methanol-iodine solution gave a measure of the relative bond strength of the P-B bond among the



trialkyl phosphites. In the series $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7$, the rate of oxidation was found to be greatest for triisopropyl phosphite and least for trimethyl phosphite; relative rates were 5.0:2.45:1.2, respectively. The addition of pyridine to the mixture did not change this trend in the series (85). This information indicates that substitution at the alpha carbon destabilizes the adduct in the ground state and apparently causes the complexing ability to decrease in the series $\text{CH}_3 > \text{C}_2\text{H}_5 > i\text{-C}_3\text{H}_7$. This trend in the basic strength is the same as that postulated for the reactivity of trialkyl phosphites to form Grignard-phosphite adducts and lends support to the argument that as the chain length increases, complexing ability decreases.

Several reports have appeared concerning the front strain in trialkyl phosphites. Some of these have presented arguments that the phosphite esters exist with the longer alkyl chains extending up and over the lone pair of electrons on phosphorus (10, 12, 57). Other reports by the same authors disclaim this and suggest that the steric effect is



inappreciable and relatively unimportant (13, 61, 62). Front strain is of major importance with amines and much work has been done concerning the effect of bulky groups on the basicity of substituted amines (73). It is assumed that this is also the case with trialkyl phosphites judging from the work discussed in this dissertation and substantiated by previous arguments (85). It appears that additional data is needed if a logical appraisal is to be made of the situation.

Normal addition of trimethyl phosphite to the Grignard reagent involves the presence of an excess of the latter during most of the addition phase. Since the displacement process is envisioned to be a series of rapid steps, this could result in product formation prior to the time when the majority of Grignard reagent is required for complexing. Very slow addition (3.5 hours) of trimethyl phosphite to the phenyl Grignard reagent substantiates this postulate. Triphenylphosphine is then produced in more than double the quantity than is observed with a rapid addition (30 minutes).

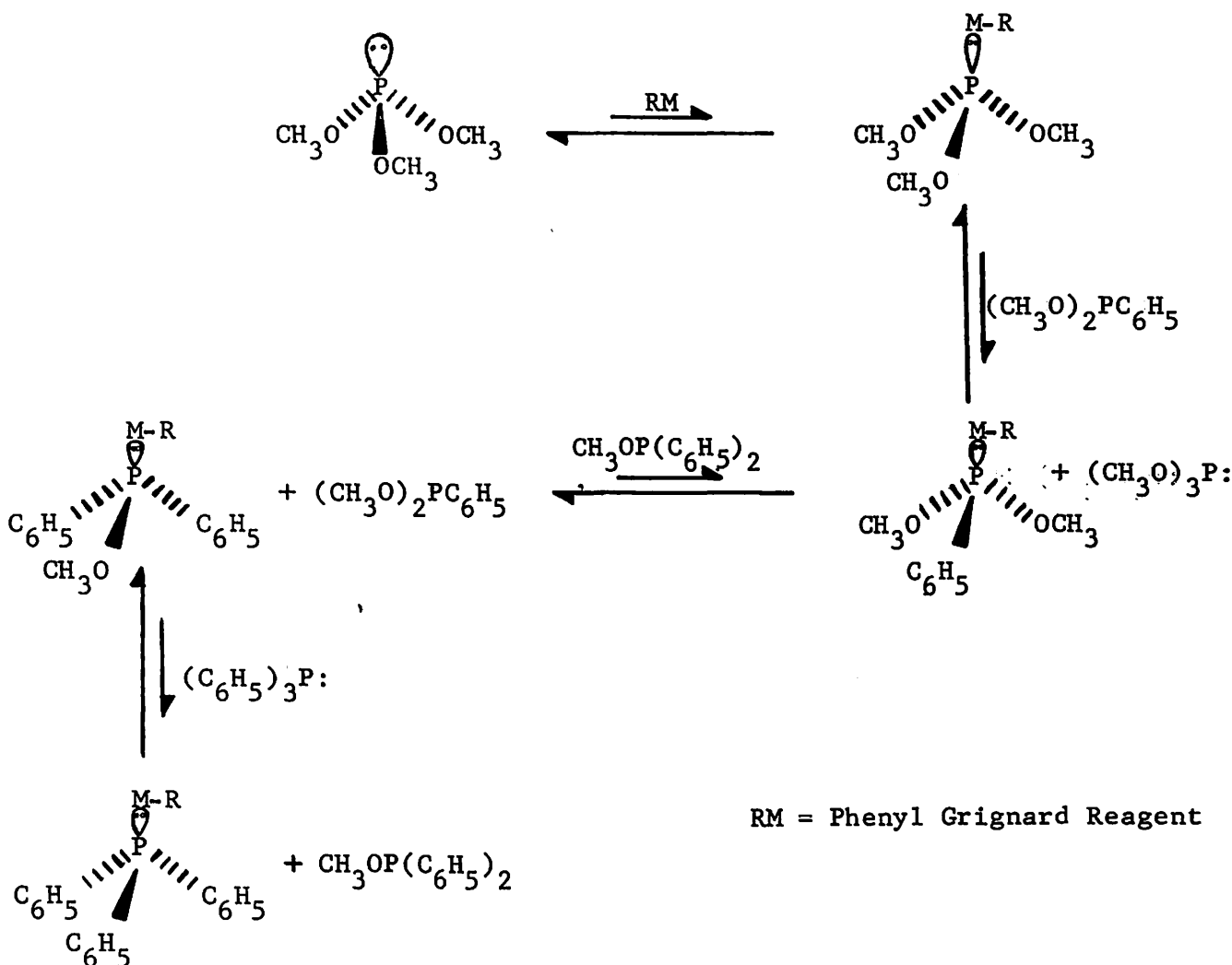
If complex formation does exist, it would be expected that bringing the reactants together in such a way that this excess of phenyl Grignard reagent is never present would greatly curtail at least one or more of the displacement steps. This has been observed. Dimethyl phenylphosphonite (41 per cent) is formed as the only major product when the Grignard reagent is added to trimethyl phosphite. Only a trace of methyl

diphenylphosphinite was detected and no triphenylphosphine was found by g.l.c. It might be tentatively assumed that trimethyl phosphite (I) and dimethyl phenylphosphonite form the more stable complexes of the ester series.

Complex formation has been reported with phosphonates (27). Magnesium bromide was found to improve the yields of phosphine oxides when it was added prior to condensation with the Grignard reagent. A similar complex is postulated for the esters of trivalent phosphorus, in which electron transfer occurs with the lone pair of electrons on phosphorus instead of the nonbonded orbitals of oxygen. It is suggested that the affinity for the magnesium of the organometallic reagent decreases in the order $(\text{CH}_3\text{O})_3\text{P} > (\text{CH}_3\text{O})_2\text{PC}_6\text{H}_5 > \text{CH}_3\text{OP}(\text{C}_6\text{H}_5)_2 > (\text{C}_6\text{H}_5)_3\text{P}$. In one experiment using magnesium bromide and the series of esters obtained from triethyl phosphite and butyl Grignard reagent, the order was found to be the reverse of that shown here (88), but it is felt that the difference is a result of changing from butyl groups attached to phosphorus to phenyl substitution. It has been shown that electron delocalization is extensive when phenyl groups are attached to trivalent phosphorus. Ultraviolet absorption of triphenylphosphine indicates the electrons to be delocalized in the benzene rings (46, 47).

Competition for the Grignard reagent is apparently operative with all intermediate esters, although trimethyl phosphite is postulated to be strongest in this sequence. This is assumed from the results in the 1:1 reverse addition reaction, and in the observations of Sander, who found that a 1:1 ratio of Grignard reagent to diethyl phenylphosphonite gave a 50-50 mixture of triphenylphosphine and phosphonite ester (recovered) when condensed with phenyl Grignard reagent (86).

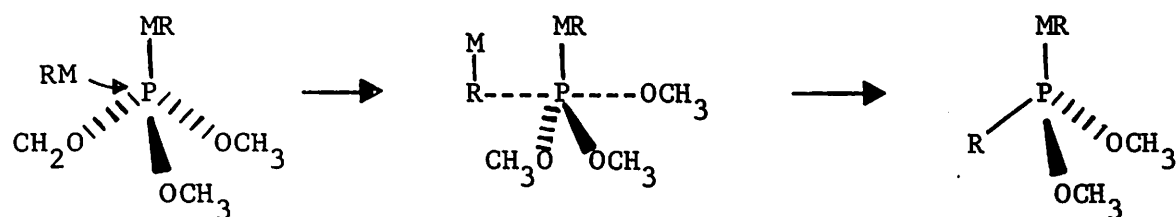
The diagram indicates the postulated equilibria among the component



esters in our studies. This seems to agree with the experimental results and can be rationalized by the fact that as the extent of phenyl substitution increases, the electron density in the nonbonded orbital on phosphorus decreases. Decrease in the complex stability would be expected to parallel the extent of phenyl substitution on the basis of previous arguments including ultraviolet data (46, 47).

Attack by the second molecule of the anionic phenyl Grignard reagent to the complexed phosphorus ester can occur by two different processes. First, a classical S_N2 (A) reaction is not unreasonable and would involve

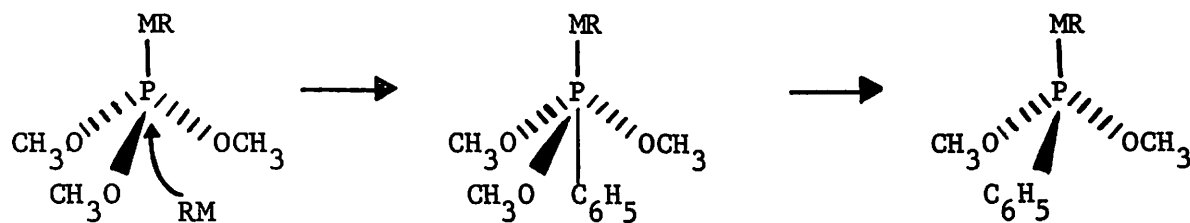
a transition state in which the reagent and the leaving group are at 180° to each other.



RM = Phenyl Grignard Reagent

A

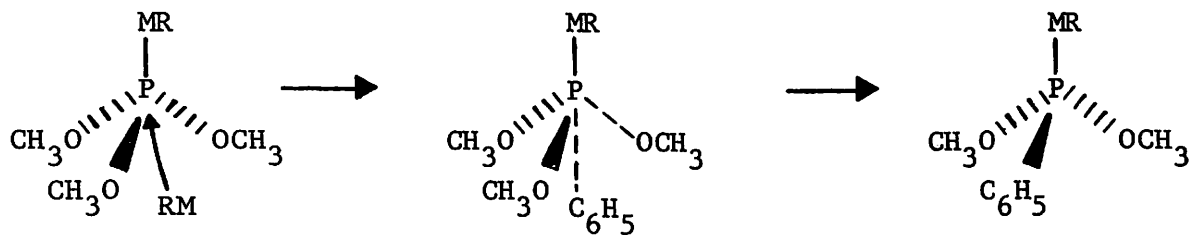
Second, a plausible sequence would involve approach by the reagent from the underside. This could follow two paths, a condensation in which a structure containing a pentacoordinate phosphorus atom is formed and subsequently collapses to the product (B), or a completely concerted



RM = Phenyl Grignard Reagent

B

mechanism may operate in which one C-P bond is formed as an O-P bond is broken (C) (the C-P-O angle could be about 90°).

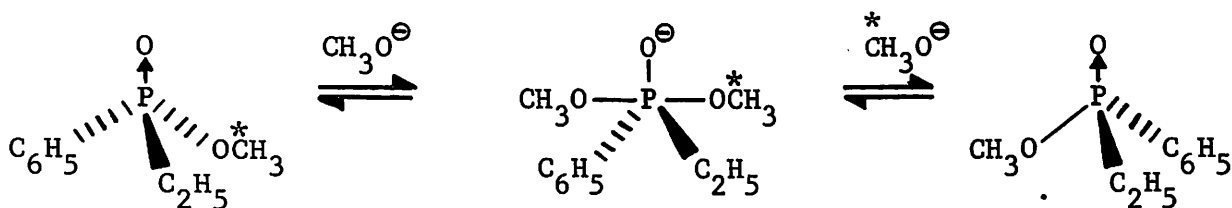


RM = Phenyl Grignard Reagent

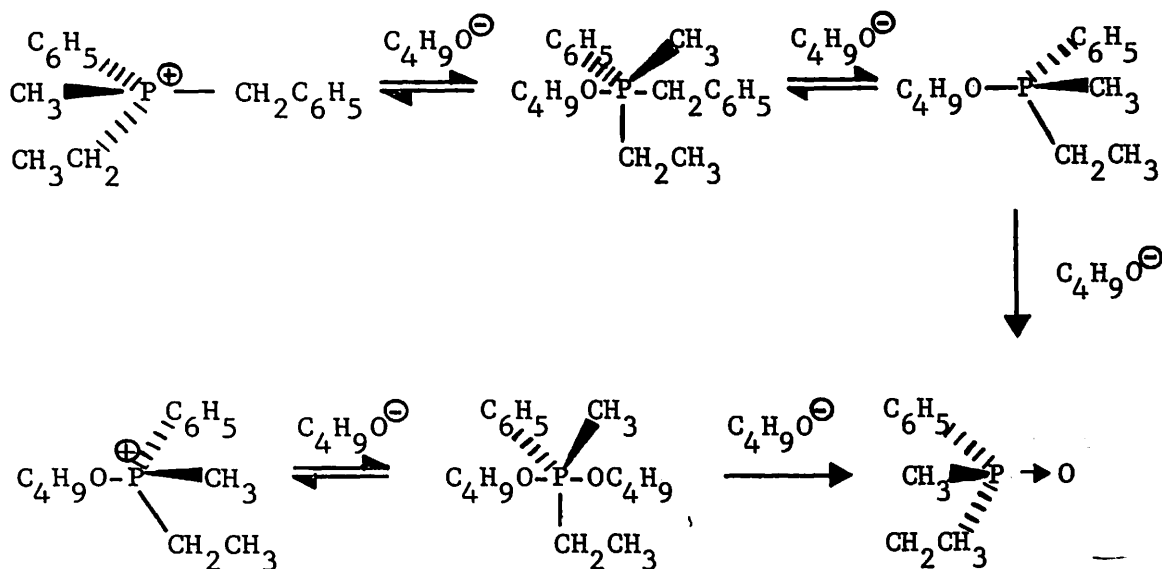
C

A review on the stereochemistry of reactions involving phosphorus atoms is available (44). The actual knowledge of bonding at phosphorus is still in its infancy with regard to hybridization of orbitals in transition states and transient reaction intermediates (43).

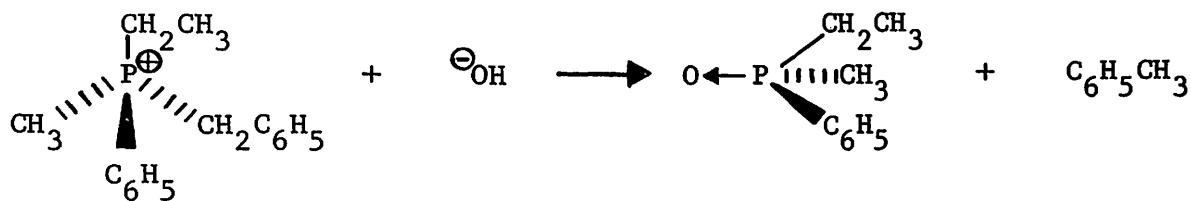
It seems impossible to differentiate between processes A and B although process C is considered less probable. Of the postulated sequences A and B, the more attractive pathway seems to be B. This involves a pentacovalent phosphorus-containing intermediate. This is permissible since 3d orbitals are available and expansion of the valence shell is allowed. Such intermediates have been postulated previously. Hudson and Green (37) have postulated that the exchange of methoxide ion with the methoxy group (isotopically labeled carbon) of a phosphinate ester proceeds through an intermediate trigonal bipyramid with inversion at the phosphorus center. The intermediate in this example



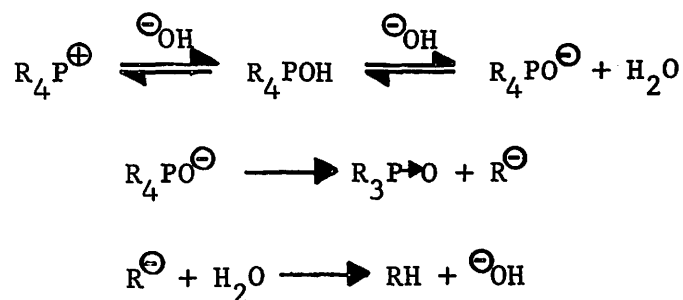
is postulated to involve pd^2 hybrid bonds between phosphorus and the incoming and leaving methoxy groups with bonding at the other three positions of the sp^2 type (37). In some cases the experimental facts can only be rationalized by a mechanism involving pentacovalent phosphorus. McEwen, et al. have shown that optically active benzylethylmethylphenylphosphonium butoxide is converted with racemization by butoxide ion to ethylmethylphenylphosphine oxide (74). The equations illustrate the postulated conversion. The products of this reaction



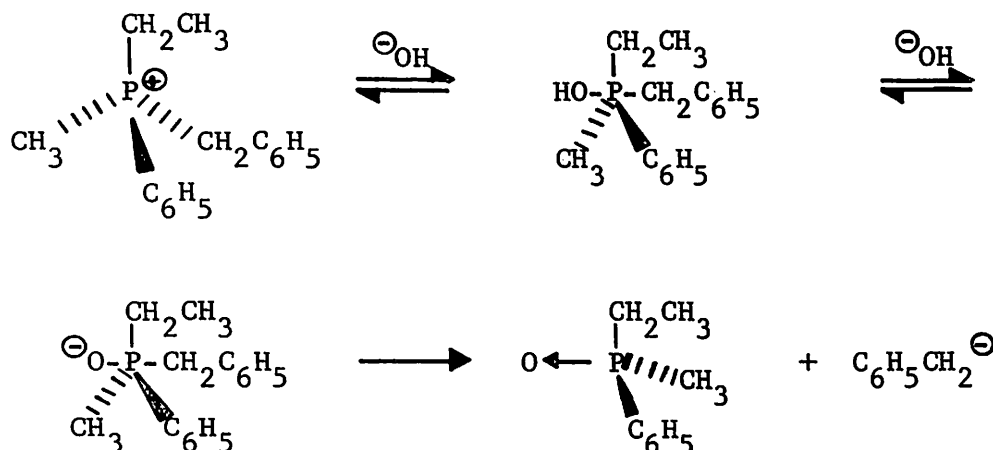
are dibutyl ether, toluene and the phosphine oxide. Pentacoordinate phosphorus intermediates in this case appear necessary to explain the data. In a more recent report, optically active benzylethylmethylphenylphosphonium iodide has been shown to decompose stereospecifically under the action of sodium hydroxide to give toluene and ethylmethylphenylphosphine oxide (66). The reaction occurs with inversion of



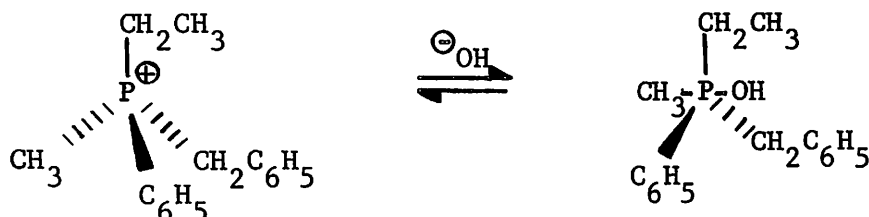
configuration at the phosphorus center. The stereochemical course of



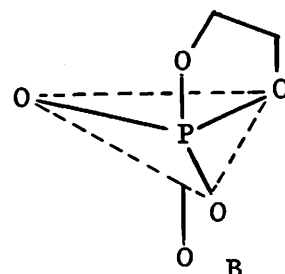
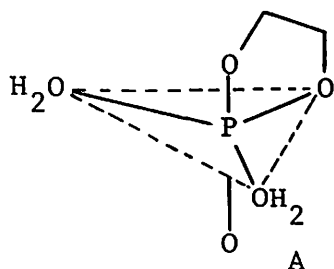
the transformation can be pictured as an attack by the hydroxide ion on the phosphonium cation to give a trigonal, bipyramidal intermediate with the hydroxyl group at an apical position. Collapse of this intermediate with expulsion of a carbanion from an apical position then occurs after conversion to the conjugate base by a second hydroxide ion. It



is evident that attack may proceed at any position opposite a hydrocarbon moiety. However, the benzyl carbanion is the better leaving group because of resonance stabilization and controls the over-all reaction. This results in retention of optical purity with inversion of configuration. Attack at positions which would give a trigonal bipyramid with the hydroxyl group and the benzyl moiety occupying basal positions is discounted since this would collapse with equal probability to give inversion and retention and net racemization of the end product. One of the possible structures of this type is illustrated. Loss of the

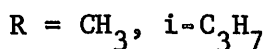
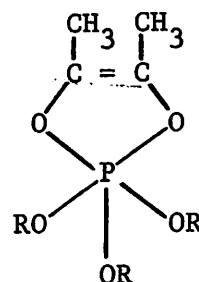
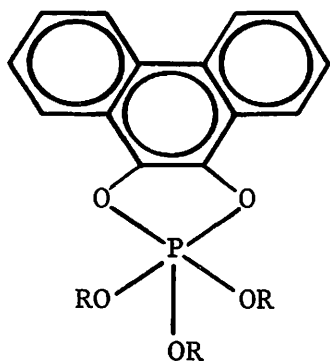


benzyl group from all of these possible structures would result in racemization. This work is in accord with the postulated mechanism of the attack of phenyl Grignard reagent on the phosphite-Grignard adduct and lends credibility to the envisioned process in our work. A trigonal bipyramidal structure was suggested by Haake and Westheimer (40) to be a good illustration of the activated complex during acid hydrolysis of ethylene hydrogen phosphate. They favored the structures pictured here and stated the evident fact that differentiation between them is impossible with the information available. Both A and B contain pentacovalent



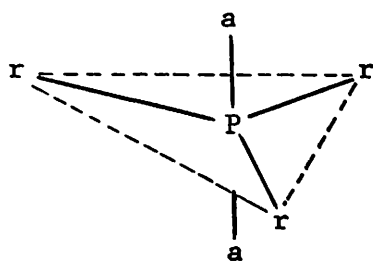
phosphorus and from this report and other similar ones, it is rather difficult to disregard the possibility that many reactions involving phosphorus may proceed through intermediates of this nature.

Many compounds involving pentacovalent phosphorus are known. Ramirez (79, 80) has prepared several of these in which phosphorus is bound to several electronegative groups and it is evident that stabilization is effected by this (43). The compounds illustrated are called



pentaoxyphosphoranes and are prepared from alpha-diketones and a tri-alkyl phosphite (79, 80).

These systems involve a phosphorus atom at the center of a trigonal bipyramid and although all bonds are equivalent in space, they are not to be assumed to have equal energy. If all bond lengths are assumed to be equal [as assumed by Duffy (30)], then the axial bonds are stronger than the radial bonds (40). On the other hand if all bonds are assumed to be of equal energy (sp^3d) then the axial bonds are longer than the

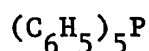


a = axial

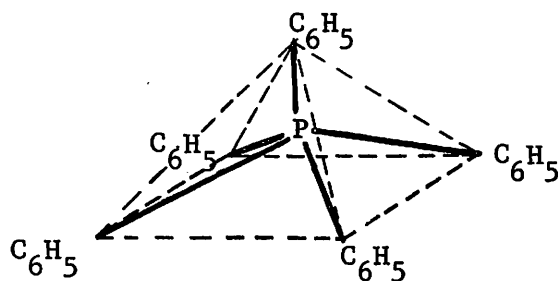
r = radial

equatorial bonds (44).

Dipole moment and x-ray diffraction studies of pentaphenylphos-



phorane have been published (97). This compound exists not as a trigonal bipyramid but has the phosphorous atom at the inside center of a square pyramidal structure (97). Consequently, both types of geometrical



arrangements, trigonal bipyramid and a square pyramid, are permissible in phosphorus molecules.

In differentiating between mechanisms A and B (page 31), it is tentatively considered that B is the most acceptable since attack by a nucleophile in this case would involve the degenerate orbital of phosphorus which contains the complexed nonbonded electrons. The lobe of this orbital, it would seem, is more available to the nucleophile.

The collapse of this intermediate is postulated to occur by an irreversible process involving precipitation of the magnesium alkoxide-bromide salt. The sequence of O-P bond breaking and salt formation is evidently rapid because the precipitate is seen within seconds after contact of the reactants.

It can be concluded that the reaction of trialkyl phosphites with aryl Grignard reagents is a very general method for preparing triarylphosphines if an excess of Grignard reagent is used. However, different alkoxy groups change the reactivity of the ester immensely. Trimethyl phosphite condenses exothermically with phenyl Grignard reagent while triethyl and tributyl phosphite react only when the temperature is increased (88). In all cases the formation of a precipitate is observed (88). Although precipitates form in condensation reactions with Grignard reagents, there is evidence that esters of tetravalent phosphorus behave differently. Precipitation of the entire organophosphorus material can occur (86). The complexes of P (III) esters have been shown by our investigations to be soluble but the complexes of P (IV) esters with Grignard reagents appear to be insoluble in ether. In Sander's report (86) Grignard reagents prepared from alkyl bromides gave solid adducts from which no phosphorus displacement products could be obtained. In contrast the chlorides gave moderate yields of products which were distillable from the unhydrolyzed reaction mixture.

Triphenylphosphine oxide did give an insoluble adduct with the Grignard reagent from bromobenzene, whereas none was observed with triphenylphosphine.

Nucleophilic displacement reactions on phosphorus atoms have an important position in organophosphorus chemistry. The entire field is progressing rapidly and can be considered to be at the threshold of some very important discoveries. In the past, the area has largely been discussed in descriptive terms but it can be expected that shortly a theoretical foundation will be available, through the type of work being pursued by R. F. Hudson, and the subject will no longer be limited to mere qualitative interpretations.

CHAPTER III

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

Preparation of Dimethyl Phenylphosphonite. A 1-liter three-necked flask was equipped with a mechanical stirrer, a reflux condenser with drying tube, a thermometer and a pressure equalizing addition

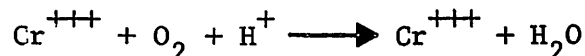
¹All melting points are corrected and all boiling points are uncorrected.

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

³The microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, and by Midwest Microlab, Inc., Indianapolis, Indiana.

⁴Gas-liquid chromatographic analyses were performed on an Aerograph Hy-Fi A-550 (hydrogen flame ionization detector) manufactured by Wilkins Instrument and Research, Inc., Walnut Creek, California. In all instances, gas liquid chromatography will be referred to as g.l.c.

⁵Commercial nitrogen was dried and deoxygenated by a method adapted from that reported (14, 93). The nitrogen was bubbled through a reservoir containing zinc amalgam rods immersed in a solution of chromic sulfate in dilute sulfuric acid. Chromium (III) is reduced to chromium (II) by zinc and then reacts with oxygen and returns to chromium (III).



Amalgamated zinc is used because the high overvoltage of hydrogen on mercury precludes the formation of hydrogen gas which would otherwise occur from the action of sulfuric acid on zinc. Water vapor was removed from the nitrogen by passing the deoxygenated gas through a scrubber of concentrated sulfuric acid and then through a column packed alternately with calcium chloride, cotton, and silica gel.

funnel connected to a supply of anhydrous, deoxygenated nitrogen. After the system had been swept with nitrogen, the funnel was charged with 25.63 g. (0.800 mole) of methanol in 100 ml. of anhydrous ether. Phenylphosphonous dichloride (63.11 g.; 0.352 mole) in 250 ml. of ether and 121.2 g. (1.0 mole) of N,N-dimethylaniline in 150 ml. of ether were added to the flask. After cooling to 6° with an ice-salt bath, the addition of the methanol-ether solution was begun (temperature below 15°). The addition was completed in 30 minutes and the resulting mixture was stirred vigorously as the contents of the flask warmed to room temperature. After heating to reflux, the contents were filtered under an inverted powder funnel connected to a nitrogen supply. The filtrate was then distilled in vacuo. After examination of the main fraction (b.p. 33-5°/0.8 mm.) by gas liquid chromatography (g.l.c.), it was evident that the material was contaminated by the N,N-dimethylaniline which had been in excess. A second distillation gave a main fraction boiling at 37-8°/0.95 mm. [lit. (42) 94.5°/13 mm.]; yield 40.6 g. (67.6 per cent). G.l.c. analysis indicated that the material was quite pure.

Preparation of Dimethyl Phenylphosphonate. To a 300-ml. three-necked flask equipped with a magnetic stirrer, a reflux condenser with drying tube, a thermometer, and a pressure-equalizing addition funnel connected to a nitrogen supply, was added 6.09 g. (0.035 mole) of dimethyl phenylphosphonite in 50 ml. of ether. In the addition funnel was placed 30 ml. of 30% aqueous hydrogen peroxide. The hydrogen peroxide was allowed to flow into the rapidly stirred contents of the flask which had been cooled to 14° with an ice-salt bath. The reaction was extremely exothermic (the first five drops raised the flask temperature

from 14° to 33°) and the addition was performed cautiously. When the addition had been completed, the mixture was stirred until it had warmed to room temperature. The mixture was then heated quickly to reflux and then, after cooling, the organic layer was cautiously separated since an excess of the peroxide was used. The water layer was extracted twice with 100-ml. portions of ether, and the combined organic layers were washed once with 50 ml. of distilled water. After the solvent was removed using a flash evaporator, the residual material was distilled in vacuo. A fraction boiling at 83-84°/2.0 mm. [lit. (39) 103°/4 mm.] was collected and shown by g.l.c. to contain only one peak when injected neat. The dimethyl phenylphosphonate obtained weighed 4.55 g. (68.2 per cent).

Preparation of Methyl Diphenylphosphinite. A 1-liter three-necked flask was equipped with a mechanical stirrer, a reflux condenser with drying tube, a thermometer, and a pressure-equalizing addition funnel connected to an anhydrous nitrogen supply. After the system had been swept with nitrogen, 81.18 g. (0.368 mole) of diphenylphosphinous chloride and 60.24 g. (0.50 mole) of N,N-dimethylaniline were added to the flask in 300 ml. of anhydrous ether. The addition funnel was charged with 16.02 g. (0.50 mole) of methanol in 50 ml. of anhydrous ether. The flask was placed in an ice-salt bath and the solution was added from the addition funnel with stirring over a period of 1.5 hours during which time the mixture was maintained at 5-10°. The reaction mixture was then stirred at reflux for 30 minutes and, after cooling, the amine salt was filtered from the mixture while maintaining the system under a nitrogen atmosphere using an inverted powder funnel. After the filtrate was concentrated in a flask evaporator, the residual oil was distilled

in vacuo through a 75-cm. Vigreux column. A fraction which distilled at $110-113^{\circ}/0.95 - 1.1$ mm., $n_D^{25^{\circ}}$ 1.6039 [lit. (7, 10) $151-2^{\circ}/10$ mm., $n_D^{20^{\circ}}$ 1.6030] was collected; yield 59.20 g. (74.4 per cent). G.l.c. indicated the material to be quite pure giving a single peak when the material was injected neat on an 8-ft. x 1/8-in. column packed with 10 per cent silicone rubber on 80/100-mesh, acid-washed Chromosorb W.

Preparation of Methyl Diphenylphosphinate. A 500-ml. three-necked flask was equipped with a mechanical stirrer, a reflux condenser with a drying tube, a thermometer, and a pressure-equalizing addition funnel connected to a supply of anhydrous nitrogen. After the entire system had been swept with nitrogen, 13.97 g. (0.0645 mole) of methyl diphenylphosphinite was dissolved in 250 ml. of ether and added to the flask. The addition funnel was charged with 20 ml. of 30 per cent hydrogen peroxide diluted to 100 ml. with distilled water. The flask was cooled to 5° with an ice-salt bath, and the addition was performed very slowly (30 minutes) with rapid stirring since the reaction is extremely exothermic (temperature rose to 23°). The solution was stirred while warming to room temperature and then heated at reflux for 45 minutes. After cooling, the organic layer was separated and the water layer was extracted with four 25-ml. portions of ether. When dried (magnesium sulfate) the organic phase was distilled in vacuo. The fraction distilling at $13.8-140^{\circ}/0.34-0.35$ mm. (18) was collected and g.l.c. showed a single peak when injected as a benzene solution. One fraction solidified upon standing. When the main fraction was seeded with a crystal of this material, it also solidified. Upon standing, this material liquified again when in contact with the atmosphere with essentially no change in its infrared spectrum.

Anal. Calcd. for $C_{13}H_{13}O_2P$: C, 67.24; H, 5.64; P, 13.78.

Found: C, 67.84; H, 5.69; P, 13.71.

Preparation of Phenyl Grignard Reagent. A 500-ml. three-necked flask was equipped with a mechanical stirrer, a reflux condenser with drying tube, a thermometer, and a pressure-equalizing addition funnel connected to an anhydrous, deoxygenated (14, 96) nitrogen supply. After the entire system was swept with nitrogen, 8.512 g. (0.35 g. atom) of magnesium was placed in the flask with just enough anhydrous ether to cover the metal. The addition funnel was charged with 50.00 g. (0.318 mole) of bromobenzene and approximately 1 ml. was added to the flask. When the reaction had been initiated by gentle agitation of the metal with the stirring rod, the bromobenzene was quickly diluted with 100 ml. of anhydrous ether, and 150 ml. of anhydrous ether was added to the flask. With stirring, under nitrogen, the bromobenzene-ether solution was added over a period of 35 minutes. The reaction mixture was held at reflux for 1.5 hours and, after cooling, was filtered through glass wool into a premarked 1-liter three-necked flask, similarly equipped, in such a way as to maintain an anhydrous and oxygen-free atmosphere. The volume was then adjusted to 300 ml. and three 1-ml. aliquots were withdrawn and added to 50.00 ml. aqueous hydrochloric acid (0.1066 meq./ml.). After heating the acidic mixture to near boiling, it was titrated to a phenolphthalein endpoint with aqueous sodium hydroxide (0.1067 meq./ml.) (35). The yield was 0.0315 mole (94.7 per cent). Of this solution, 375 ml. (0.276 mole) was used immediately in the next reaction.

Reaction of Phenyl Grignard Reagent with Trimethyl Phosphite (3:1).

The addition funnel of the previously described apparatus was charged

with 11.43 g. (0.0921 mole) of trimethyl phosphite in 225 ml. benzene. This solution was added, with stirring, under nitrogen, over a period of 23 minutes during which time the temperature rose throughout addition from 23° to 40°. Benzene (100 ml.) was added to the flask and the reaction mixture was heated to reflux (20 minutes required) and then held at 53-55° during the entire reaction period (10 hours). The mixture was then cooled to -1° with an ice-salt bath and 300 ml. of 20 per cent aqueous ammonium chloride was added at such a rate that the temperature remained below 15°. The mixture was then stirred for 1 hour at room temperature and then transferred to a separatory funnel. The organic layer was separated quickly and placed under nitrogen. The water layer was extracted twice with 100-ml. portions of ether and twice with 100-ml. portions of benzene. The combined organic layers, after drying over magnesium sulfate, were concentrated at aspirator pressure on a steam bath in an apparatus which had previously been flushed with nitrogen. The concentrated mixture (117 ml.) was then analyzed by g.l.c. using an 8-ft. by 1/8-in. column composed of 10 per cent silicone rubber on 80/100-mesh, acid-washed Chromosorb W. The flow rates for the nitrogen carrier gas and for the hydrogen were 30 and 25 ml. per minutes, respectively. Qualitative analysis showed the presence of triphenylphosphine (retention time of 14.8 minutes at 243°), methyl diphenylphosphinite (15.8 minutes at 174°), biphenyl (5.7 minutes at 174°) and trimethyl phosphite (1.3 minutes at 119°). None of the possible oxidation products were observed. All analyses were confirmed by mixed injections with authentic samples. Trace quantities of several unknowns were present but were not identified. These peaks occurred between trimethyl phosphite and dimethyl phenylphosphonite in retention times. No

dimethyl phenylphosphonite was found. Quantitative analyses was performed by making repeated injections of the reaction mixture alternately with a prepared standard mixture (4.2319 g. of triphenylphosphine in 25 ml. benzene).

Average area for standard solution -- $1050 \text{ mm}^2/0.60\mu\text{l}$

Average area for triphenylphosphine in reaction -- $1070 \text{ mm}^2/0.80 \mu\text{l}$

Standard solution: $\frac{0.01613 \text{ mole}}{25 \text{ ml.}} \times \frac{10^{-3} \text{ ml.}}{\mu\text{l}} = 6.454 \times 10^{-7} \text{ mole}/\mu\text{l}$

Theoretical yield of triphenylphosphine: $\frac{0.09213 \text{ mole}}{117 \text{ ml.}} \times \frac{10^{-3} \text{ ml.}}{\mu\text{l}}$
 $= 7.874 \times 10^{-7} \text{ mole}/\mu\text{l}$

Actual yield of triphenylphosphine: $\frac{\frac{1070 \text{ mm}^2}{0.80 \mu\text{l}} (6.454 \times 10^{-7} \text{ mole}/\mu\text{l})}{\frac{1050 \text{ mm}^2}{0.60 \mu\text{l}}}$
 $= 4.935 \times 10^{-7} \text{ mole}/\mu\text{l}$

Percentage yield triphenylphosphine: $\frac{4.935 \times 10^{-7} \text{ mole}/\mu\text{l}}{7.874 \times 10^{-7} \text{ mole}/\mu\text{l}} \times 100$
 $= 62.68 \text{ per cent.}$

From the molar ratios of triphenylphosphine and methyl diphenylphosphinite obtained from a standard solution, and from the observed ratio of the areas of these components in the reaction mixture, the calculated yield of methyl diphenylphosphinite was found to be 4.2 per cent. A full description of the methods used for the quantitative analyses is contained in the next section.

Average area of methyl diphenylphosphinate: 37 mm^2 .

Molar ratio of areas of triphenylphosphine to methyl diphenylphosphinite: 1.9/1.

Yield of methyl diphenylphosphinite:

$$\frac{(4.935 \times 10^{-7} \text{ mole}/\mu\text{l})(37 \text{ mm}^2)(1.9)}{(7.84 \times 10^{-7} \text{ mole}/\mu\text{l})(1050 \text{ mm}^2)} \times 100 = 4.2 \text{ per cent.}$$

Reaction of Phenyl Grignard Reagent with Trimethyl Phosphite (1:1).

To 132 ml. of phenyl Grignard solution (0.120 mole) prepared similarly to that described previously in a 500-ml. flask equipped similarly was added over a period of 20 minutes 14.89 g. (0.120 mole) of trimethyl phosphite in 100 ml. benzene with stirring, under anhydrous, deoxygenated nitrogen. The reaction was exothermic and the temperature rose during the first half of the addition to 48°, but during the latter half of the addition, the temperature dropped to 40°. The addition resulted in the formation of a finely divided, white precipitate immediately upon contact of the two solutions. Heat was applied and the mixture was brought quickly to reflux (48°) over a period of 15 minutes. Upon addition of 50 ml. of benzene, the mixture was brought to reflux and held at 53-55° for 10 hours. The mixture was then cooled to -4° immediately with an ice-salt bath. Decomposition was effected with 200 ml. of 20 per cent aqueous ammonium chloride solution (temperature maintained below 13°). After stirring at room temperature for 1 hour, the mixture was transferred to a separatory funnel under nitrogen, and the organic layer was quickly separated and stored under nitrogen. Six 75-ml. portions of benzene were used to extract the water layer. The combined organic layers after drying (magnesium sulfate) were concentrated at reduced

pressure (aspirator) on a steam bath using an apparatus which had previously been filled with nitrogen. G.l.c. was used to analyze the concentrated solution (151 ml.). Aqueous hydrochloric acid was used to acidify the water layer. After standing 24 hours, it was extracted four times with 75-ml. portions of benzene. The combined organic layers were dried over magnesium sulfate and upon evaporation to dryness, no residue was observed. This confirms that essentially no hydrolysis of the reaction intermediates occurred.

Gas Liquid Chromatographic Analysis of Mixture from Reaction of Phenyl Grignard Reagent and Trimethyl Phosphite (1:1). The following is typical of the methods used to analyze all reaction mixtures in this series.

Qualitative Analysis. All components observed were identified by comparison of retention times with those of known samples dissolved in the same solvents. In all cases mixed injections were made to confirm the identity of each unknown component. An 8-ft. x 1/8-in. column composed of 10 per cent silicone rubber on 80/100-mesh, acid-washed Chromosorb W was used to separate the products. The flow rates for nitrogen and hydrogen were 30 and 26 ml. per minute, respectively. None of the possible oxidized phosphorus products were observed although when reaction mixtures were allowed to remain in contact with the atmosphere, oxidation occurred and oxidation products could be readily detected. For this reason, all of the trivalent phosphorus compounds were placed in solution in vials filled with nitrogen and capped with rubber septums. A sample of the solution was withdrawn by inserting the syringe needle through the septum.

TABLE III

QUALITATIVE G.L.C. ANALYSIS OF THE MIXTURE FROM THE REACTION OF PHENYL GRIGNARD REAGENT AND TRIMETHYL PHOSPHITE (1:1)

Components	Temperature ($^{\circ}\text{C}$)	Retention Time (min.)
$(\text{C}_6\text{H}_5)_3\text{P}$	240	14.2
$\text{CH}_3\text{OP}(\text{C}_6\text{H}_5)_2$	170	15.0
$(\text{CH}_3\text{O})_2\text{PC}_6\text{H}_5$	144	6
$(\text{CH}_3\text{O})_3\text{P}$	116	1.4
$\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$	170	5.6

Quantitative Analysis of Mixture from Reactions of Phenyl Grignard Reagent and Trimethyl Phosphite (1:1). A standard solution of the following compounds was prepared by dissolving the compounds in 50.0 ml. benzene and diluting to 100 ml. in a volumetric flask with ether.

TABLE IV

COMPOSITION OF STANDARD SOLUTION

$(\text{C}_6\text{H}_5)_3\text{P}$	1.480 g. (0.00564 mole)
$\text{CH}_3\text{OP}(\text{C}_6\text{H}_5)_2$	1.220 g. (0.00564 mole)
$(\text{CH}_3\text{O})_2\text{PC}_6\text{H}_5$	1.9501 g. (0.0114 mole)
$(\text{CH}_3\text{O})_3\text{P}$	3.3993 g. (0.0273 mole)

Using this standard solution, several injections were made to determine the molar ratios of the areas of the components in this mixture.

$$\frac{\text{Area (triphenylphosphine)}}{\text{Area (methyl diphenylphosphinite)}} = \frac{1.90}{1}$$

$$\frac{\text{Area (methyl diphenylphosphinite)}}{\text{Area (dimethyl phenylphosphonite)}} = \frac{3.33}{1}$$

Repeated injections of the reaction mixture gave the following results.

$$\frac{\text{Area (triphenylphosphine)}}{\text{Area (methyl diphenylphosphinite)}} = \frac{1.61}{1}$$

$$\frac{\text{Area (methyl diphenylphosphinite)}}{\text{Area (dimethyl phenylphosphonite)}} = \frac{1.77}{1}$$

From this information, the following mole ratios for the product distribution was obtained. Triphenylphosphine:methyl diphenylphosphinite:dimethyl phenylphosphonite was 1:1.2:2.3. Using the standard solution containing 1.480 g. (0.0057 mole) of triphenylphosphine in 100 ml. benzene and ether, several injections were made alternately with injections of the reaction mixture. From the injection size in both cases it was possible to determine the concentration of triphenylphosphine in the reaction mixture. In addition, with knowledge of the molar ratios of the areas of the different products, it was possible to calculate the percentage yield based on available trimethyl phosphite. In all cases the areas were determined by the peak height multiplied by the width at half height (92). It is apparent that reproduction of injection sizes is difficult and we later employed the internal standard method to circumvent this problem.

Injection No.	Area of triphenylphosphine in standard solution (mm ²)
1	457
2	460
3	464
4	484
5	446
6	479
7	446
8	488

Injection No.	Area of Triphenylphosphine in reaction mixture (mm ²)
1	268
2	285
3	304
4	276
5	385
6	312
7	280
8	304

Average area of triphenylphosphine in standard solution: 464 mm².

Average area of triphenylphosphine in reaction mixture: 289 mm².

Concentration of triphenylphosphine in standard solution:

$$5.643 \times 10^{-8} \text{ mole}/\mu\text{l}.$$

Injection size for standard solution: 1.0 μl .

Injection size for reaction mixture: 0.5 μl .

$$\frac{(289 \text{ mm}^2)(1.0 \mu\text{l})(5.643 \times 10^{-8} \text{ mole}/\mu\text{l})}{(0.5 \mu\text{l})(465 \text{ mm}^2)} = \frac{7.011 \times 10^{-8} \text{ mole}/\mu\text{l}}{79.47 \times 10^{-8} \text{ mole}/\mu\text{l}}$$

$$\frac{0.1200 \text{ mole}}{0.151 \text{ l}} \times \frac{10^{-6} \text{ l}}{\mu\text{l}}$$

Percentage yield for triphenylphosphine based upon moles of trimethyl phosphite was found to be

$$\frac{7.001 \times 10^{-8} \text{ mole}/\mu\text{l}}{79.47 \times 10^{-8} \text{ mole}/\mu\text{l}} \times 100 = 8.82 \text{ per cent.}$$

From previous relationships which were calculated, the following was found.

$$(8.82)(1) = 8.82 \text{ per cent triphenylphosphine}$$

$$(8.82)(1.2) = 10.6 \text{ per cent methyl diphenylphosphinite}$$

$$(8.82)(2.3) = 20.3 \text{ per cent dimethyl phenylphosphonite}$$

$$\text{Total conversion} = 39.7 \text{ per cent.}$$

Reaction of Phenyl Grignard Reagent and Trimethyl Phosphite (4:1).

To a 1-liter flask equipped similarly to that previous described was added 350 ml. of a solution of phenyl Grignard reagent (0.416 mole) in ether prepared as described previously. Trimethyl phosphite (12.92 g.; 0.104 mole) in 225 ml. benzene was added slowly under nitrogen to the stirred solution over a period of 30 minutes during which time the temperature rose gradually from 23° to 44°. The mixture was brought quickly to reflux and held at 54-55° for 10 hours. The mixture was cooled to 2° with an ice-salt bath and hydrolyzed with 350 ml. of 20 per cent aqueous ammonium chloride solution while maintaining the reaction mixture below 15°. The mixture was then stirred at room temperature for 1 hour and then transferred to a separatory funnel (under nitrogen). Again the organic layer was quickly separated and stored under nitrogen. The water layer was extracted four times with 100-ml. portions of benzene. After the combined organic layers had been dried (magnesium sulfate), the solution was concentrated and after the volume was measured, g.l.c. was used for analysis. By previously described methods, qualitative analysis using an 8-ft. x 1/8-in. column packed with 10 per cent silicone rubber on 80/100-mesh, acid-washed Chromosorb W showed the solution to contain triphenylphosphine and an unmeasurable trace of methyl diphenylphosphinite. Neither trimethyl phosphite nor dimethyl phenylphosphonite could be detected even at maximum sensitivity by g.l.c.. The yield of triphenylphosphine was quantitative.

Reaction of Phenyl Grignard Reagent and Trimethyl Phosphite (1:1; Reverse Addition). To the addition funnel of the previously described apparatus was added 150 ml. of phenyl Grignard reagent (0.113 mole) prepared as previously described in ether. Into the 500-ml. three-

necked flask was placed 14.07 g. (0.113 mole) of trimethyl phosphite in 100 ml. of benzene. With stirring under anhydrous, deoxygenated nitrogen, the phenyl Grignard reagent was added over a period of 15 minutes while the temperature rose continuously throughout the addition from 23° to 42°. The mixture was then held at reflux (53-55°) for 10 hours and, after cooling to -3° with an ice-salt bath, decomposition was accomplished by hydrolysis with 200 ml. of aqueous ammonium chloride solution (20 per cent). After stirring for 1 hour, at room temperature, the mixture was separated with a separatory funnel, and the organic layer stored under nitrogen immediately. The water layer was then extracted with four 75-ml. portions of benzene. The combined organic layers were dried over magnesium sulfate, and concentrated (125 ml.). G.l.c. analysis was performed using an 8-ft. x 1/8-in. column packed with 10 per cent silicone rubber on 80/100-mesh, acid-washed Chromosorb W. The flow rates for nitrogen and hydrogen were 31 and 23 ml. per minute, respectively. Qualitative analysis by methods previously described indicated dimethyl phenylphosphonite to be the only major product. Trimethyl phosphite was the only other component present in sufficient quantity to measure.

Quantitative analysis was accomplished by application of the methods previously described.

Average area for dimethyl phenylphosphonite in standard solution:

$$302 \text{ mm}^2/\mu\text{l.}$$

Average area of dimethyl phenylphosphonite in reaction mixture:

$$496 \text{ mm}^2/0.5 \mu\text{l.}$$

Concentration of standard solution: 1.146×10^{-7} mole/ $\mu\text{l.}$

Yield of dimethyl phenylphosphonite:

$$\frac{(496 \text{ mm}^2)(1.146 \text{ mole}/\mu\text{l})(125 \text{ ml.})}{(302 \text{ mm}^2)(0.1134 \text{ mole})(0.5 \mu\text{l})(1 \times 10^{-3} \text{ ml}/\mu\text{l})} \times 100$$

= 41.6 per cent.

TABLE V

COMPOSITION OF MIXTURE FROM REACTION OF PHENYL GRIGNARD REAGENT AND TRIMETHYL PHOSPHITE (1:1; REVERSE ADDITION)

Component	Temperature ($^{\circ}\text{C}$)	Retention Time (min.)	Occurrence in Mixture
$(\text{C}_6\text{H}_5)_3\text{P}\rightarrow\text{O}$	281	11.6	absent
$(\text{C}_6\text{H}_5)_3\text{P}$	281	5.2	absent
$(\text{C}_6\text{H}_5)_2\overset{\text{O}}{\uparrow}\text{POCH}_3$	281	3.7	present
$(\text{C}_6\text{H}_5)_2\text{POCH}_3$	202	7.8	present
$\text{C}_6\text{H}_5\overset{\text{O}}{\uparrow}\text{P}(\text{OCH}_3)_2$	202	4.9	present
$\text{C}_6\text{H}_5\text{P}(\text{OCH}_3)_2$	202	2.5	present
$(\text{CH}_3\text{O})_3\text{P}\rightarrow\text{O}$	134	2.4	present
$(\text{CH}_3\text{O})_3\text{P}$	134	1.0	present
$\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$	202	4.3	present

This value is based upon trimethyl phosphite. Since it was impossible to measure accurately the amounts of the trace components present, a rough estimated placed the value of all of these taken together at between 4 and 8 per cent.

Reaction of Phenyl Grignard Reagent with Trimethyl Phosphite (1:1; 1 Hour Reaction Time). To a 500-ml. flask, equipped similarly to that described previously and containing 150 ml. of phenyl Grignard reagent (0.202 mole) was added over a period of 35 minutes 25.08 g. (0.202 mole) of trimethyl phosphite in 80 ml. of benzene. The entire operation was conducted with stirring under an anhydrous, oxygen-free nitrogen atmosphere. As the trimethyl phosphite came in contact with the Grignard reagent, a white, finely divided precipitate was formed as usual. Although the process was exothermic, heat evolution occurred only during the first half of the addition (24-40°) while the latter half was accompanied by a drop in temperature (40 to 35°). Heat was applied and the reaction mixture was brought to reflux (53°) and, after boiling the mixture 1 hour at reflux, the flask was quickly immersed in ice water. After dismantling, the flask was transferred to a dry box and the solid was separated from the liquid portion of the reaction mixture. This was accomplished by filtering the mixture through filter paper, using the gravity flow method. The solid was a very finely divided material and filtration and subsequent washing of the precipitate was a slow and tedious operation, requiring more than six hours to complete. The ether-washed solid was then dried by passing anhydrous nitrogen into the flask containing the material for a period of 12 hours. An infrared spectrum of this material (potassium bromide pellet) indicated that no absorption was present other than that due to water. An ash test was performed by burning a sample on the end of a spatula. Very little combustion occurred and a heavy ash deposit was left. Hydrolysis of the solid was extremely exothermic; it was accomplished by adding 200 ml. of aqueous ammonium chloride (20 per cent) to the solid suspended

in 100 ml. of ether at room temperature (25°). Upon addition of five drops of the ammonium chloride solution, the ether suspension began boiling (34°) and an ice-salt bath was employed to control the temperature of decomposition. Even with the aid of the cold bath, addition was slow requiring 35 minutes to complete. After stirring an additional 1 hour at room temperature, the organic layer was separated and the water layer was extracted six times with 50-ml. portions of ether. The combined organic layers and extracts were dried over magnesium sulfate and distilled (34°) through a 75-cm. Vigreux column until the residual material in the distilling flask measured 17 ml. G.l.c. was then employed to analyze this material using an 8-ft. x 1/8-in. column of 10 per cent silicone rubber on 80,100 mesh, acid-washed Chromosorb W. Quantitative analysis of this material indicated that very little of the total amount of phosphorus compounds produced in this reaction was present in this 17 ml. of concentrated solution from the hydrolysis of the solid material which precipitated during the reaction. Of those compounds identified, none were of the trivalent oxidation state. Triphenylphosphine oxide was by far the largest component present although methyl diphenylphosphinate and dimethyl phenylphosphonate were also detected. Benzene was also identified, as well as traces of diphenylmethylphosphine oxide and biphenyl. The filtrate obtained from separation of the heterogeneous reaction mixture which had remained at room temperature under nitrogen for a period of 36 hours was hydrolyzed under nitrogen with 250 ml. of aqueous 20 per cent ammonium chloride solution. It is important to note that no evolution of heat occurred. The temperature throughout the addition did not change even though it was performed without the use of any external cooling. After stirring

the mixture for one hour at room temperature, the organic layer was separated and the water layer was extracted four times with 50-ml. portions of benzene. Concentration of the combined organic layers after drying over magnesium sulfate was accomplished with a flask evaporatory. G.l.c. analysis was performed on the concentrated solution (94 ml.), and qualitative analysis by previously described techniques indicated the presence of triphenylphosphine oxide, triphenylphosphine, methyl diphenylphosphinate, dimethyl phenylphosphonate, and biphenyl. Neither methyl diphenylphosphinite nor dimethyl phenylphosphonite was detected. It should be noted also that no diphenylmethylphosphine oxide was found in this portion of the reaction mixture.

TABLE VI

COMPOSITION OF PRODUCTS OF REACTION OF TRIMETHYL PHOSPHITE
AND PHENYL GRIGNARD REAGENT (1:1;
1 HOUR REACTION TIME)

Component	Yield (per cent)	
	Solid from Mixture	Filtrate from Mixture
$(C_6H_5)_3P \rightarrow O$	0.7	8.4
$(C_6H_5)_2P(O)(OCH_3)$	0.4	2.3
$C_6H_5P(O)(OCH_3)_2$	--- ¹	--- ¹
$(C_6H_5)_3P$		10.4

¹Dimethyl phenylphosphonate was present only in the extract of the solid and not in sufficient quantity to measure by g.l.c.

As mentioned previously, other components were identified by they were present in exceedingly small amounts and were not measured. The total percentage conversion to the displacement products was 22.2 per cent based upon trimethyl phosphite.

TABLE VII

SUMMARY OF RESULTS FROM REACTIONS OF TRIMETHYL PHOSPHITE
AND PHENYL GRIGNARD REAGENT

Reaction No.	Molar Ratio	$\frac{\text{RM}^1}{(\text{CH}_3\text{O})_3\text{P}}$	Reaction Time (hours)	Yield (per cent) ²		
				$(\text{C}_6\text{H}_5)_3\text{P}$	$(\text{C}_6\text{H}_5)_2\text{POCH}_3$	$\text{C}_6\text{H}_5\text{P}(\text{OCH}_3)_2$
1	1	1	10	8.8	10.6	20.3
2	1 ³	1	10	---	--- ⁴	41.6
3	1 ⁵	1	7.5	17.4	--- ⁶	--- ⁶
4	1	1	1	18.8 ⁷	2.7 ⁸	--- ⁴
5	3	3	10	62.7	4.2	--- ⁴
6	4	4	10	Quant.	--- ⁴	---
7	5.5	5.5	18	Quant.	---	---
8	7	7	3	95.9 ⁹	---	---

¹RM is used to denote the phenyl Grignard reagent.

²Percentage conversion is based upon trimethyl phosphite. The sum of each horizontal row represents the percentage of trimethyl phosphite (in moles) which has reacted with the Grignard reagent.

³This reaction was accomplished by a reverse addition technique in which the Grignard reagent was added to the phosphite.

⁴The products indicated here were detected but were not measured because of the extremely small amounts which were present.

⁵A 3.5-hour addition time was utilized in this reaction to determine its effect on the yield of triphenylphosphine and although the other products were present, they were not measured quantitatively. Triphenylphosphine was isolated by elution with low petroleum ether from acid-washed alumina.

⁶These products were detected but were not measured although it was evident from g.l.c. that they were present in much smaller quantities than from the reaction involving a normal addition process.

⁷The figure here represents the triphenylphosphine which was converted to the oxide also.

⁸This includes also that material converted to the phosphinate.

⁹This product was obtained from elution of reaction mixture from 600 g. of acid-washed alumina with low-boiling petroleum ether.

TABLE VIII

SUMMARY OF RESULTS FROM THE REACTIONS OF TRIMETHYL PHOSPHITE
AND PHENYL GRIGNARD REAGENT

Reaction No.	Addition Time (hours)	Ratio of Components (in moles)				Grignard reagent ¹ consumed (per cent)
		$(C_6H_5)_3P$	$(C_6H_5)_2POCH_3$	$C_6H_5P(OCH_3)_2$	$(CH_3O)_3P$	
1	0.3	1	1.2	2.3	6.8	67.9
2	0.25	---	---	1	1.5	41.6
3	3.5	1	---	---	4.7	52.2 ²
4 ³	0.5	7	1	---	26.4	61.8
5	0.3	15.4	1	---	7.7	65.5
6	0.5	Quant.	---	---	---	75.0
7	0.75	Quant.	---	---	---	--- ⁴
8	1.5	Quant. ⁵	---	---	---	--- ⁴

¹This figure represents the percentage of the phenyl Grignard reagent which was consumed in the production of triphenylphosphine, methyl diphenylphosphinite, and dimethyl phenylphosphonite.

²This figure is only a close approximation. See Footnote 5 and 6 in Table V.

³See Footnote 7 and 8 in Table V.

⁴The Grignard reagent in this case was present in large excess.

⁵See Footnote 9 in Table V.

Reaction of Phenyl Grignard Reagent and Methyl Diphenylphosphinite

(3:1). To a 500-ml., three-necked flask equipped similarly to that described earlier containing 250 ml. of phenyl Grignard reagent (0.7887 mole) in ether, was added, with stirring, under anhydrous, deoxygenated nitrogen, 13.60 g. (0.0629 mole) of methyl diphenylphosphinite. The addition required 45 minutes and no precipitate was observed. The reaction was only slightly exothermic, the temperature rising from 24 to 38° during the addition. At the end of the addition, the color of the solution was essentially unchanged from that of the phenyl Grignard reagent mixture. However, within 10 minutes after heating was initiated, the mixture cleared and deposited a greenish-yellow viscous material on the bottom of the flask which interfered with the stirring action. The mixture was heated at 50 to 55° for 8 hours and, after cooling to 0° with an ice-salt bath, it was hydrolyzed with 100 ml. of 20 per cent aqueous ammonium chloride solution (temperature kept below 15°). After stirring for 1 hour at room temperature, the mixture was transferred to a separatory funnel and an additional 200 ml. of the same ammonium chloride solution was added. After vigorous agitation, the organic layer was separated and the water layer was extracted three times with 100-ml. portions of benzene. The combined organic layers were dried (magnesium sulfate) and the solution was concentrated in vacuo. The concentrated solution (48 ml.) was analyzed by g.l.c. Qualitative analysis, by methods described previously, indicated triphenylphosphine to be the only major product. No starting material was detected. Quantitative analysis by methods previously described confirmed the qualitative observation giving a value of 97.5 per cent for the yield based upon methyl diphenylphosphinite. It should be noted at this

point that thorough examination of the reaction mixture did not reveal the presence of diphenylmethylphosphine oxide.

Reaction of Phenyl Grignard Reagent and Dimethyl Methylphosphonate

(3:1). To 150 ml. of an ether solution of phenyl Grignard reagent (0.396 mole) prepared as previously described in a 500-ml. three-necked flask equipped as usual was added 16.39 g. (0.1321 mole) of dimethyl methylphosphonate in 50 ml. of benzene. The addition, which required 30 minutes, was performed under anhydrous nitrogen with stirring and produced no change in the color of the Grignard mixture. The addition did not result in precipitation and only a slight increase in temperature was noted. After 15 minutes at reflux (50°), the mixture abruptly cleared and a heavy, viscous material was deposited on the bottom of the flask. The semi-solid had a brownish-green color and had a tendency to ball up thereby interfering with the stirring action. The mixture was boiled at $50-55^{\circ}$ for 15 hours and, after cooling to 5° with an ice-salt bath, was hydrolyzed with 200 ml. of 20 per cent. aqueous ammonium chloride solution. An additional 200 ml. of the ammonium chloride solution was added to the mixture after transferring to a separatory funnel. When the organic layer had been separated, the water layer was extracted four times with 50-ml. portions of benzene. The combined organic layers were dried (magnesium sulfate) and the solution was concentrated in vacuo. Qualitative analysis by previously described methods showed only diphenylmethylphosphine oxide to be present. No dimethyl methylphosphonate could be detected. A sample of the solution was concentrated further and a solid material was deposited. This material upon recrystallization from benzene-heptane gave no depression when a mixture melting point determination was performed with an authentic sample of diphenyl-

methylphosphine oxide; yield quantitative.

Reaction of Trimethyl Phosphite and Anhydrous Magnesium Bromide. A

500 ml. three-necked flask was equipped with a mechanical stirrer, a reflux condenser fitted with a calcium chloride drying tube, a thermometer, and a pressure-equalizing addition funnel connected to a supply of anhydrous, deoxygenated nitrogen. After purging the system with nitrogen, 18.42 g. (0.10 mole) of freshly fused and pulverized magnesium bromide was placed in the flask and covered with 100 ml. anhydrous benzene and 75 ml. anhydrous ether. This mixture was stirred vigorously while the addition funnel was charged with 12.41 g. (0.10 mole) of trimethyl phosphite in 25 ml. of anhydrous benzene and 75 ml. of anhydrous ether. The addition was made over a period of ten minutes and no temperature increase was observed. After the vigorously stirred mixture (heterogeneous) was held at reflux for ten hours (51 to 55^o), hydrolysis was accomplished with 200 ml. of aqueous ammonium chloride solution (15 per cent) in an exothermic process. The organic layer was separated, the water layer was extracted four times with 50-ml. portions of benzene, and the combined organic layers were dried (magnesium sulfate). Concentration of the solution was accomplished by distillation through a 75-cm. silvered vacuum-jacketed Vigreux column. The concentrated solution (60 ml.) was analyzed by g.l.c. on an 8-ft. x 1/8-in. column packed with 10 per cent silicone rubber on 80/100-mesh, acid-washed Chromosorb W. Trimethyl phosphite, trimethyl phosphate, ether, and benzene were identified. Four other components were detected but could not be identified using samples which were available. Neither dimethyl hydrogenphosphonate nor dimethyl methylphosphonate were present. Procedures used for the analyses were the same as those previously

recorded. Some type of transformation is apparently initiated by the magnesium bromide since in a similar procedure in the absence of magnesium bromide, g.l.c. analysis indicated only unchanged starting material.

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PART II

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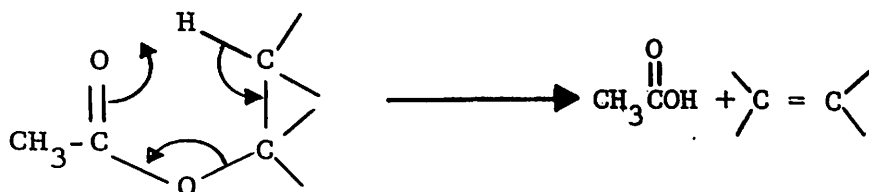
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CHAPTER I

HISTORICAL

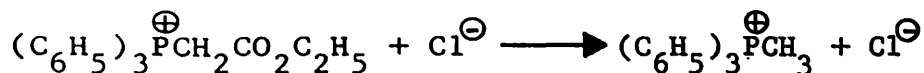
The thermal decomposition of organic compounds to produce olefins has been known for over a century (29). A few of these reactions are of synthetic importance for the preparation of alkenes in high yields. The more common elimination reactions include the decomposition of esters of carboxylic acids, xanthates, and amine oxides.

The accepted mechanism for these reactions are very similar and it is postulated that a concerted process is operative in most instances. A cyclic transition state with abstraction of cis hydrogen is envisioned as the predominant pathway for the transformation. The reaction sequence is depicted for the thermolysis of an acetate, but the mechanism of the elimination is similar for amine oxides and xanthates (29).



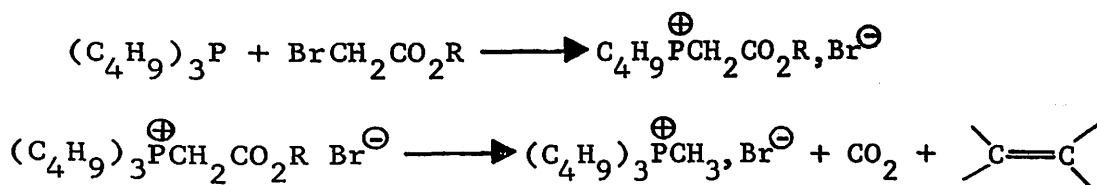
The thermal decomposition of organophosphorus compounds to produce olefins has become the object of active investigation only recently, although some early fragmentary reports are available. Michaelis and Gimborn (58) noted that upon heating the quaternary phosphonium salt obtained from triphenylphosphine and ethyl chloroacetate, slow decomposition occurred at 100^o to give methyltriphenylphosphonium chloride.

They drew the reasonable conclusion that the other products of the



reaction were carbon dioxide and ethylene, but these were neither detected nor isolated. A similar reaction was reported by Piaux who found that dimethylphenylcarbethoxymethylammonium iodide yielded phenyltrimethylammonium iodide when treated similarly (66).

To obtain further insight concerning the scope and utility of this transformation, Bailey and co-workers prepared several of these quaternary salts and subjected them to thermally induced decomposition (26). In all cases, the quaternary phosphonium compounds gave a new phosphonium salt, carbon dioxide, and an olefin derived from the alcohol portion of the ester moiety of the salt. Triphenylphosphine and tributylphosphine were used with both bromo and chloro esters to produce the quaternary phosphonium compounds. Improved yields of olefin under milder conditions were obtained when tributylphosphine was used as the starting material for the preparation of the phosphonium intermediate. The temperatures



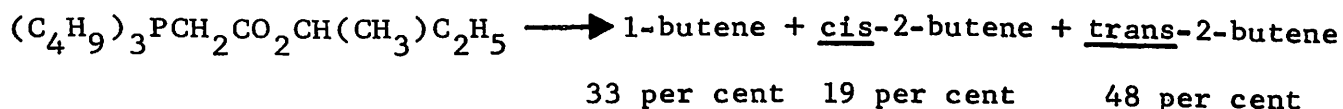
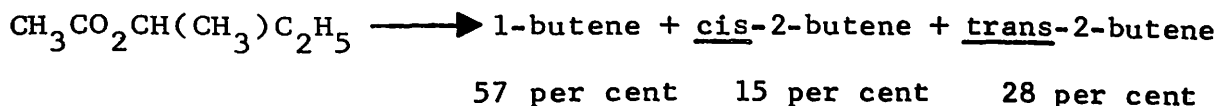
(R is derived from primary, secondary, and tertiary alcohols)

required for this decomposition (130-225^o) were quite mild compared to those normally used for the pyrolysis of acetates (300-550^o)

The yields of alkenes obtained by this method were in most cases

extremely good and the experimental procedure was fairly simple. In a typical reaction sequence, tributyl phosphine (20.0 g.; 0.10 mole) and 2-octyl bromoacetate (23.0 g.; 0.10 mole) were mixed with cooling. Although purification of the phosphonium intermediate was possible, it was not necessary, and this crude mixture was then heated (190°) for a period of 3 hours and the olefin which distilled was collected. Distillation of this material yielded 76 per cent of mixed octenes.

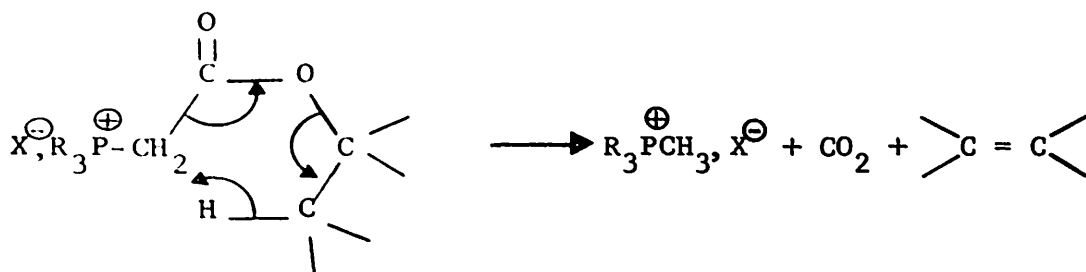
In the preparation of terminal olefins by this procedure, it was found that unless reduced pressure was used to rapidly remove the olefin as it was formed, extensive isomerization of the alkene occurred (27). Skeletal rearrangements were observed when pyrolysis of compounds prepared from secondary alcohols were performed. In all cases, the product distribution from the decompositions varied greatly from that observed for the corresponding acetates. Pyrolysates from secondary butyl acetate (33) and the quaternary phosphonium salt of tributylphosphine and butyl bromoacetate (27) contained the following components:



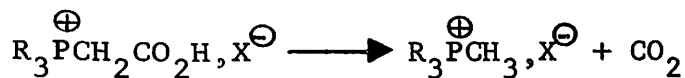
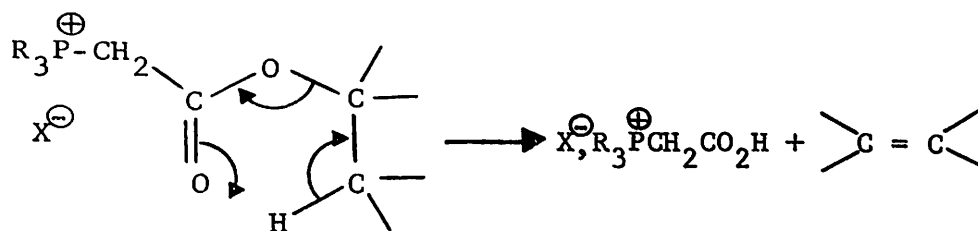
The pyrolysis of the salt from cis-2-phenylcyclohexanol gave mixtures of 1- and 3-phenylcyclohexene (27), whereas the acetate of cis-2-phenylcyclohexanol yielded primarily 3-phenylcyclohexene (1).

In a preliminary report (26), the authors suggested a mechanism for

this reaction which involved the transfer of hydrogen to carbon. Although the assumption was speculative, it was certain that this decom-



position was quite different mechanistically from *cis* eliminations observed previously. It is possible to write a reasonable mechanism for this reaction which involves transfer of hydrogen from carbon to oxygen.

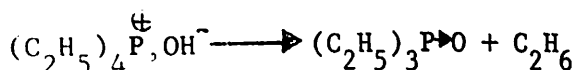


The intermediate carboxymethylphosphonium salt pictured here has been shown to decarboxylate (28) under conditions identical to those used for the pyrolysis of carbethoxymethylphosphonium halides (27). Experimental data does not however support a transition state of this type since it would be expected that the product distribution would be similar to that found in acetate decomposition and this is contrary to the facts.

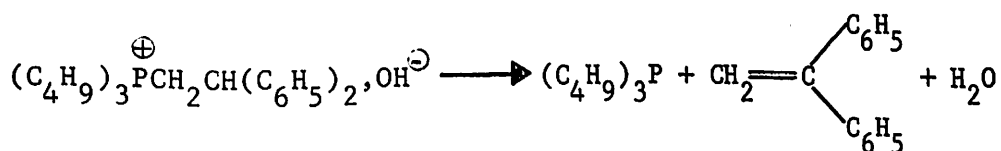
Denney and Smith (28) have pyrolyzed phosphobetaines obtained from the treatment of carboxymethylphosphonium salts with aqueous alkali to

subject has also been covered in a more recent review (67).

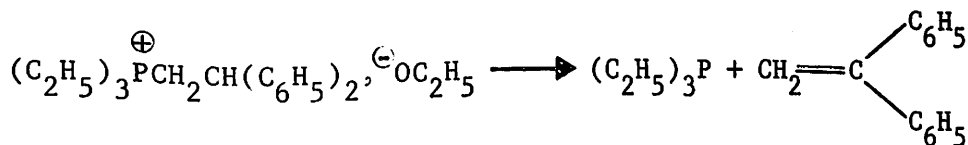
The thermal decomposition of quaternary phosphonium hydroxides gives in most cases a tertiary phosphine oxide and a hydrocarbon derived from one of the attached alkyl groups (42). This is in contrast to the results obtained from pyrolysis of quaternary amine hydroxides (Hofmann degradation) which give olefins and a tertiary amine. By varying the nature of the attached substituent, Hey and Ingold (42) were able to obtain olefins. Tetraethylphosphonium hydroxide yielded



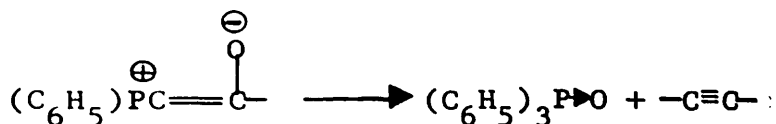
triethylphosphine oxide and ethylene upon heating the phosphonium hydroxide. However, when tributyl(2,2-diphenylethyl)phosphonium hydroxide was decomposed, 1,1-diphenylethylene (90 per cent) was



obtained. Similar results were observed when the corresponding alkoxides were used.

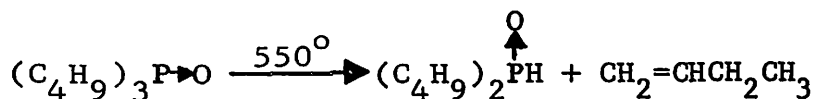


Substituted acetylenes have been prepared by the thermal decomposition of an intermediate obtained by the reaction of α -halo ketones with tertiary phosphines followed by neutralization with base (34, 35, 72).



The yields of substituted acetylenes are appreciable only when the enolate anion is conjugated with an aromatic nucleus or a similar functional group capable of delocalizing the negative charge. In a recent article (75) decompositions of this type which are not truly thermolysis reactions are discussed with references to the literature.

Thermal decomposition of tertiary amine oxides has been the subject of numerous reports (29). However, the corresponding reaction of the structurally similar phosphorus compounds has received little study and only a single report (6) has appeared in which a purely thermolytic method was used to cleave the carbon-phosphorus bond. The thermolysis of tertiary phosphine oxides in the presence of base has received some attention (17, 44). Bailey (6) has shown that tertiary phosphine oxides, usually considered to be one of the most thermally stable classes of compounds known, undergo scission of the carbon-phosphorus bond to give secondary phosphines and alkenes at elevated temperatures. The formation

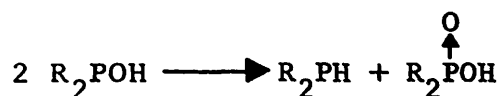


of the secondary phosphine oxide results from rearrangement of the unstable phosphinous acid by a prototropic process. This equilibrium has

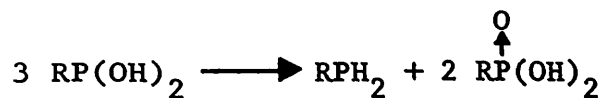


been shown to favor the phosphine oxide (47). Bailey and Fox have

reported that the presence of a hydrogen-phosphorus bond in conjunction with a phosphoryl group does not, however, imply the existence of tautomers in a specific family of compounds (4). In some cases the pyrolysis of tertiary phosphine oxides was accompanied by the formation of the corresponding phosphinic acid which was suggested to occur by disproportionation of the initially formed phosphinous acid similar to that



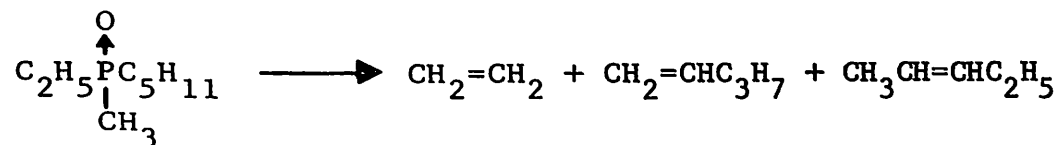
observed for the conversion of phosphonous acids to primary phosphines and phosphonic acids (57). Trimethyl- and triphenylphosphine oxide are



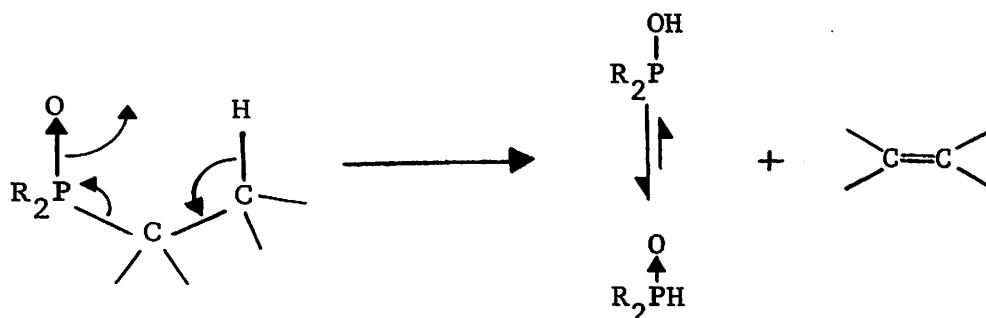
thermally stable to 700°; this stability is attributed to the absence of β-hydrogen in these compounds. The high thermal stability of the tertiary phosphine oxides is indicated by the carbon-phosphorus bond strength. A value of 62 kcal./mole has been reported (46) for the carbon-phosphorus bond compared to the accepted value for the carbon-carbon bond of 64 kcal./mole. The temperatures required for the decomposition of the tertiary phosphine oxides ranged from 490 to 665° for a minimum of 50 per cent decomposition (6). This compares to a maximum temperature of 150° for similar decomposition of tertiary amine oxides (24).

The pyrolysis of tributylphosphine oxide yielded only 1-butene at 550°, but increased amounts of isomeric butenes were found when the decomposition temperature was increased to a maximum of 650°. This indicated that possible acid-induced isomerization comparable to that

observed in ester pyrolysis (7) was operative. The pyrolysis of ethylmethylamylphosphine oxide at temperatures ranging from 410 to 565° gave proportionately higher yields of alkenes as the temperature was increased, but also resulted in increased amounts of isomerized materials. At 410°, the yield of olefin was 16 per cent; it was composed of 83 per cent ethylene and 17 per cent 1-pentene. At 565° the yield of olefinic compounds was 67 per cent, and product analysis showed 24 per cent ethylene, 23 per cent 1-pentene, 28 per cent trans-2-pentene, 21 per cent cis-2-pentene, and 4 per cent of other isomers. Because of the absence

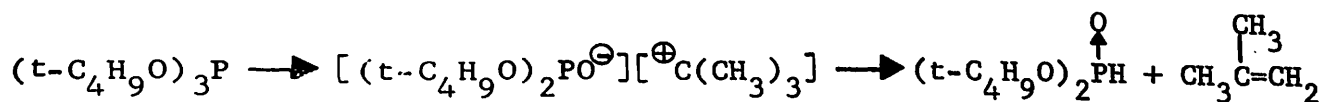


of isomeric olefins at lower pyrolysis temperatures and the stability of these compounds in the absence of β -hydrogen atoms, a cyclic transition state is an attractive mechanism for the reaction. The predominantly cis steric course observed for the thermal decomposition of amine oxides (29), which results from the abstraction of cis hydrogen in the transition state, has not been shown to exist with the similar thermolysis of phosphine oxides. Because of the absence of data concerning this aspect of the reaction, a mechanism cannot be definitively stated. However, a reasonable mechanism based on available data involving a



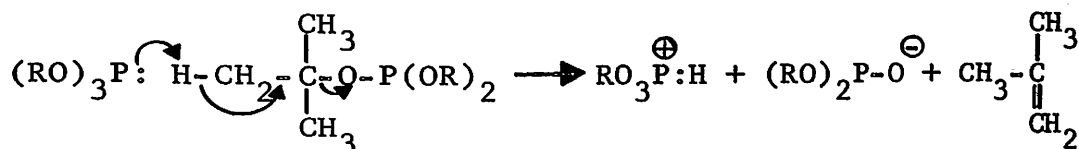
similar transition state can be envisioned (6).

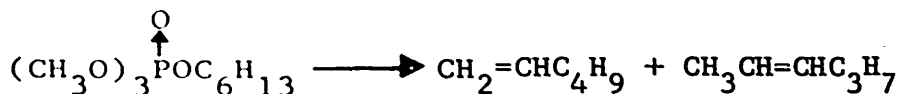
The pyrolysis of esters of phosphorus acids has not been investigated extensively. A single report concerning the preparation of tri-*t*-butyl phosphite (54) indicates that the compound is not thermally stable (54). When prepared and stored under nitrogen below 0°, the material could be preserved. However, upon heating above 50° in vacuo, rapid evolution of isobutylene occurred and after 2 hours at 80° and 50 mm., a quantitative yield of di-*t*-butyl hydrogenphosphonate resulted. Speculation as to the manner in which the tri-*t*-butyl phosphite undergoes decomposition gives rise to several possible courses for the transformation. An E₁ elimination cannot be wholly disregarded because of the



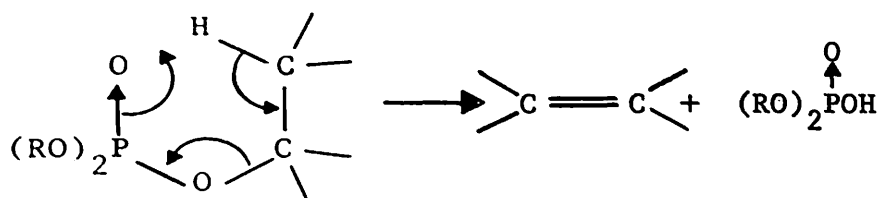
extreme ease with which the *t*-butyl cation is formed. The fact that formation of isobutylene occurred during the reaction of tri-*t*-butyl phosphite with methyl iodide (Michaelis-Arbuzov rearrangement) at room temperature also indicates that the reaction may be E₁ in nature.

Another reasonable pathway could possibly result from the attack of the phosphite on a second molecule of the compound. A somewhat similar type of transformation is pictured by the authors (54) as perhaps representative of the reaction pathway leading to isobutylene during the Michaelis-Arbuzov rearrangement.

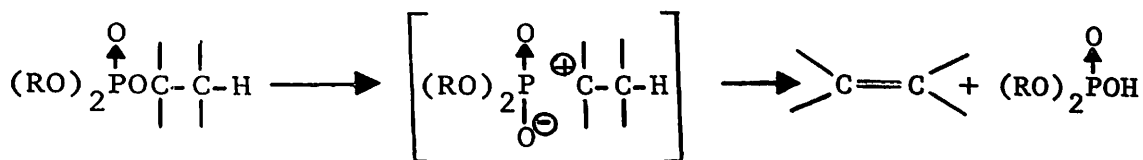




cis-substituted double bond, and a trans-substituted double bond. A mechanism involving a cyclic transition state can be written for this reaction analogous to that for the pyrolysis of esters of carboxylic acids. However, in contrast to acetate pyrolysis, the thermal decomposition of these alkyl phosphates gave large amounts of isomerization.



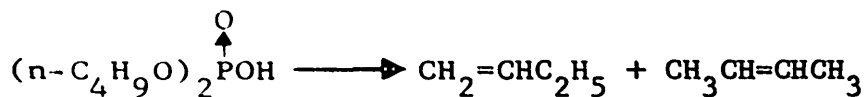
A more reasonable mechanism is one which involves ionic intermediates, and results are in agreement with this postulate (9). The formation



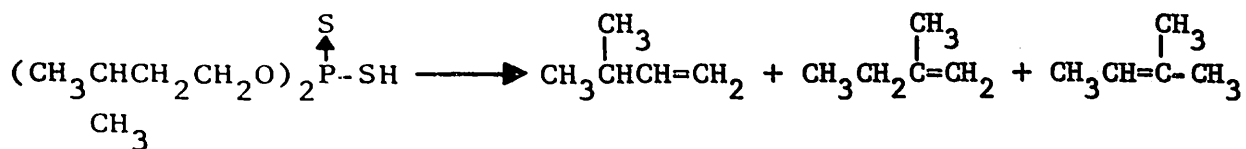
of ionic intermediates then is the probable pathway for this transformation either exclusively or in competition with a cyclic process. The arguments of Berti (18) in support of an ionic mechanism for the thermolysis of alkyl sulfites appear to be applicable to the cleavage of phosphates in this case.

Hanneman and Porter (39) have studied the thermal decomposition (215-302°) of some phosphoric acid derivatives. Lead and zinc salts of these derivatives have also been investigated (65). The pyrolyses were performed in the heated injection block of a gas-liquid chromatography unit (52). The decomposition of the dialkyl hydrogen phosphates (39) gave a mixture of olefins in all cases. In one example (39) the

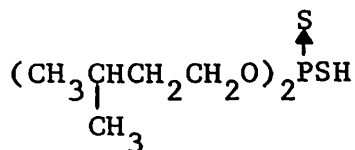
pyrolysis of di-n-butyl hydrogen phosphate gave 28 per cent 1-butene, 32 per cent cis-2-butene, and 40 per cent trans-2-butene. A similar



reaction using di-isoamyl hydrogen dithiophosphate gave 2-methyl-1-butene (13 per cent), 2-methyl-1-butene (23 per cent), 2-methyl-2-



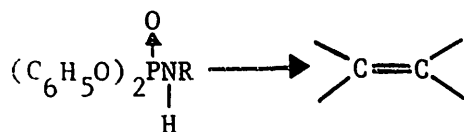
butene (59 per cent), and 5 per cent of a mixture of butenes, 1-pentene, and cis-2-pentene. The decomposition 0,0-diisoamyl S-3-bornyl dithiophosphate gave essentially the same product distribution (39). Results



were approximately the same also for the pyrolysis of zinc 0,0,diisoamyl dithiophosphate. This information tends to rule out any type of concerted process since isomerization is extensive in all cases, although skeletal rearrangements were not always significant. The decomposition of the neopentyl esters cannot occur by a cyclic process because of the absence of a β -hydrogen. The authors (39) suggest a carbonium-ion mechanism and results indicate this to apply. In all examples, the products are those which would result from loss of hydrogen from the thermodynamically most stable carbonium ion. Pyrolysis in the presence of added base (to neutralize any acidic products) did not alter the product composition. The reaction was shown to be acid-catalyzed by

the addition of different acidic materials; as the pH was increased, the temperature required for decomposition decreased. All data is in keeping with a carbonium-ion intermediate.

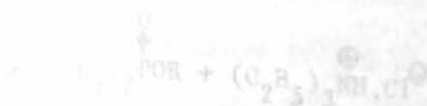
Dimethyl N-alkylphosphoramidates were shown to decompose upon heating at 350 to 400° to give mixtures of olefins (10). The olefins were extensively isomerized, and the presence of tertiary amines in the pyrolyzate indicated that the alkylamine underwent methylation in this process. The substitution of methoxy groups by phenoxy groups in an attempt to eliminate one or both of these problems was only partially successful (11). The cyclohexyl, hexyl, decyl, and 2-ethylhexyl esters of diphenylphosphoramidic acid were pyrolyzed at temperatures ranging



from 350 to 450° and gave yields of alkenes ranging from 56 to 95 per cent (crude). Analysis (g.l.c.) indicated several (3 to 7) components present except from the cyclohexyl ester. A measure of the extent of isomerization was made by dividing the amount of expected olefin by the total amount of olefinic matter present. This measurement ranged from 42 per cent for the hexyl ester to 95 per cent for the 2-ethylhexyl compound. Non-olefinic products from this reaction were not identified chemically. The presence of phenol was apparent from its odor, and traces of material containing NH and NH₂ groups may have been present as indicated by infrared analysis, but isolation of the expected diphenylphosphoramidate was not accomplished. Isomerization of the olefins was attributed to the presence of acidic products resulting from the reaction. It is evident that changes in the structure of this phosphorylated

amine will be necessary before the pyrolysis can be effectively utilized as a synthetic method.

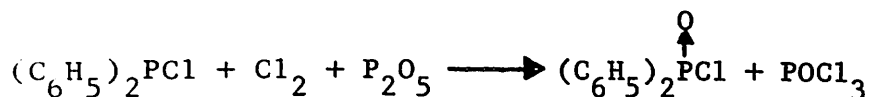
In conclusion, it is apparent that no reaction comparable to the pyrolysis of carboxylic acid esters which involves an organophosphorus intermediate has been reported. Compounds structurally similar to acetates are known (15) but no work has been recorded concerning their thermal stability.



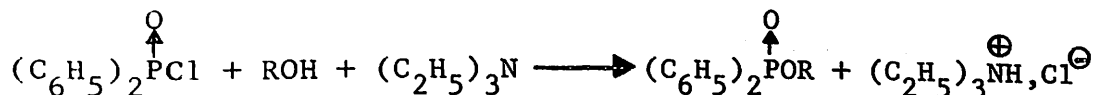
CHAPTER II

DISCUSSION OF RESULTS AND CONCLUSIONS

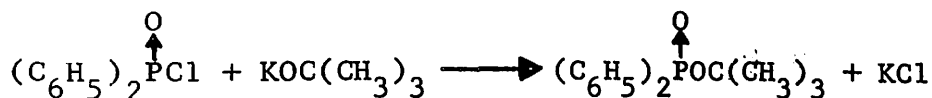
Several esters of diphenylphosphinic acid were prepared. The esterification of diphenylphosphinic chloride, obtained by oxidative



chlorination of diphenylphosphinous chloride in the presence of phosphorus pentoxide, was effected with the appropriate alcohol using



triethylamine as a proton acceptor. The preparation of t-butyl diphenylphosphinate required different conditions which utilized the condensation



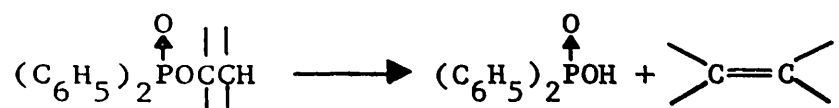
of potassium t-butoxide with diphenylphosphinic chloride. The yields of all esters were excellent (Table II), and the purified compounds gave satisfactory elemental analyses.

Infrared and nuclear magnetic resonance (n.m.r.) spectroscopy gave the expected absorption for these compounds (Table III). Infrared analysis revealed absorption by the phosphoryl group at 8.1 to 8.2 μ

while the P-O-C linkages displayed peaks from 9.6 to 10.95 μ (63, 71). In addition, the P-phenyl bond was observed at 6.93 μ . Examination of the esters by n.m.r. showed complex multiplets for α -protons due to H^1-P^{31} coupling. With isopropyl diphenylphosphinate (Plate XII), a symmetrical eight-line pattern was visible (each line of the pattern showed splitting also) for the tertiary hydrogen. If all the splitting due to H^1-P^{31} coupling and that due to H^1-H^1 coupling were visible in the n.m.r., the compound should show a multiplet of 14 lines. The observed multiplet may arise from the overlap of two heptets, one appearing as a result of CH-CH₃ coupling and the other from H-P³¹ coupling, assuming the J_{CH-CH_3} and $J_{CH-P^{31}}$ were equal (or nearly equal) in value. It has been demonstrated that J_{CH-CH_3} and $J_{H-P^{31}}$ are equal in triethyl phosphite and give rise to a symmetrical five-line grouping without further splitting (8, 41). Similar results were obtained from β -phenethyl diphenylphosphinate (Plate XVII). A symmetrical four-line pattern was observed and was attributed to the overlap of two triplets, one resulting from CH-CH₃ coupling and the other due to H-P³¹ coupling. Additional n.m.r. data is provided in Table III.

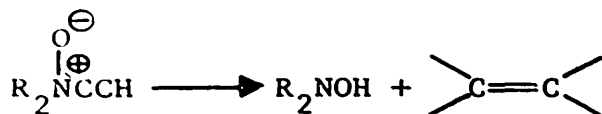
A representative group of these esters were subjected to pyrolysis in a static system under a nitrogen atmosphere at atmospheric pressure and the products (collected at dry ice-acetone temperatures) were analyzed by g.l.c. The group of compounds chosen included esters prepared from primary and secondary alcohols, and from alcohols in which the hydroxyl group was attached to a cyclic hydrocarbon moiety, and also one in which the hydroxyl group was situated in a beta position relative to an aromatic nucleus. The data obtained from these reactions is summarized in Table IV.

A thermometer placed directly in the reaction mixture allowed the temperature to be observed throughout the pyrolysis. The decomposition was found to occur rapidly after initiation and usually required no longer than 15 to 20 minutes to reach completion. The temperatures required for the transformation were quite moderate, ranging from 200 to 250°. The products of this reaction were found to be diphenylphosphinic acid and an olefin derived from the alcohol portion of the ester.

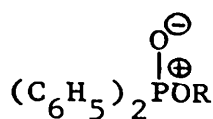


In each experiment it was necessary to filter the olefinic distillate since a small amount of diphenylphosphinic acid was present in the receiver. Surprisingly, g.l.c. analysis of the filtrate showed the olefinic products to be relatively free from other impurities. In some instances no further purification was necessary since the refractive indices of the olefins isolated were essentially the same as those observed with samples of known purity and g.l.c. also indicated a high degree of purity.

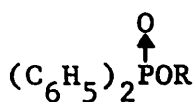
The residue from the decomposition showed little discoloration. In one example, that from cyclohexyl diphenylphosphinate, the observed melting point of the residual material taken immediately after cooling was 189-192° compared to 193-4° for an authentic sample of diphenylphosphinic acid. The acid formed from this particular reaction was recovered and purified (99.7 per cent yield). Although diphenylphosphinic acid is produced in this reaction, apparently it is not acidic enough to induce isomerization of the simple alkenes. The amount of 2-octene present in the pyrolyzate from the decomposition of octyl



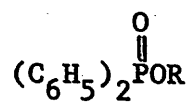
N-O bond present in amine oxides is a true semi-polar bond since no d orbitals are available for nitrogen to utilize and all 2p orbitals are occupied. The C-O bond of the acetate carbonyl group, however, is a covalent bond with $p\pi-p\pi$ bonding between carbon and oxygen. The P-O bond of the phosphoryl group of the phosphinate ester is intermediate in nature between these two extremes (38) and has characteristics of



A



B



C

a semi-polar bond (A) and a covalent bond (C). This results via $p\pi-d\pi$ bonding which is permissible since phosphorus has available 3d orbitals; structure B illustrates this phenomenon. A thorough discussion concerning the phosphoryl and carbonyl groups is available (64). A review is also available which compares the bonding in phosphorus and nitrogen compounds (45).

Kinetic studies have shown that the pyrolyses of acetates (62) and xanthates (61) are unimolecular processes and evidence indicates that the same is true for amine oxides (24). A study of the energy values for the pyrolysis of acetates is indicative of a concerted process involving a cyclic transition state (20). The entropies of activation for t-butyl and isopropyl acetate were found to be -10.7 e.u. and -4.9 e.u. respectively at 800° K (20). Almost identical values were recorded for the corresponding vinyl ethers (19, 21). This is in keeping with a mechanism which involves little freedom in the transition state.

Reactions which proceed by a cyclic transition state are usually found to have high negative values of entropy of activation. Diels-Alder type reactions have such high negative values. Amine oxide decomposition would then be expected to exhibit a negative entropy of activation. No data concerning the kinetics of the similar phosphinate transformation is yet available but this reaction would also be expected to have a negative entropy of activation if a concerted process involving a cyclic transition state were operative.

Although the similarities of the pyrolysis of acetates and amine oxides are well known (29) some differences are important to note. The major difference is the much lower temperature required for the decomposition of amine oxides and reasons for this have been discussed (29). There also appears to be a slight change in the transition state and in the decomposition of amine oxides. The carbon-carbon double bond appears to be formed to a much greater extent than in similar transformations involving acetates though little charge separation is evident (19). In most cases which have been studied, the pyrolysis of acetates and amine oxides give an essentially statistical distribution of olefinic products (19, 33). However, Bailey (5) has shown that in the pyrolysis of *t*-amyl acetate at lower temperatures, Saytzeff elimination actually predominates over Hofmann elimination. At 400° the ratio of 2-methyl-1-butene to 2-methyl-2-butene in the pyrolyzate was 70:30 whereas at 225° the ratio was 42:58.

A comparison of the product distribution is shown in Table I from the pyrolysis of an acetate, an amine oxide, and a phosphinate all derived from secondary alkyl moieties will illustrate the similarities and differences in these three processes.

TABLE I
PRODUCT DISTRIBUTION FROM PYROLYSES

Compound	1-alkene ¹	<u>cis</u> -2-alkene ¹	<u>trans</u> -2-alkene ¹
$\begin{array}{c} \ominus \\ \\ (\text{CH}_3)_2\text{N}^+\text{CH}(\text{CH}_3)\text{C}_2\text{H}_5 \end{array}$	67	12	21
$\begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{COCH}(\text{CH}_3)\text{C}_2\text{H}_5 \end{array}$	57	15	28
$\begin{array}{c} \text{O} \\ \uparrow \\ (\text{C}_6\text{H}_5)_2\text{P}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{C}_6\text{H}_{13} \end{array}$	21	21	58

¹The values are percentage distributions.

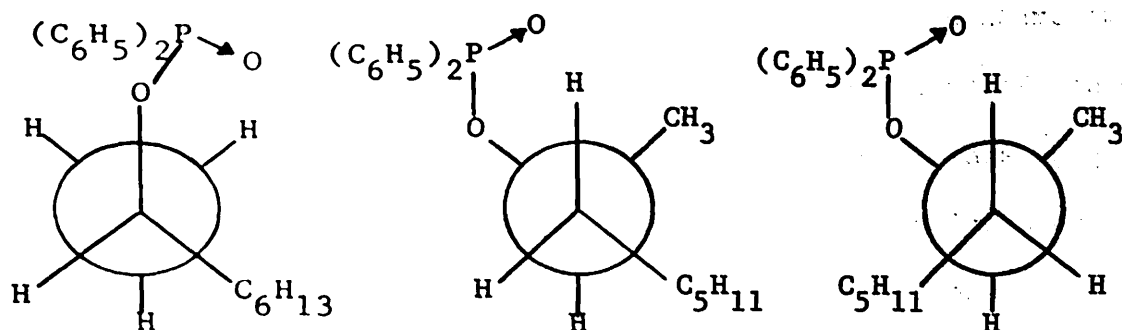
The ratio of 1-alkene to 2-alkene for these three reactions, assuming statistical elimination, is 60:40 and, of course, the trans isomer is expected to predominate over the cis isomer. The acetate ester yields a 57:43 ratio and the amine oxide gives a 67:33 ratio, which are close to the predicted value. However, a ratio of 21:79 is found for the phosphinate ester. This striking difference might tend to rule out the possibility that similar mechanisms are involved but other data concerning the pyrolysis of alkyl diphenylphosphinates seem to suggest these three decompositions are similar in nature.

The distribution of products obtained from the pyrolysis of 2-octyl diphenylphosphinate is similar to that observed from the thermodynamic equilibration of alkenes. Voge and May (74) isomerized isomeric butenes over several acidic catalysts. At temperatures approximating those used

for the decomposition of 2-octyl diphenylphosphinate, the butene isomerization yielded 14.5 per cent 1-butene, 33.2 per cent cis-2-butene, and 50.3 per cent trans-2-butene. The ratio here of 1-alkene to 2-alkene is 14.5:85.5 (compared to 21:79 for the pyrolysis reaction). Similar results using iodine as an initiator for the isomerization have been reported (14). The possibility thus arises that the thermal decomposition might occur through a carbonium-ion intermediate. Such an intermediate is not indicated by data from the pyrolysis of octyl diphenylphosphinate, which gave high yields of 1-octene. Had a carbonium ion been generated, it would have been expected to rearrange to the more stable secondary carbonium ion which would have resulted in the formation of isomeric octenes. This was not observed. Only 1- and 2-octene were found in the distillate from the pyrolysis of 2-octyl diphenylphosphinate. If a carbonium ion mechanism were operative, other isomeric octenes should have been present. No 3-octene or 4-octene were found by g.l.c. analysis. From these results, it appears that the products from this reaction are formed as a result of kinetic control and not from isomerization during the reaction. In support of this conclusion, is the observation that at the boiling point of 1-octene and cis-2-octene, no isomerization occurs in the presence of diphenylphosphinic acid. When cis-2-octene was held at reflux for 2.5 hours (123-5°) in the presence of diphenylphosphinic acid, g.l.c. analysis on the recovered olefin was unchanged.

Examination of molecular models suggests there is little steric compression in the conformations required to produce either 1-octene or trans-2-octene from the 2-octyl ester. As expected, a more pronounced effect is evident for the conformation which leads to the formation of cis-2-octene.

Consideration of Newman projections (Fig. 1) indicates there are fewer



A (Gives 1-isomer)

B (Gives cis isomer)

C (Gives trans isomers)

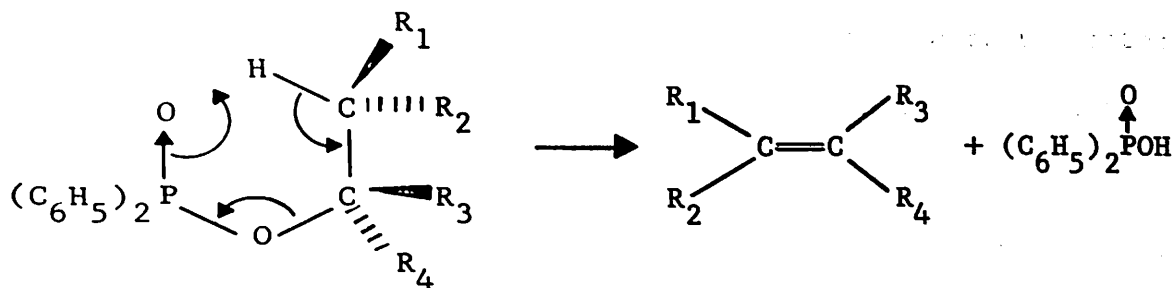
Figure 1. Newman Projections of Conformations Leading to Observed Olefin Distribution

nonbonding interactions in C than in B. However, on steric grounds alone, A would appear to be the preferred conformation. Geometric requirements for six-membered rings containing phosphorus may not necessitate coplanarity of all member atoms because of the size of the phosphorus atom. A survey has been made concerning the conformations of phosphorus ring compounds and the effects of the conformation on the infrared stretching frequencies (32). Possible gauche interactions between the alkyl groups are offered to explain the predominance of trans-2-octene over cis-2-octene but this does not rationalize the over-all predominance of 2-isomer. From the data available it is postulated that the transition state leading to 2-octene is inherently favored over that leading to 1-octene in the pyrolysis of 2-octyl diphenylphosphinate.

The pyrolysis of β -phenethyl diphenylphosphinate yielded styrene (quantitative) and no tendency of this product to polymerize was noted during the reaction. The absence of polymerization during the actual reaction tends to rule out any mechanism involving homolytic cleavage of the ester bond and production of free radicals. It is also important

to note that the distillation of α -naphthyl diphenylphosphinate was accomplished without decomposition even though the temperature at the distilling head was in excess of 250° and the temperature of the contents of the distillation flask was probably close to 300° . This suggests that in the absence of active β -hydrogen atoms, no pyrolysis of the nature described herein occurs with the phosphinate esters.

The existing data is most consistent with and is reasonably viewed as to include a mechanism with a cyclic transition state in the pyrolysis



of alkyl diphenylphosphinates giving rise to olefins by a concerted process. The degree of bond-breaking and bond-formation in the transition states cannot be wholly defined. Arguments given tend to discredit the possibility of a radical intermediate and the formation of fully ionic intermediates does not appear justifiable in view of the results obtained from pyrolysis and of the isomerization studies with the octenes. The predominance of Saytzeff products in the pyrolysis of 2-octyl diphenylphosphinate seems anomalous but even in this reaction, no evidence is present which is in serious disagreement with the postulated sequence. Bailey observed that even with acetates, pyrolysis at lower temperatures sometimes gives predominantly Saytzeff products (5).

Thermolysis of cholesteryl diphenylphosphinate resulted in a quantitative conversion but gave a mixture which showed two spots with thin-layer chromatography (t.l.c.) on silica gel with petroleum ether. Instrumental evidence (infrared; ultraviolet, Plate XXI; nuclear magnetic

resonance spectra) indicates that at least one and probably both of these components are conjugated dienes. The material possessed an observed positive rotation, but from the absorption spectra in the ultraviolet, one of the products is believed to be $\Delta^{3,5}$ -cholestadiene (36).

This reaction has several advantages over other reported pyrolytic olefin-forming reactions. The starting material is much easier to obtain than in most recorded elimination processes. The preparation of phosphinate esters is readily accomplished and in most cases the esters are fairly easy to purify although purification may not be necessary in most preparative work.

The actual decomposition of the phosphinate esters is very simple and no special equipment of the type required for the pyrolysis of acetates is required. Decomposition is rapid with the esters and requires only 15 to 20 minutes for completion from the time of initiation. The products are surprisingly free from impurities and in some cases require no further purification, and isolation of the pure products is easily accomplished. Other pyrolytic olefin syntheses from phosphorus compounds give rise to extensive isomerization (6, 9, 11) and skeletal rearrangements (9, 11, 27). Neither of these factors appears to be important in the pyrolysis of phosphinate esters.

Since only moderate temperatures (200-250°) are required for the decomposition of alkyl diphenylphosphinates, the possibility of isomerization and skeletal rearrangements resulting from thermal excitation is minimized. Acetate pyrolysis requires high temperatures (29) as does the thermolysis of tertiary phosphines oxides (6).

The by-product of this reaction, diphenylphosphinic acid, is a

high-melting solid (194-5°) and is very stable thermally. The material is practically insoluble in most organic liquids and is thus easily removed from the pyrolyzate. In cases where the olefin is not volatile, simple washing with bicarbonate solution will effectively remove the acid since it reacts to give the diphenylphosphinic acid anion. This is possible when the olefin is not sensitive to weakly basic solutions.

The pyrolysis of alkyl diphenylphosphinates appears to an extremely useful synthetic method for the preparation of olefins. Further study concerning the possibility of obtaining sensitive olefins and strained dienes should determine the actual scope of this pyrolytic elimination reaction. The effect of substituents on the aromatic nuclei attached to phosphorus in the ester would also seem to be relevant in determining the ease of elimination in this reaction. More information is needed before it can be confirmed that the transformation actually follows a predominantly cis steric course. This can be achieved by the analysis of the products resulting from the pyrolysis of cis-2-methylcyclohexyl diphenylphosphinate. By the use of the methods employed in the mechanistic studies of other pyrolytic elimination reactions, evaluation of the parameters controlling the pyrolysis of the esters of diphenylphosphinic acid should be greatly facilitated.

CHAPTER III

EXPERIMENTAL^{1,2,3,4,5,6,7}

Preparation of Diphenylphosphinic Chloride.⁸ A cylinder of chlorine was connected through a trap to a 3-l. three-necked flask equipped with a mechanical stirrer, a condenser with a drying tube, a thermometer, and a fritted glass delivery tube for passing in chlorine gas. To the flask was added 1323.6 g. (6.0 moles) of diphenylphosphinous chloride (neat).

¹All melting points are corrected and all boiling points are uncorrected.

²The infrared spectra were determined on Beckman IR-5 and IR-5A spectrometers as films on sodium chloride cells 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 an internal standard.

⁴Gas chromatographic analyses were performed using an Aerograph Hy-Fi Model A-550 with a hydrogen flame ionization detector from Wilkins Instrument and Research, Inc., Walnut Creek, California.

⁵The microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

⁶The ultraviolet spectra were obtained from a Cary Model recording spectrophotometer using quartz cells.

⁷Grateful acknowledgment is made to Dr. E. J. Eisenbraun and API Project 58A for furnishing some of the hydrocarbon samples.

⁸This method was adapted from a procedure obtained from Victor Chemical Company (personal communication). We thank Dr. W. D. Ebert and Dr. E. L. Kubiak for generous samples of diphenylphosphinous chloride.

Phosphorus pentoxide (270 g., 1.9 moles) was slowly added to the flask with gentle stirring and a suspension of the solid in the acid chloride was obtained. With vigorous stirring, chlorine gas was passed into the flask through the fritted glass tube at such a rate that the exothermic reaction produced a slow rise in temperature. When the temperature reached 70° (45 minutes), a water bath was applied and the temperature was held between 70 and 70° . Chlorination of the mixture was continued until a greenish color developed in the reaction mixture (color change occurred abruptly). A slow stream of chlorine gas was then used while the mixture was heated slowly to 110° at which point the chlorination was terminated. The mixture was then boiled for 1.5 hours (maximum temperature attained was 145°). Distillation of the phosphorus oxychloride was accomplished at aspirator pressure using a potassium hydroxide-calcium oxide trap between the apparatus and the water aspirator. The mixture was heated ($71-76^{\circ}$) until 250 ml. of phosphorus oxychloride had been collected and the distillation was terminated. Transfer of the reaction mixture to a 2-l. distillation flask was accomplished under anhydrous conditions. Diphenylphosphinic chloride was distilled in vacuo [$165-70^{\circ}/0.35-0.4$ mm; lit. (43) $135-6^{\circ}/0.07$ mm]; yield 1213.7 g. (85.6 per cent) [n_D^{26} 1.6095; lit. (43) n_D^{20} 1.6068].

Preparation of Cyclohexyl Diphenylphosphinate (Method A). A 1-l., three-necked flask was equipped with a mechanical stirrer, a condenser with drying tube, a thermometer, and a pressure-equalizing addition funnel connected to a supply of anhydrous nitrogen. After purging the system with nitrogen, 40.04 g. (0.40 mole) of cyclohexanol and 50.57 g. (0.50 mole) of triethylamine were placed in the flask and diluted with a total of 350 ml. of anhydrous ether. The funnel was charged with

78.80 g. (0.333 mole) of diphenylphosphinic chloride diluted with 100 ml. of anhydrous ether. Vigorous stirring was maintained while the diphenylphosphinic chloride-ether solution was added. External cooling (ice-salt bath) was employed during the first phase of the addition but was discontinued because the reaction was only moderately exothermic. At the end of the addition process (30 minutes), the reaction mixture was allowed to warm to room temperature and heat was applied. The rapidly stirred, heterogeneous mixture was held at reflux (39°) for 1 hour. After cooling to room temperature, the precipitate (triethylamine hydrochloride) was removed by filtration and washed four times with 100-ml. portions of boiling anhydrous ether. The ether washings and the filtrate were combined and concentrated at aspirator pressure. Filtration of the solid which was deposited from the solution was necessary when approximately three-fourths of the solvent had been removed because the material was not appreciably soluble in ether. The remaining solution was evaporated to dryness and the combined solid (89.8 g., m.p. $110-4^{\circ}$) was recrystallized. After dissolving the solid in hot benzene, heptane was added slowly until the ester began precipitating from the solution, and then the mixture was set aside to cool. This mixed solvent system was about 75:25 of heptane:benzene. Cyclohexyl diphenylphosphinate (78.5 g.; 78.5 per cent) obtained was characterized by its elemental analysis, by its nuclear magnetic resonance (n.m.r.) spectrum (Plate XIV), and by its infrared spectrum (Plate IV). Table II shows the principal infrared absorption bands and the chemical shifts for the n.m.r. spectrum of the ester. Diphenylphosphinic acid was obtained from the filtered triethylamine hydrochloride; it was apparently formed by hydrolysis of the acid chloride during the reaction

and precipitated because of its insolubility in ether. It was characterized by its melting point [$192-3^{\circ}$; lit. (51) $194-5^{\circ}$], and a mixture melting point determination with an authentic sample showed no depression. The amount of diphenylphosphinic acid was not determined.

Preparation of α -Naphthyl Diphenylphosphinate (Method B). A 1-1. three-necked flask was equipped with a mechanical stirrer, a condenser with drying tube, a thermometer, and a pressure-equalizing addition funnel connected to a supply of anhydrous nitrogen. The entire system was purged with nitrogen and the flask was charged with 23.07 g. (0.160 mole) of freshly distilled α -naphthol dissolved in 200 ml. of benzene and 25.30 g. (0.250 mole) of triethylamine diluted with 100 ml. of benzene. Diphenylphosphinic chloride (34.37 g.; 0.145 mole) was diluted with 100 ml. of benzene and added to the addition funnel. The temperature of the solution in the flask at the time the addition was started had reached 41° . When the reagents were added to the flask initially, the mixing procedure resulted in an exothermic process. The addition of the acid chloride to the rapidly stirred contents of the flask required 20 minutes during which time the temperature rose from 41 to 57° . With continuous stirring, the mixture was heated to 67° and then held between 67 and 71° for 1.5 hours. The entire reaction mixture was transferred to a separatory funnel after cooling to room temperature. Although the mixture was colorless at the beginning of the reaction sequence, at the time it was placed in the separatory funnel, it had developed an intense reddish-brown color like that of the unpurified α -naphthol. This was evidently a result of oxidation during the reaction to produce naphthoquinones. Four 100-ml. portions of aqueous sodium hydroxide (10 per cent) were used to wash the reaction mixture.

This method was found to remove the excess diphenylphosphinic chloride and the hydrochloric acid from the hydrolysis of triethylamine hydrochloride as well as any unreacted α -naphthol. The aqueous sodium hydroxide was extracted three times with 100-ml. portions of benzene and the combined organic layers were dried over anhydrous magnesium sulfate. Concentration of the dried solution to approximately 100 ml. was accomplished on a steam bath at aspirator pressure. The addition of 150 ml. of heptane to the hot benzene solution precipitated the ester when the benzene-heptane solution was cooled and then chilled. The crude material had a definite brownish appearance and repeated recrystallizations from benzene-heptane did not remove the color. A yield of 46.34 g. (92.7 per cent) of α -naphthyl diphenylphosphinate (m.p. 123-4 $^{\circ}$) was obtained. Distillation (150-2 $^{\circ}$ /1.1 mm.) of a sample of this material yielded a white crystalline material; m.p. 123-4 $^{\circ}$. The α -naphthyl diphenylphosphinate was characterized by its elemental analysis, by its infrared spectrum (Plate IX), and by its n.m.r. spectrum (Plate XIX). Table II shows the principal absorption bands in the infrared and the n.m.r. data for this compound. Acidification [aqueous hydrochloric acid (10 per cent)] of the sodium hydroxide solution which was used to wash the reaction mixture did not precipitate any diphenylphosphinic acid when the water solution was chilled overnight.

Preparation of 2-Octyl Diphenylphosphinate (Method C). A 1-1. three-necked flask was equipped with a mechanical stirrer, a condenser with a drying tube, a thermometer, and a pressure-equalizing addition funnel connected to a supply of anhydrous nitrogen. After the system had been purged with nitrogen, 39.41 g. (0.303 mole) of 2-octanol

(diluted with 150 ml. of anhydrous ether) and 50.60 g. (0.500 mole) of triethylamine (diluted with 150 ml. of anhydrous ether) were added to the flask. Diphenylphosphinic chloride (94.64 g.; 0.400 mole) was diluted with 100 ml. of anhydrous ether and added to the addition funnel. The addition of the diphenylphosphinic chloride-ether solution to the vigorously stirred contents of the flask required 30 minutes, during which time the temperature rose from 19 to 31°. Heat was applied and the heterogenous mixture was held at reflux (39°) for 2 hours. After cooling to room temperature, the reaction mixture was transferred to a separatory funnel. Aqueous sodium bicarbonate solution (10 per cent) was used to neutralize the hydrochloric acid from the hydrolysis of the triethylamine hydrochloride. When two 200-ml. portions of this solution failed to destroy all of the solid which was present in the reaction mixture, the solid was removed by filtration. This solid material was washed with distilled water and set aside for characterization. A 100-ml. portion of aqueous sodium hydroxide (10 per cent) was then used to wash the reaction mixture to insure removal of all of the unreacted diphenylphosphinic chloride. The triethylamine which was used in excess was removed from the base-extracted reaction mixture by consecutive washings with three 100-ml. portions of 3 N aqueous hydrochloric acid. Distilled water (3 x 100 ml.) was employed to remove all traces of the hydrochloric acid from the organic phase. After drying the organic layer over magnesium sulfate, the ether was removed under aspirator pressure. The residual oil was transferred to a distilling flask equipped with a magnetic stirrer and a capillary tube connected to a nitrogen supply. The capillary tube was immersed in the vigorously stirred liquid and with nitrogen passing through the mixture, it was

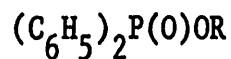
heated in vacuo to $90^{\circ}/3.5$ mm. over a 1-hour period. Heating was continued and the temperature increased from 95° to $125^{\circ}/2.5$ mm. during an additional 2 hours and then terminated. This procedure effectively removed the solvent and any unreacted 2-octanol and was necessary because the ester underwent decomposition below the temperature required for distillation. Thin layer chromatography (t.l.c.) showed a single spot on the silica gel with low-boiling petroleum ether, using iodine vapor as the developer. 2-Octyl diphenylphosphinate (72.5 g.; 72.5 per cent) was further characterized by elemental and instrumental analysis [n.m.r. (Plate XVI) and infrared spectra (Plate VI)]. The refractive index of this compound was determined ($n_D^{28^{\circ}}$ 1.5302). Table II gives pertinent information obtained from n.m.r. and infrared analyses. The solid which was filtered from the reaction mixture after treatment with sodium bicarbonate was characterized as follows. Infrared analysis showed absorption for P=O (8.1μ) and P-C₆H₅ (6.95μ) but showed no peak for P-O-C, which is at 10.1μ for 2-octyl diphenylphosphinate. One absorption band at 10.4μ was indicative of a P-O-P anhydride bond (13). The n.m.r. spectrum of this solid material showed no absorption for protons bonded to aliphatic carbon, but did show a strong band for aromatic hydrogen. Diphenylphosphinic acid reacted rapidly and dissolved in aqueous sodium bicarbonate, whereas this solid material did not. However, the action of aqueous sodium hydroxide (10 per cent) on the isolated solid material produced an extremely exothermic reaction and upon acidification of the basic solution with aqueous hydrochloric acid, diphenylphosphinic acid was obtained. From this data the solid was established as the anhydride of diphenylphosphinic acid [m.p. $142-3^{\circ}$; lit. (60) 143°] and was postulated to form in the original

condensation via the reaction of diphenylphosphinic chloride with diphenylphosphinic acid (from hydrolysis of the acid chloride) in the presence of triethylamine.

Preparation of Potassium t-Butoxide (30). To a 1-l. three-necked flask equipped with a mechanical stirrer, a condenser, a thermometer, and a pressure-equalizing addition funnel connected to a supply of anhydrous nitrogen, was added 300 ml. of t-butyl alcohol. Potassium metal (11.73 g.; 0.300 g.-atom) was cut into small pieces (3-5 mm. in diameter) and added slowly to the vigorously stirred alcohol. When the last piece of potassium had dissolved, the system was flushed with nitrogen and the contents of the flask were heated slowly to reflux and then cooled to 35°.

Preparation of t-Butyl Diphenylphosphinate (Method D). To the addition funnel of the previously described apparatus was added diphenylphosphinic chloride (43.13 g.; 0.182 mole) diluted with 100 ml. of benzene. The addition of the acid chloride-benzene solution was performed under nitrogen while the material in the flask was stirred rapidly. During the addition process (30 minutes), the temperature rose from 35 to 56°. The mixture was then heated at reflux (69-71°) for 1.5 hours and after cooling was transferred to a separatory funnel. Two 150-ml. portions of aqueous ammonium chloride (15 per cent) were used to destroy the excess potassium t-butoxide. After extracting the aqueous solution of ammonium chloride with benzene (4 x 100 ml.) the combined organic layers were washed with two 150-ml. portions of distilled water and dried over magnesium sulfate. The solvent was removed at aspirator pressure until a volume of approximately 100 ml. remained. Heptane (100 ml.) was added to this hot solution and the precipitate

PREPARATION AND PROPERTIES OF ALKYL DIPHENYLPHOSPHINATES



R	Yield (per cent)	Method of Preparation	Physical Data	Analysis (per cent)						Reference
				Calculated			Found			
				C	H	P	C	H	P	
CH_3- (I)	92.5	B	b.p. $178^\circ/2.4$ mm. ²							5
$i\text{-C}_3\text{H}_7-$ (II)		A	m.p. $97-9^\circ$ ³	69.22	6.58	11.90	70.12	6.33	11.72	
$t\text{-C}_4\text{H}_9-$ (III)	80.1	D	m.p. $111-2^\circ$	70.06	6.98	11.29	70.28	6.94	11.34	
$\text{C}_6\text{H}_{11}-$ (IV)	78.5	A	m.p. $119-20^\circ$	71.98	7.05	10.31	71.86	6.80	10.36	
$1\text{-C}_8\text{H}_{17}-$ (IV)	98.7	C	$n_D^{29^\circ}$ 1.5318 ⁴	72.72	8.24	9.38	72.38	8.21	9.62	7
$2\text{-C}_8\text{H}_{17}-$ (VI)	72.5	C	$n_D^{29^\circ}$ 1.5302	72.72	8.24	9.38	72.38	8.39	9.48	
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2-$ (VII)	88.4	B	m.p. $65-6^\circ$	74.52	5.94	9.61	74.45	6.20	9.84	
C_6H_5- (VIII)	97.9	B	m.p. $135-6^\circ$ ⁵							8
$1\text{-C}_{10}\text{H}_7-$ (IX)	92.7	B	m.p. $123-4^\circ$	76.74	4.98	9.00	76.45	4.91	9.10	
Cholesteryl- (X)	80.1	B	$[\alpha]_D$ -20.1° (CHCl_3) m.p. $153-4^\circ$	79.82	9.45	5.28	79.50	9.43	5.37	

¹This title refers to the four methods found in the experimental part which describes the preparation of these esters.

²The reported value (16) is $140^\circ/0.34$ mm.

³The literature (2) gives a melting point of $97-9^\circ$.

⁴The recorded (70) index of refraction for this compound is $n_D^{25^\circ}$ 1.5330.

⁵The melting point reported (59) for this material is $135-6^\circ$.

TABLE III

N.M.R. AND I.R. SPECTRAL CHARACTERISTICS OF ALKYL DIPHENYLPHOSPHINATES

Compound	Infrared Bands (μ)		Chemical Shifts (δ) ¹					
	P→O	P=O-C	CH ₃	CH ₂	CH	-OCH	-OCH ₂ -	C ₆ H ₅
I	8.1	9.6	3.70-d ²					7.25-8.20-m
II	8.2	10.1	1.28-d		4.64-o			7.28-8.25-m
III	8.2	10.2	1.45-s					7.25-8.05-m
IV	8.2	10.1		1.57-m	4.45-m			7.28-8.25-m
V	8.1	10.2		1.25-m ³				7.25-8.15-m
VI	8.1	10.2		1.30-m ³	4.33-m			7.25-8.15-m
VII	8.1	9.9		3.00-t			4.20-q	7.15-8.10-m
VIII	8.2	10.85						6.92-8.28-m
IX	8.2	10.95						7.08-8.45-m
X	8.2	9.8		1.60-m ³	4.25-m	5.20-m		7.25-8.15-m

¹The chemical shifts are given in p.p.m. (δ) downfield from internal standard tetramethylsilane (T.M.S.).

²The lower case letters s, d, t, q, o, and m refer to the multiplicity of the signal and signify singlet, doublet, triplet, quartet, octet, and multiplet, respectively.

³The methyl protons were not resolvable from the methylene protons in this multiplet.

which was deposited upon standing was collected by filtration. There was obtained 40.05 g. (80.1 per cent) of t-butyl diphenylphosphinate (m.p. $111-2^{\circ}$). This compound was characterized by instrumental methods [n.m.r. (Plate XIII) and infrared (Plate III)], and by elemental analysis. Table II gives the principal infrared absorption bands and the chemical shifts from the n.m.r. analysis.

Pyrolysis of Cyclohexyl Diphenylphosphinate. The following procedure is typical of that used for the thermolytic decomposition of those alkyl diphenylphosphinates which produced volatile alkenes. Table IV lists the pertinent information for these decomposition reactions. Cyclohexyl diphenylphosphinate was heated (125°) in a vacuum oven at 28.8 pounds (versus air) for 1 hour. This freshly fused material (14.45 g.; 0.0481 mole) was transferred directly to a 100-ml. three-necked flask equipped with a magnetic stirrer, a thermometer, and a nitrogen inlet tube connected to a supply of anhydrous nitrogen. A 4-in. adapter was inserted into the center neck of the flask and to this was attached a one-piece pyrolysis trap system. This apparatus consisted of three 20-ml. receivers connected in series and designed in such a way that the receivers could be immersed in dry ice acetone baths. The outlet tube of the trap system was equipped with a silica gel drying tube. After the receivers were in place, anhydrous nitrogen was allowed to flow through the entire system to remove all traces of water vapor. The receivers were then immersed in 1-l. Berzelius beakers filled with dry ice and acetone. A heating mantle filled with small-mesh sea sand was used as the heat exchanger for the pyrolysis flask. With a slow stream of nitrogen passing through the system, the contents of the flask were heated slowly until a melt was achieved and from this

time until the termination of the reaction, vigorous stirring was maintained. The temperature (observed directly from the thermometer immersed in the fused material) was increased quickly to 195° by means of a Variac. The Variac was then adjusted to give a gradual increase in temperature. At 200° the decomposition became evident and vapor could be observed passing into the first receiver. Glass wool was quickly placed around the pyrolysis flask and the vertical and horizontal delivery tubes. For 15 minutes the temperature was held at $200-205^{\circ}$ and during this interval, gaseous material passed rapidly into the receiver system. Apparently the reaction was complete within this short time because upon further heating (from 205° to 230° in 20 minutes) no additional condensation was observed. The apparatus was then disassembled and the receivers were emptied. A very small amount of solid material which was present in the first receiver was removed by filtration. Gas liquid chromatography (g.l.c.) using a 6-ft. x 1/8-in. column packed with 5 per cent silicone 30 on 60/80 mesh acid-washed Chromosorb G pretreated with dimethyldichlorosilane showed one major component and a trace amount of another more volatile compound. The infrared spectrum (film on sodium chloride cells) of this distillate was identical to that of an authentic sample of cyclohexene; yield 3.56 g., 96.2 per cent. Refractive index measurements on the distillate and a sample of reagent grade Fisher A.C.S. cyclohexene gave n_D^{22} 1.4462 and n_D^{22} 1.4455, respectively [lit. (12) $n_D^{15.1}$ 1.4492]. In a similar reaction sequence on a larger scale (36.67 g.; 0.122 mole of cyclohexyl diphenylphosphinate), a quantitative yield (99.6 per cent) of cyclohexene was isolated. Table IV gives a summary of the results from all the pyrolysis reactions. The solid residue in the pyrolysis flask

showed an observed melting point of $189-92^{\circ}$ and was only slightly discolored. A 100-ml. portion of an aqueous sodium hydroxide solution (10 per cent) was used to dissolve the solid residue. This aqueous solution was washed thoroughly in a separatory funnel with a solution of ether-benzene (100 ml. -25 ml.). After extraction of the organic layer with one 50-ml. portion of distilled water, the combined water layers were acidified by the addition of concentrated hydrochloric acid solution. When the further addition of hydrochloric acid caused no additional precipitation of the solid material, the mixture was chilled and filtered. Diphenylphosphinic acid [m.p. 19203.5° ; lit. (51)] was obtained in high yield (99.7 per cent, 10.47 g.) after drying 5 hours at 110° . The solid removed from the pyrolysis receiver as well as some solid which was obtained from the horizontal delivery tube melted from 180 to 192° .

Pyrolysis of Cholesteryl Diphenylphosphinate. To the pyrolysis flask of an apparatus identical to that described in the previous experiment was added 15.92 g. (0.0271 mole) of cholesteryl diphenylphosphinate. After flushing the system with anhydrous nitrogen, the receivers were immersed in dry ice-acetone baths. Heat was applied and stirring was begun when the material melted (155°). During the first 45 minutes the temperature was increased to 255° . The reaction mixture was then held at $255-257^{\circ}$ for another 20 minutes. The material was then heated quickly (15 minutes) from 257° to 270° and the reaction was terminated. Examination of the pyrolysis receivers showed no condensate present. A small amount of solid material was observed on the walls of the vertical and horizontal portions of the delivery tube. After the pyrolysis flask had cooled to room temperature, successive

additions of a mixture of aqueous sodium hydroxide solution (10 per cent) and ether to the residue dissolved the material. Six portions (50 ml. of ether and 25 ml. of sodium hydroxide solution) were used and each time the contents of the flask were vigorously stirred. All of the pyrolysis residue was thus transferred to a separatory funnel and the layers were separated. The organic layer was then extracted successively with 10 per cent aqueous sodium hydroxide (2 x 25 ml.) and distilled water (3 x 50 ml.). After drying over anhydrous magnesium sulfate, the organic layer was concentrated at aspirator pressure on a steam bath to a viscous oil. This residue was transferred to a column filled with 200 g. of activated alumina (Merck acid-washed) and eluted with low-boiling petroleum ether. Fractions of 50 ml. were taken and, after concentration, all hydrocarbon fractions (as determined by infrared analysis) were combined. Solvent was then removed in vacuo (3.0 mm.), a capillary tube being used to pass anhydrous nitrogen across surface of the residue. After 3 hours on the vacuum system, crystallization did not occur and the material (9.53 g.) was rechromatographed similarly on 100 g. of activated alumina (Merck acid-washed). Repeated attempts failed to cause the material to crystallize after the second chromatography. A sample of this substance (3.174 g.) was dissolved in 10 ml. of chloroform and optical rotation was determined. An average of six readings using a 5 ml. cell gave $\{[\alpha]_D^{24} + 13^\circ (\text{CHCl}_3)\}$. Thin layer chromatography (t.l.c.) on silica gel with low-boiling petroleum ether showed two spots after development with iodine vapor. The material exhibited no absorption for P-O, P-O-C, or P-phenyl as indicated by infrared analysis, nor was there any absorption characteristic of an alcohol group. The spectrum showed slight absorption in

the 6.1 μ region where carbon-carbon double bonds usually exhibit their stretching frequencies. Characteristic absorption for carbon-hydrogen deformation common to alkenes at 10.4 and 14.5 μ were observed. Thus it appears that the material obtained from the thermolytic decomposition of cholesteryl diphenylphosphinate is composed of unsaturated hydrocarbons. The ultraviolet spectrum (Plate XXI) of a sample of this material in cyclohexane (2.6×10^{-4} g./ml.) showed strong absorption with maxima at 237 $m\mu$ (shoulder at 230 $m\mu$). These bands are characteristic of conjugated dienes but are different from those expected for the products of this decomposition reaction. One of the products is believed to be 3,5-cholestadiene, lit. (36) λ_{\max} 235 $m\mu$, 2-propanol, but since the specific rotation was positive ($+13^\circ$), it is probably present in less than 50 per cent lit. (69) $\alpha_D^{20} - 129^\circ$ (CHCl_3). The other decomposition product from the reaction was not fully characterized.

Gas Liquid Chromatographic Analysis of the Pyrolysate from the Thermolysis of 2-Octyl Diphenylphosphinate. The following procedure is typical of the methods required for the quantitative analyses of the decomposition products from the pyrolysis of the alkyl diphenylphosphinates. Several column packings and substrates were investigated (20 per cent Apiezon L on 60/80-mesh, acid-washed Chromosorb W; 10 per cent dibutyl phthalate on Fluoropak; 22 per cent silver nitrate-glycerol on Celite G; 15 per cent X E 60 on 80/100-mesh, acid-washed Chromosorb W) but best results were obtained using a 6-ft. x 1/8-in. column packed with 5 per cent silicone 30 on 60/80-mesh, acid-washed Chromosorb G which had been pre-treated with dimethyldichlorosilane. An injection size of 0.5 μ l was maintained throughout the entire study. The nitrogen and hydrogen gauge pressures were 5 and 9 lbs, respectively. A standard

olefin solution was prepared by mixing pure 1-octene with a mixture of cis- and trans-2-octene, the analysis of which was known.

Wt. of 1-octene: 0.9150 g.; percentage (by wt.) = 24.0

Wt. of cis-2-octene: 0.8423 g.; percentage (by wt.) = 22.8

Wt. of trans-2-octene: 2.0621 g.; percentage (by wt.) = 53.2

This mixture was then injected on the gas chromatograph and the chromatograms were measured by triangulation. A typical set of calculations is given for the comparison of actual measurements with the known composition of the olefin mixture.

Total area = 4119 mm.²

Area of 1-octene = 945 mm.²

Area of cis-2-octene = 2331 mm.²

Area of trans-2-octene = 943 mm.²

$$\frac{945 \text{ mm.}^2}{4119 \text{ mm.}^2} \times 100 = 22.9 \text{ per cent 1-octene (theory, 24.0)}$$

$$\frac{2331 \text{ mm.}^2}{4119 \text{ mm.}^2} \times 100 = 56.6 \text{ per cent } \underline{\text{cis}}\text{-2-octene (theory, 53.2)}$$

$$\frac{943 \text{ mm.}^2}{4119 \text{ mm.}^2} \times 100 = 22.9 \text{ per cent } \underline{\text{trans}}\text{-2-octene (theory, 22.8)}$$

Because of the inability to completely resolve cis- and trans-2-octene by g.l.c., a second standard olefin mixture was prepared using only 1-octene and cis-2-octene (these were easily resolved). An inert hydrocarbon (cyclohexane) was used to dilute the isomeric octenes to achieve the approximate concentrations which were found in the actual decomposition reactions.

Wt. of 1-octene: 1.799 g.; Wt. per cent = 21.0

Wt. of cis-2-octene: 2.1891 g.; Wt. per cent = 26.1

Wt. of cyclohexane: 3.8519 g.; Wt. per cent = 52.9

The percentage distribution of 1-octene and cis-2-octene in the standard solution was calculated.

$$\frac{1.7999 \text{ g.}}{3.9890 \text{ g.}} \times 100 = 45.1 \text{ per cent}$$

$$\frac{3.1891 \text{ g.}}{3.9890 \text{ g.}} \times 100 = 54.9 \text{ per cent}$$

Injections were made and the results obtained from average measurements of the chromatograms gave the following data.

Average 1-octene found = 45.4 per cent (theory, 45.1)

Average cis-2-octene found = 54.6 per cent (theory 54.9)

From the results of these two studies, it is evident that when equal weights of the isomeric octenes are used, measurement of the corresponding areas are equal. Using this information, the product distribution for the decomposition of 2-octyl diphenylphosphinate was determined. Because of the inability to completely resolve the cis and trans isomers of 2-octene by g.l.c., two methods are described and the results are compared. A tracing of a typical chromatogram (Figure 2) is pictured and the symbols which are given are used in the description. The area of 1-octene (A) was measured by multiplying its peak height times its width at half height (68). The area of trans-2-octene was taken as the area of (B + C + D + F) - (D). The area of B + C + D + F was obtained by measuring the peak height of this surface and the width at half height of this same surface. The area of cis-2-octene was taken as the area of (C + D + E + G) - (C). The area of this surface was obtained using similar measurements. The triangles C and D were then measured and these values were properly subtracted.

$$\text{Area of 1-octene (A)} = 55 \text{ mm.} \times 14.5 \text{ mm.} = 798 \text{ mm.}^2$$

$$\text{Area of (B + C + D + F)} = 96 \text{ mm.} \times 24 \text{ mm.} = 2304 \text{ mm.}^2$$

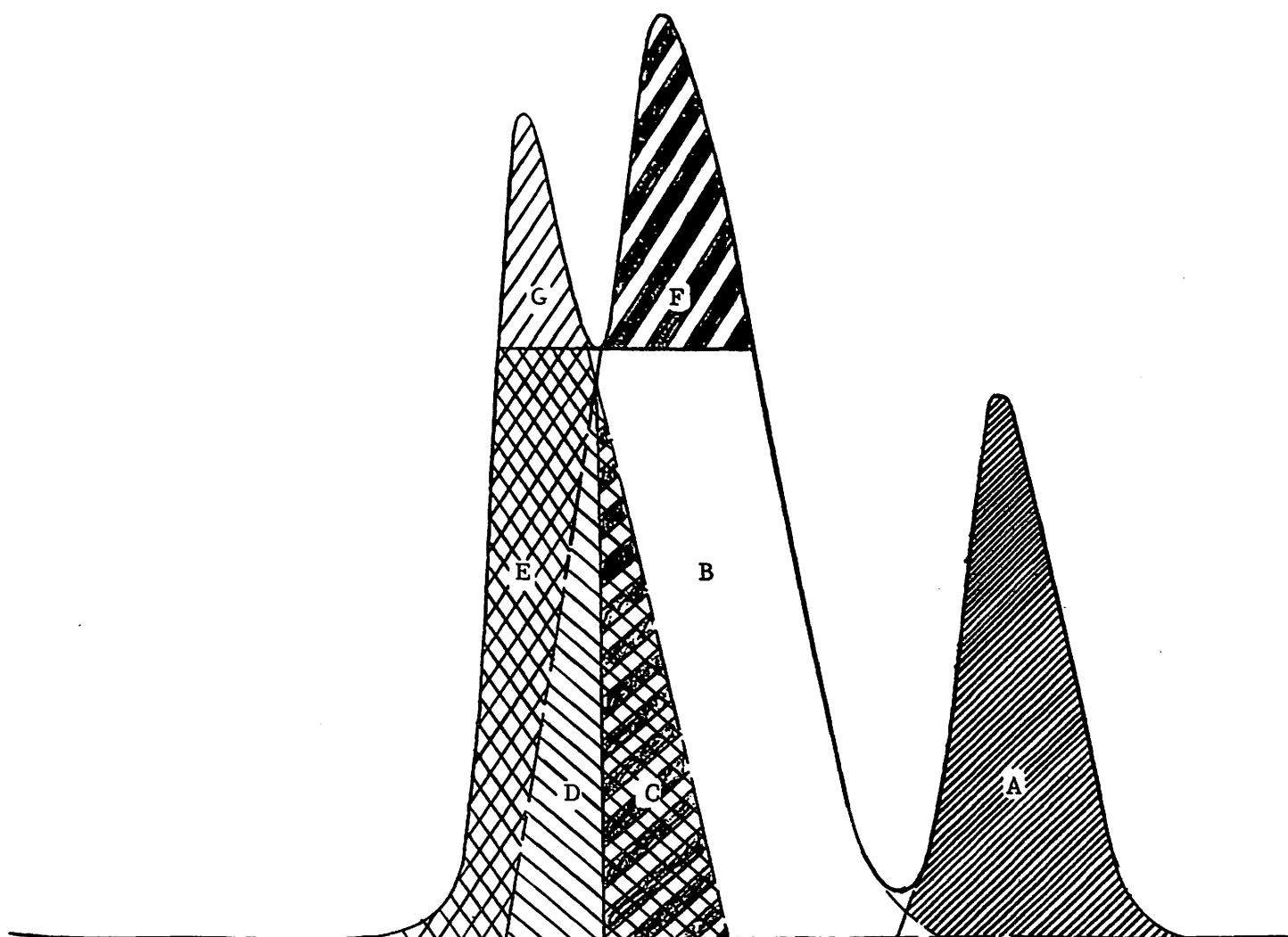


Figure 2. Typical Chromatogram of Pyrolyzate from Decomposition of 2-Octyl Diphenylphosphinate

$$\text{Area of (C + D + E + G)} = 84 \text{ mm.} \times 16. \text{mm.} = 1344 \text{ mm.}^2$$

$$\text{Area of C} = 1/2 (56 \text{ mm.} \times 12.5 \text{ mm.}) = 350 \text{ mm.}^2$$

$$\text{Area of D} = 1/2 (55.5 \text{ mm.} \times 9.5 \text{ mm.}) = 264 \text{ mm.}^2$$

$$\begin{aligned} \text{Area of } \underline{\text{trans}}\text{-2-octene} &= (\text{B} + \text{C} + \text{D} + \text{F}) - (\text{D}) = 2304 \text{ mm.}^2 - 264 \text{ mm.}^2 \\ &= 2040 \text{ mm.}^2 \end{aligned}$$

$$\begin{aligned} \text{Area of } \underline{\text{cis}}\text{-2-octene} &= (\text{C} + \text{D} + \text{E} + \text{G}) - (\text{C}) = 1344 \text{ mm.}^2 - 350 \text{ mm.}^2 \\ &= 994 \text{ mm.}^2 \end{aligned}$$

$$\text{Total area} = 3832 \text{ mm.}^2$$

$$\text{Percentage of 1-octene} = \frac{798 \text{ mm.}^2}{3832 \text{ mm.}^2} \times 100 = 20.9 \text{ per cent}$$

$$\text{Percentage of } \underline{\text{cis}}\text{-2-octene} = \frac{994 \text{ mm.}^2}{3832 \text{ mm.}^2} \times 100 = 25.9 \text{ per cent}$$

$$\text{Percentage of } \underline{\text{trans}}\text{-2-octene} = \frac{2040 \text{ mm.}^2}{3832 \text{ mm.}^2} \times 100 = 53.3 \text{ per cent}$$

In another series of experiments the amount (per cent) of cis- and trans-2-octene was obtained by measuring only the upper portions (F, G) of the curves since in the procedure described above, error can occur when the perpendicular line is drawn to separate the two peaks. Although they are symmetrical, they are not of the same height. When the heights are approximately equal, very accurate results can be obtained using this method (40). From the areas of surface F and G, the following percentages were obtained.

$$1\text{-octene} = 20.9 \text{ per cent}$$

$$\underline{\text{cis}}\text{-2-octene} = 22.3 \text{ per cent}$$

$$\underline{\text{trans}}\text{-2-octene} = 56.8 \text{ per cent}$$

Although the figures obtained by the two procedures vary, the difference is not extensive and the latter method seemed more attractive. From the average of several calculations similar to those described, the

following results were obtained.

1-octene = 20.9 per cent

cis-2-octene = 20.5 per cent

trans-2-octene = 57.6 per cent

Table IV gives a summary of the results obtained from the pyrolysis reactions.

TABLE IV
SUMMARY¹ OF RESULTS OF THE PYROLYSES OF (C₆H₅)₂⁰POR

R	Pyrolysis Temperature (°C)	Olefin Isolated (per cent)	Product Distribution (per cent) ²
C ₆ H ₁₁ -	195-230	quant.	---
C ₆ H ₅ CH ₂ CH ₂ -	240-270	quant.	---
1-C ₈ H ₁₇ -	245-280	82.2	96% 1-octene 4% 2-octene
2-C ₈ H ₁₇ -	215-235	quant.	21% 1-octene 21% <u>cis</u> -2-octene 58% <u>trans</u> -2-octene
C ₂₇ H ₄₅	255-260	96	--- ³

¹A minimum of two pyrolyses was examined with each ester.

²These figures represent the amount of olefin isolated in high purity as shown by g.l.c.

³Mixture was not fully characterized.

Attempted Isomerization of cis-2-Octene with Diphenylphosphinic Acid. A 15-ml. round-bottom flask was equipped with a thermometer (inserted into flask), a condenser with a drying tube, and a magnetic stirrer. Freshly purified diphenylphosphinic acid (0.604 g.; 0.0027 mole) and 6.036 g. (0.0538 mole) of cis-2-octene were added to the flask. The heterogenous mixture was heated at reflux (125°) with vigorous

stirring for 2.5 hours. G.l.c. analysis was performed on the mixture using a 6-ft. x 1/8-in. column packed with 5 per cent silicone 30 on 60/80-mesh, acid-washed Chromosorb G which had been pre-treated with dimethyldichlorosilane. The chromatogram indicated a single component and this was shown to be cis-2-octene by the method of mixed injections. Thus isomerization had not occurred.

Attempted Isomerization of 1-Octene with Diphenylphosphinic Acid.

To a 25-ml. round-bottom flask equipped with a magnetic stirrer, a thermometer (inserted into flask), and a small Vigreux fractionating column connected to a distilling head, was added 4.98 g. (0.0445 mole) and 0.830 g. (0.038 mole) of diphenylphosphinic acid. The acid was recrystallized and dried (110° ; 8 hours) immediately prior to its use. Distillation at atmospheric pressure yielded four fractions (b.p. $112-120^{\circ}$). G.l.c. analysis on a 6-ft. column packed with 5 per cent silicone 30 on 60/80-mesh, acid-washed Chromosorb G pre-treated with dimethyldichlorosilane showed that all fractions were identical. By the method of mixed injections this single component was shown to be 1-octene. Of the 1-octene which was added to the distilling flask, 4.54 g. was recovered (91.2 per cent).

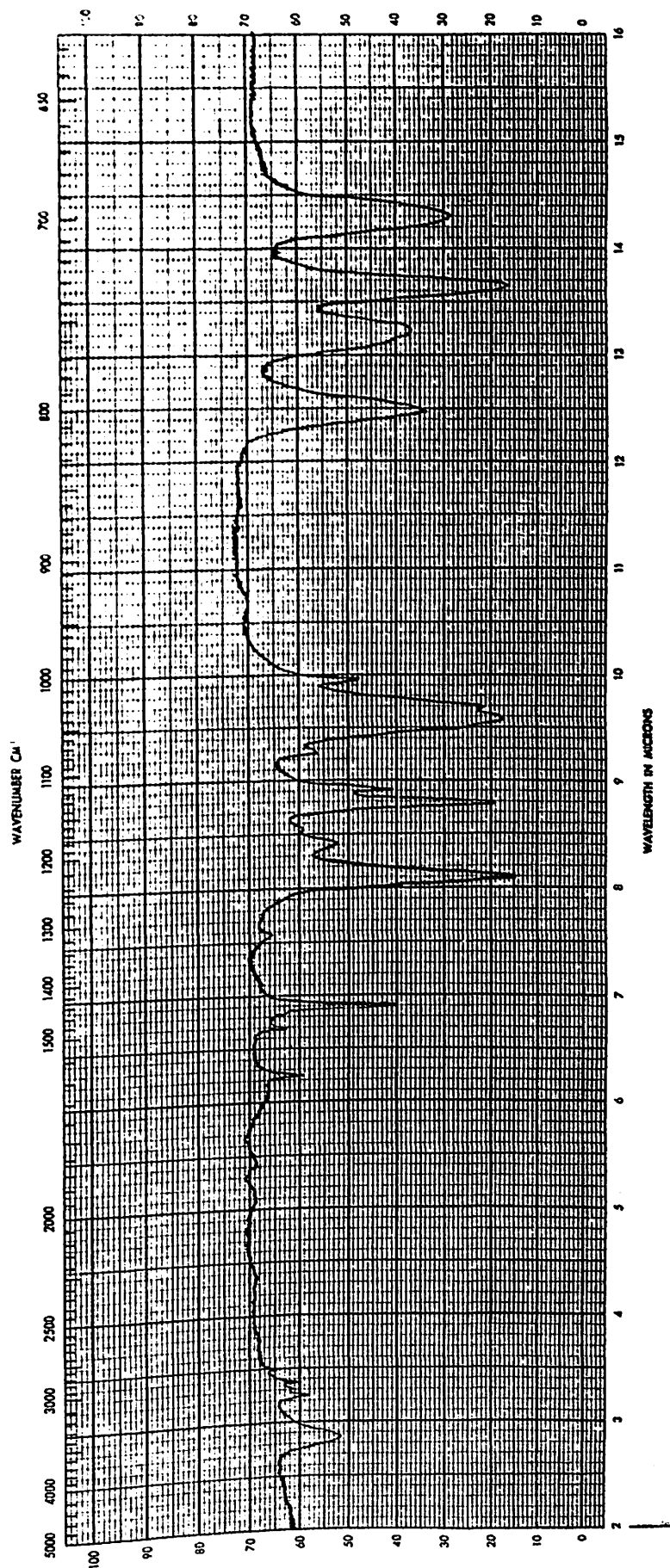
Attempted Acid Hydrolysis of Phenyl Diphenylphosphinate. A 250-ml. round-bottom flask was equipped with a magnetic stirrer, a condenser, and a thermometer (inserted into flask). Phenyl diphenylphosphinate (5.048 g.; 0.0171 mole) was dissolved in 50 ml. of benzene and placed in the flask. A 50-ml. portion of aqueous hydrochloric acid solution (6 N) was then added to the flask. This vigorously stirred mixture was then heated at reflux ($73-75^{\circ}$) for 13 hours. After cooling, aqueous sodium bicarbonate (10 per cent) was used to neutralize the reaction mixture. The

organic layer was separated and washed twice with 25-ml. portions of the bicarbonate solution and then with three 50-ml. portions of distilled water. The organic phase (after drying over anhydrous magnesium sulfate) was concentrated and to this was added cold heptane. Unreacted starting material precipitated. Phenyl diphenylphosphinate (4.992 g.) was recovered (98.9 per cent). Acidification (6 N aqueous hydrochloric acid) of the alkaline phase yielded no diphenylphosphinic acid. Under these conditions, phenyl diphenylphosphinate does not hydrolyze.

Alkaline Hydrolysis of Phenyl Diphenylphosphinate. A 200-ml. round-bottom flask equipped with a magnetic stirrer, a condenser, and a thermometer (inserted into the flask) was charged with 5.021 g. (0.0171 mole) of phenyl diphenylphosphinate dissolved in 50 ml. of benzene. A 50-ml. portion of aqueous sodium hydroxide (6 N) was added to the contents of the flask and with vigorous stirring the mixture was heated at reflux ($72-3^{\circ}$) for 13 hours. After cooling to room temperature, the organic phase was separated and the aqueous layer was extracted with three 50-ml. portions of benzene. The combined organic layers were washed with a single 50-ml. portion of distilled water and dried over magnesium sulfate. Removal of the organic solvent under aspirator pressure on a steam bath did not leave a residue. The alkaline phase from the reaction mixture and the aqueous extract of the organic layer were combined and acidified by the dropwise addition of concentrated hydrochloric acid solution. When the addition of the acid solution resulted in no further precipitation, the heterogenous mixture was chilled and the solid was collected. The diphenylphosphinic acid isolated (3.956 g.; 96.5 per cent) melted at $192-3.5^{\circ}$ [lit. (51) $194-5^{\circ}$].

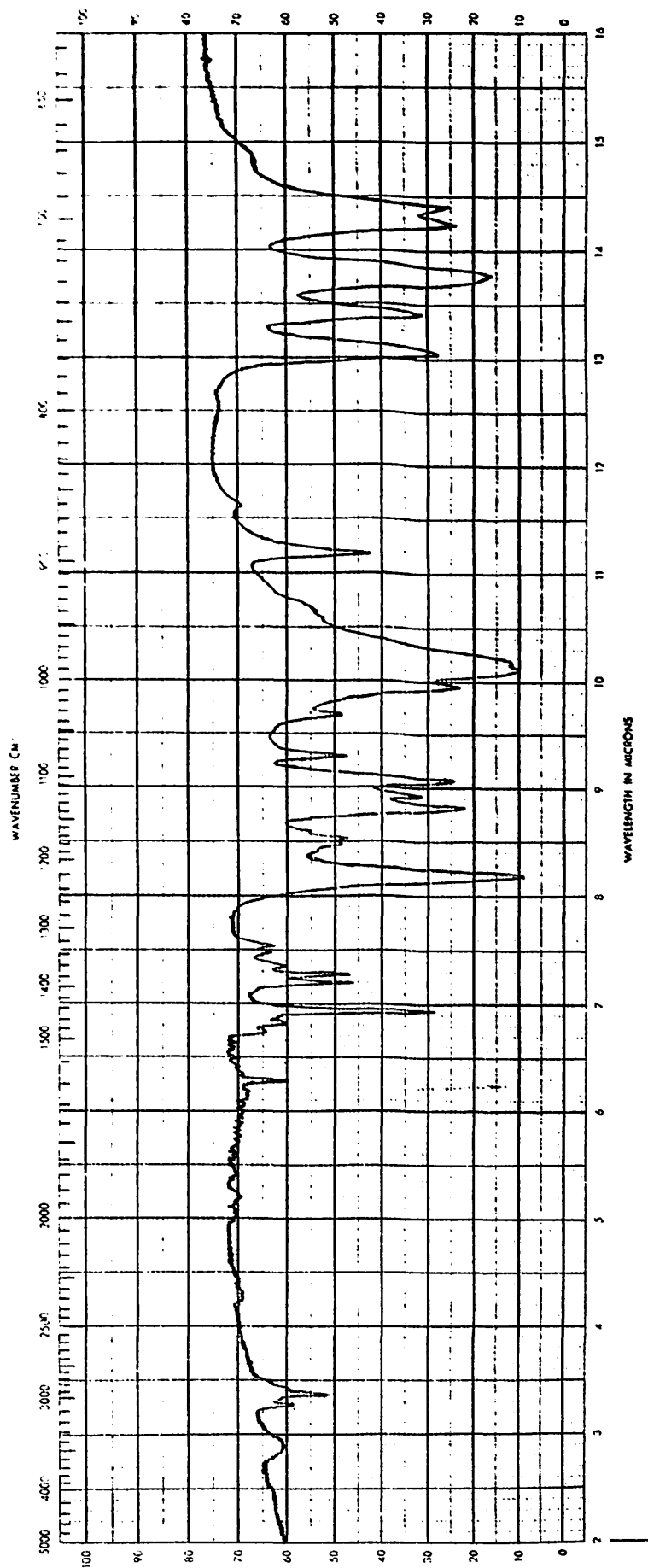
Alkaline hydrolysis under these conditions results in total conversion of phenyl diphenylphosphinate to diphenylphosphinic acid.

Plate I



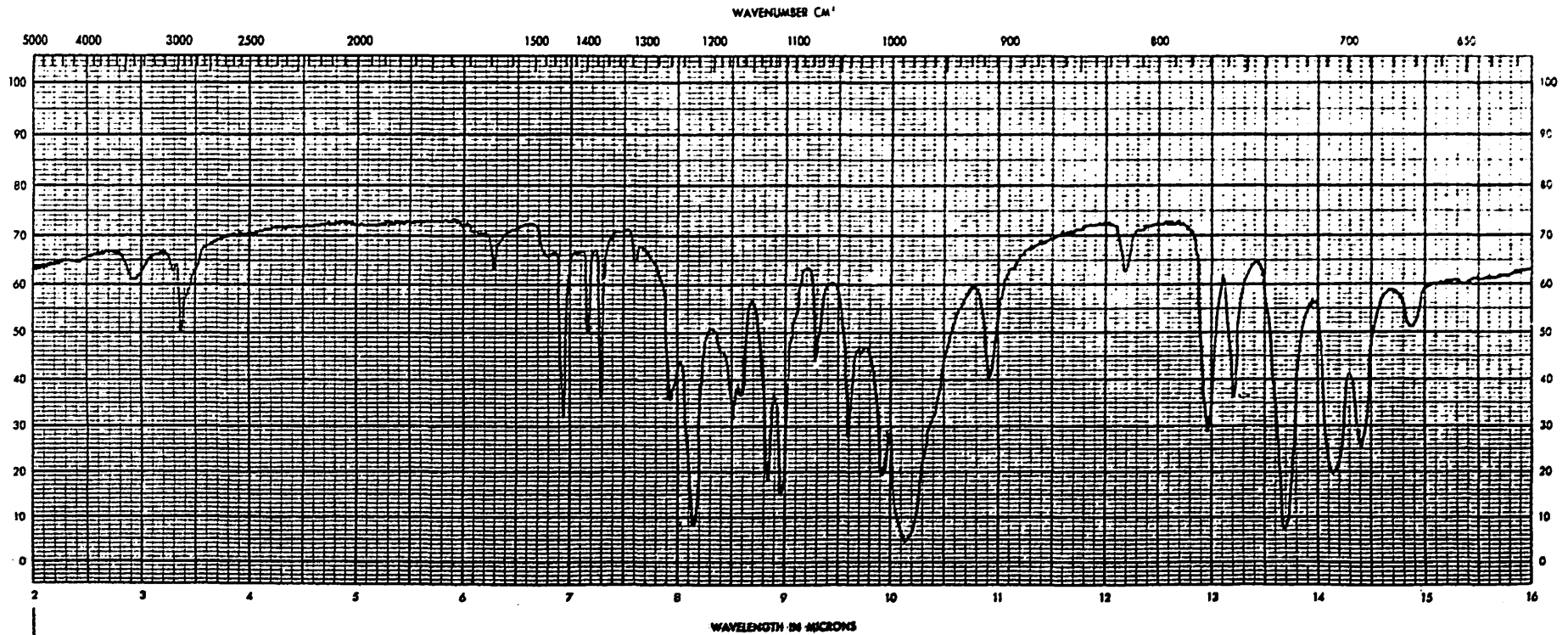
Methyl Diphenylphosphinate, KBr Pellet

Plate II



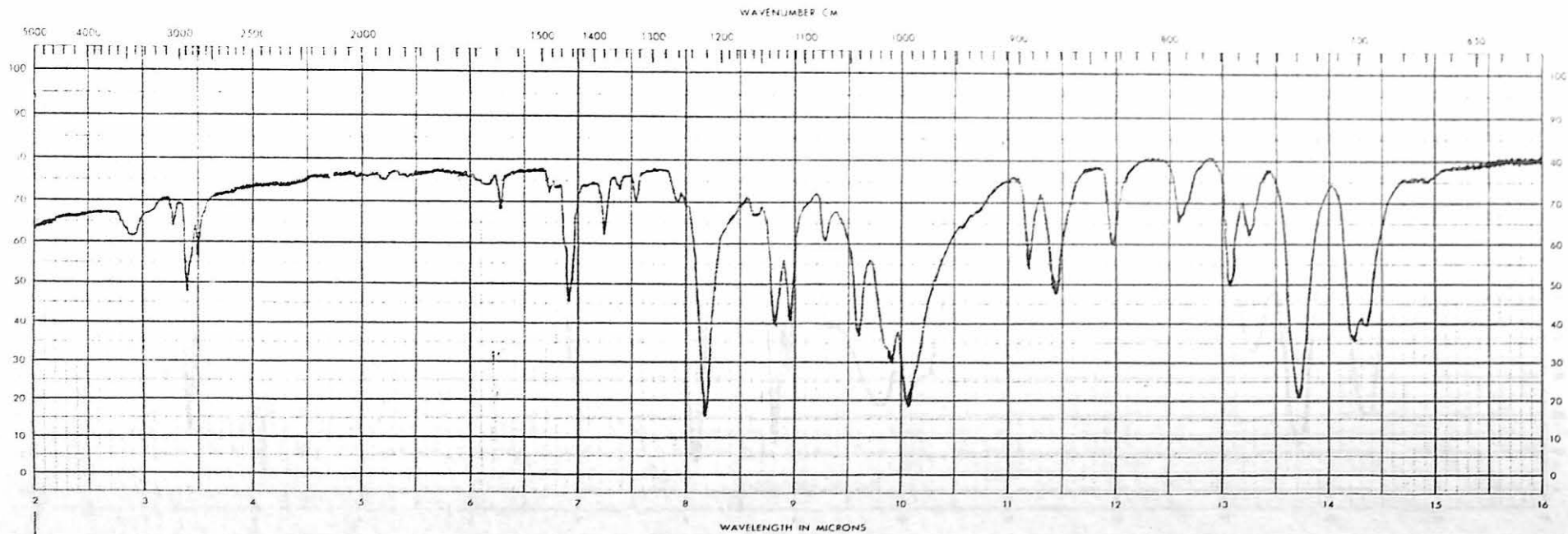
Isopropyl Diphenylphosphinate, KBr Pellet

Plate III



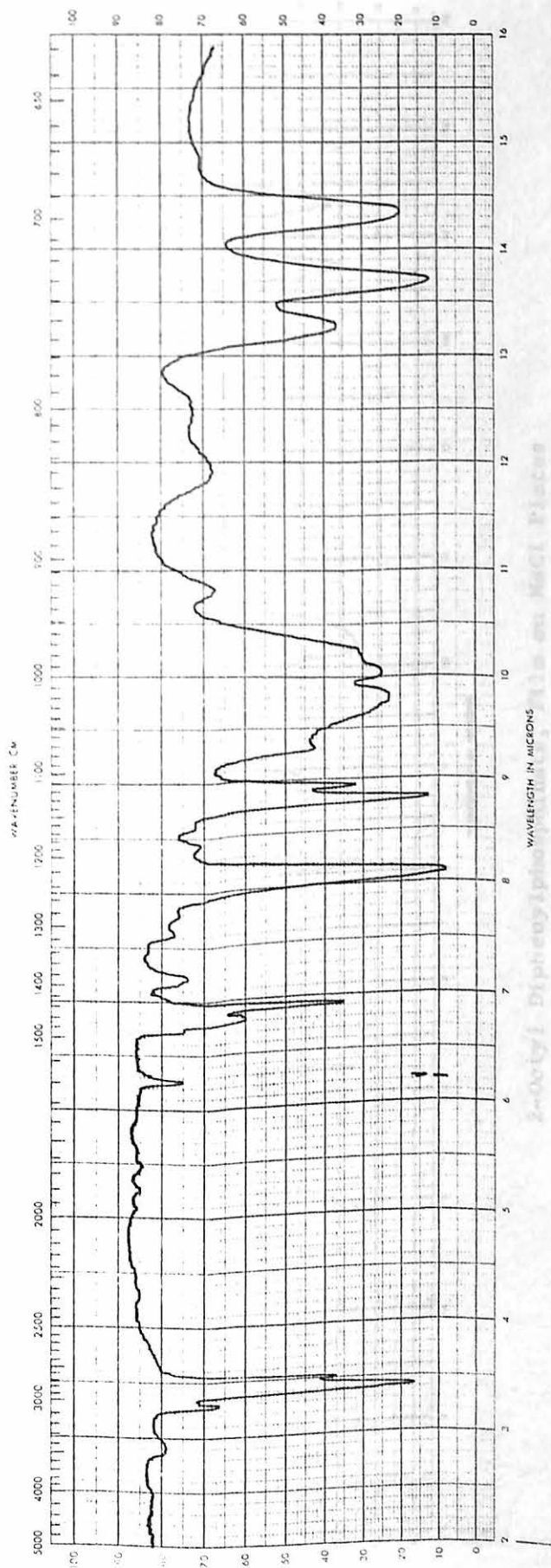
t-Butyl Diphenylphosphinate, KBr Pellet

Plate IV



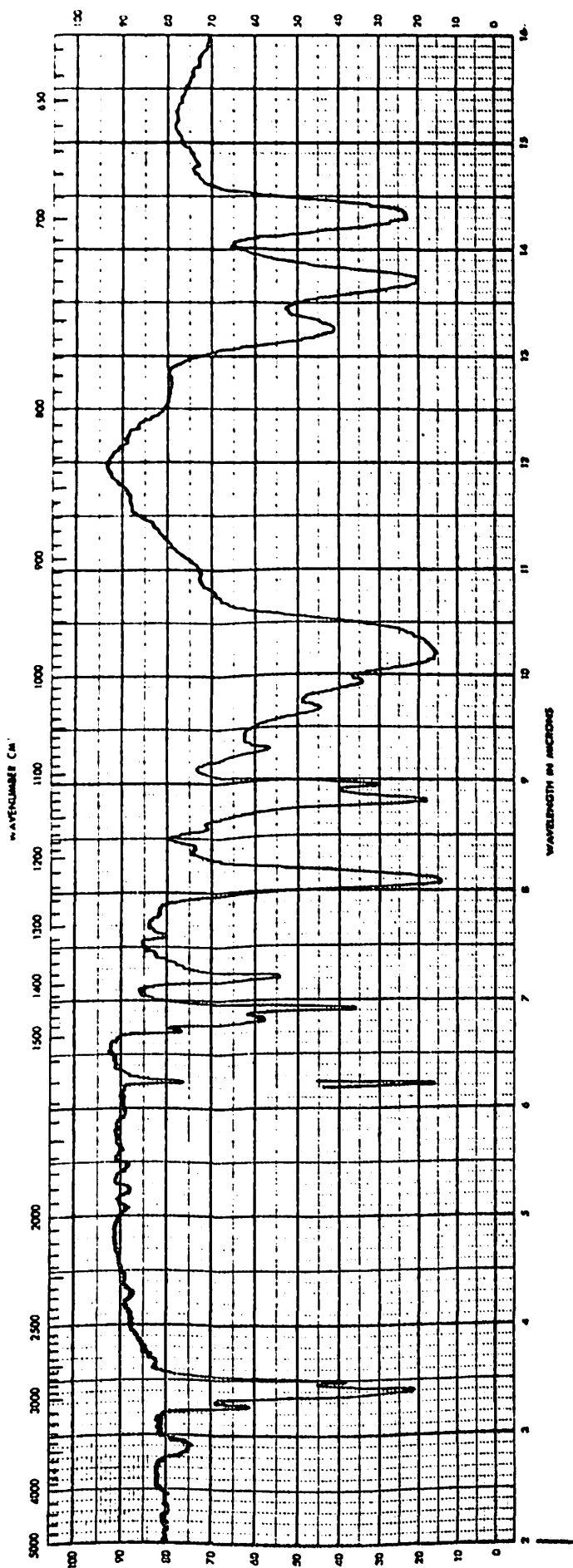
Cyclohexyl Diphenylphosphinate, KBr Pellet

Plate V



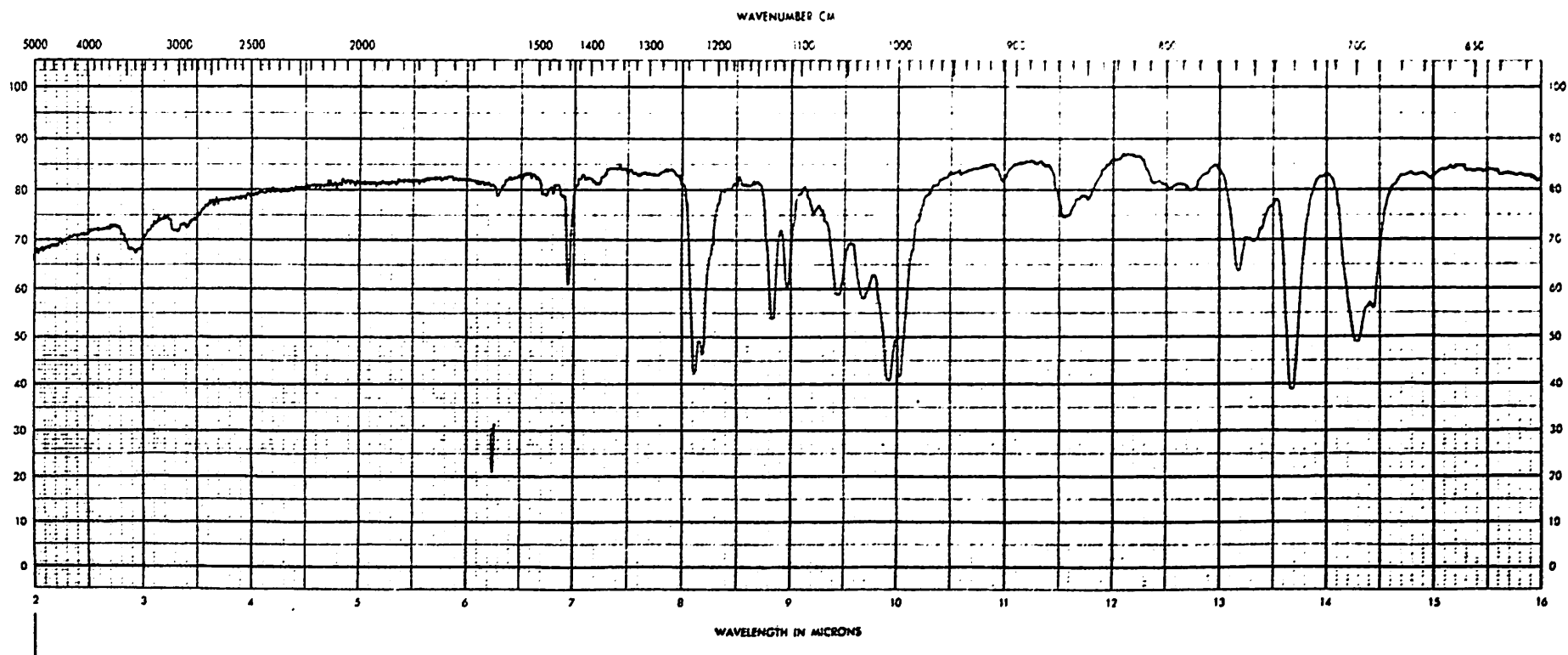
Octyl Diphenylphosphinate, Film on NaCl Plates

Plate VI



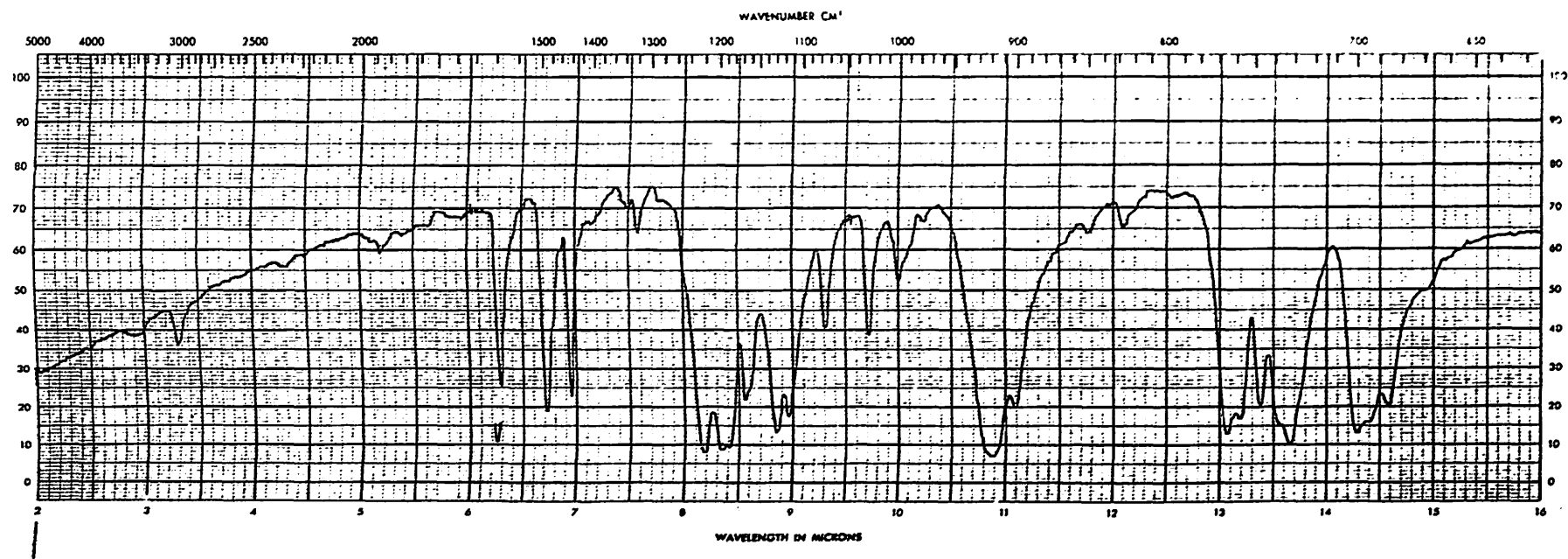
2-Octyl Diphenylphosphinate, Film on NaCl Plates

Plate VII



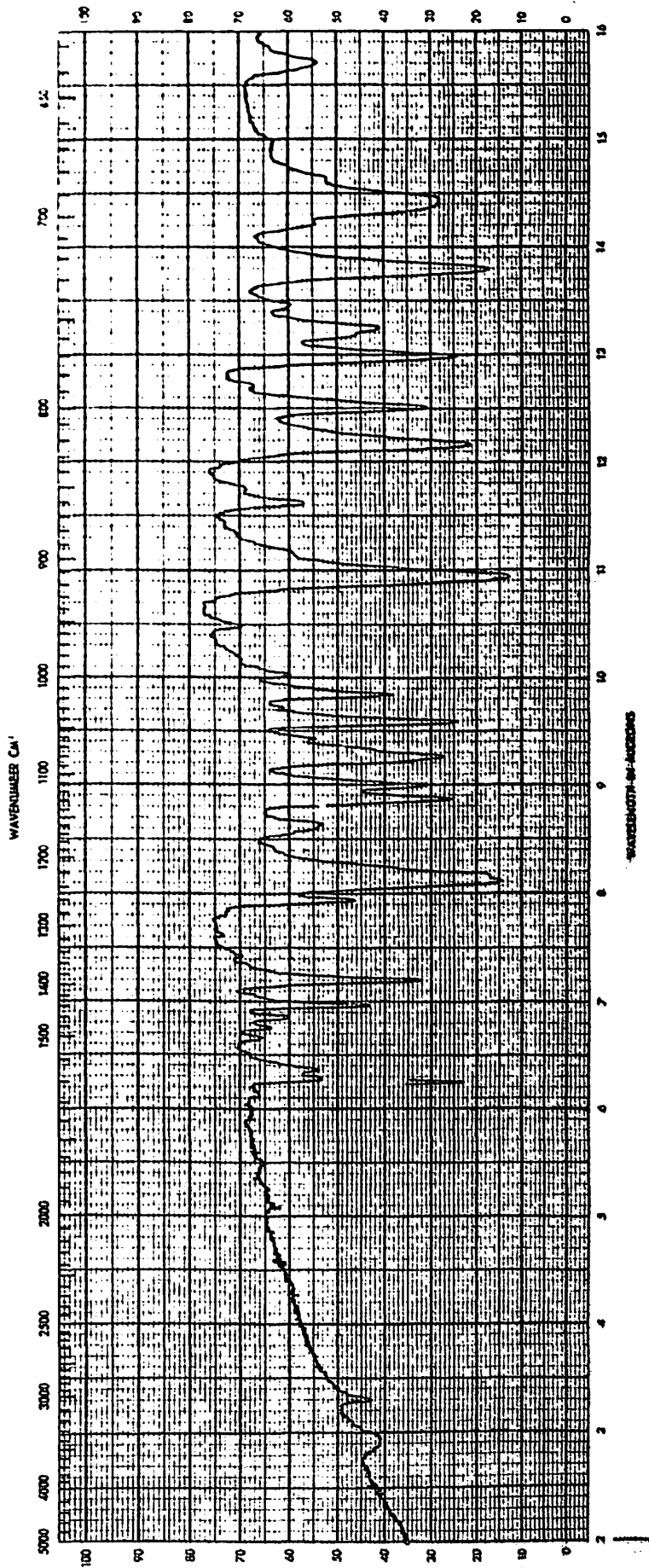
β -Phenethyl Diphenylphosphinate, KBr Pellet

Plate VIII



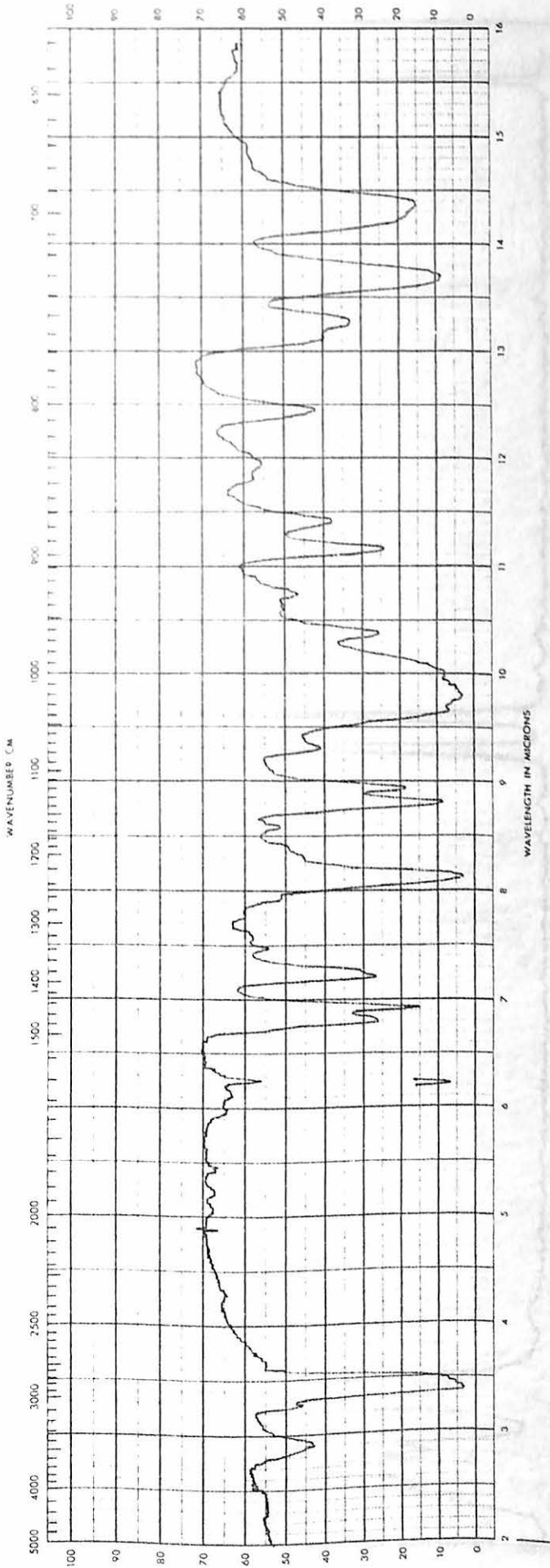
Phenyl Diphenylphosphinate, KBr Pellet

Plate IX



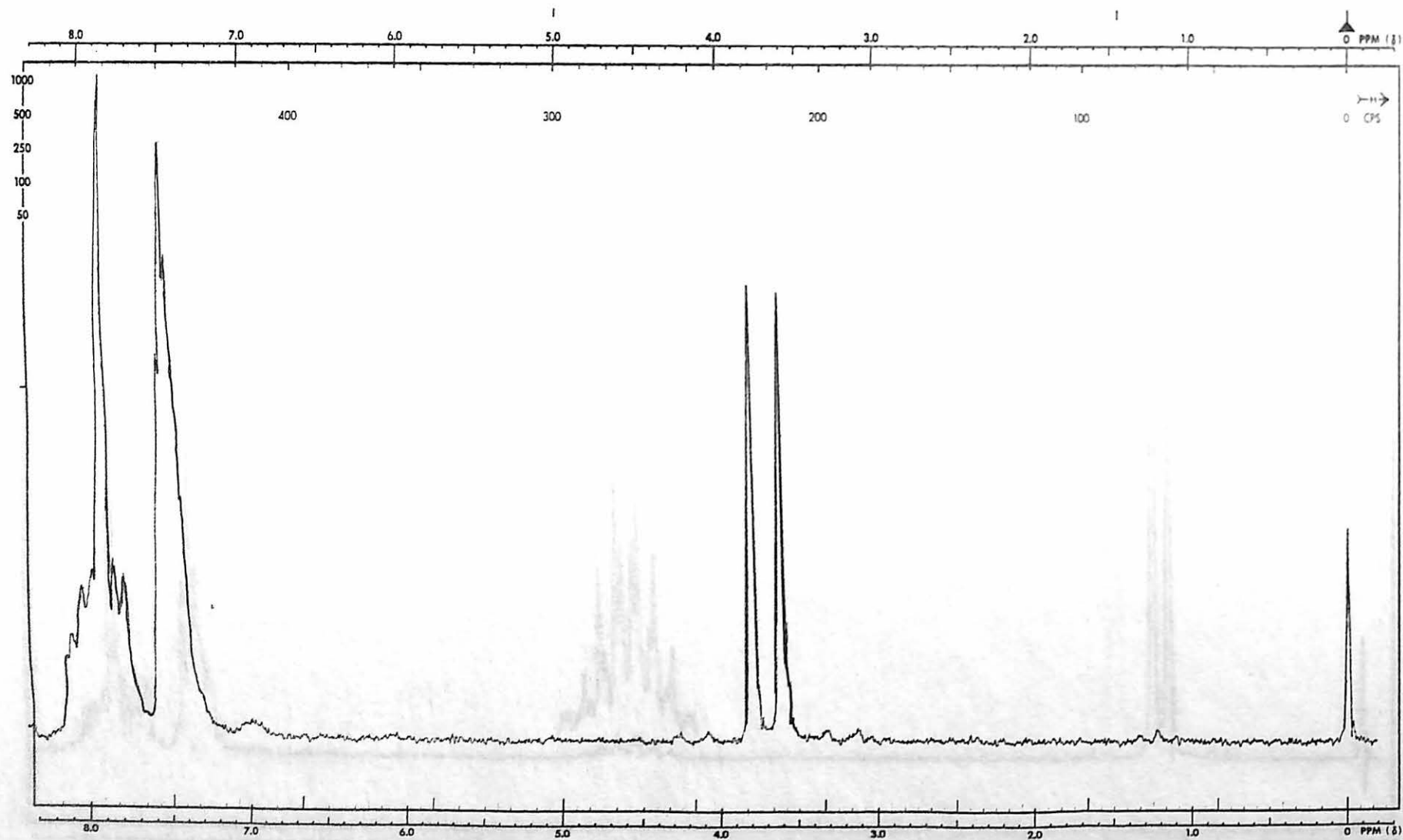
α -Naphthyl Diphenylphosphinate, KBr Pellet

Plate X



Cholesteryl Diphenylphosphinate, KBr Pellet

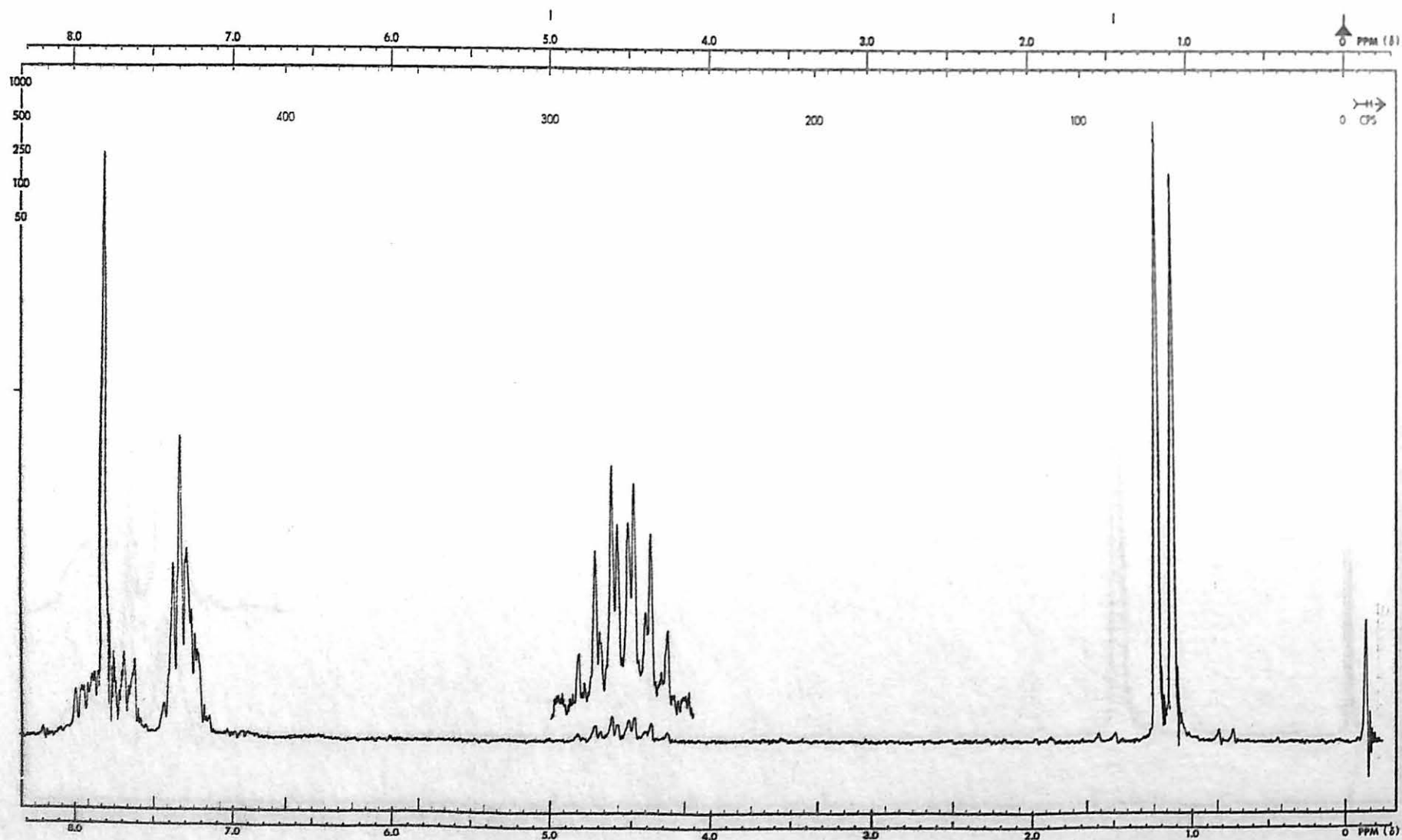
Plate XI



Methyl Diphenylphosphinate

Solvent	CHCl_3	R.F. Field	0.22 mG	S.W.	500 cps	S.A.	4.0
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

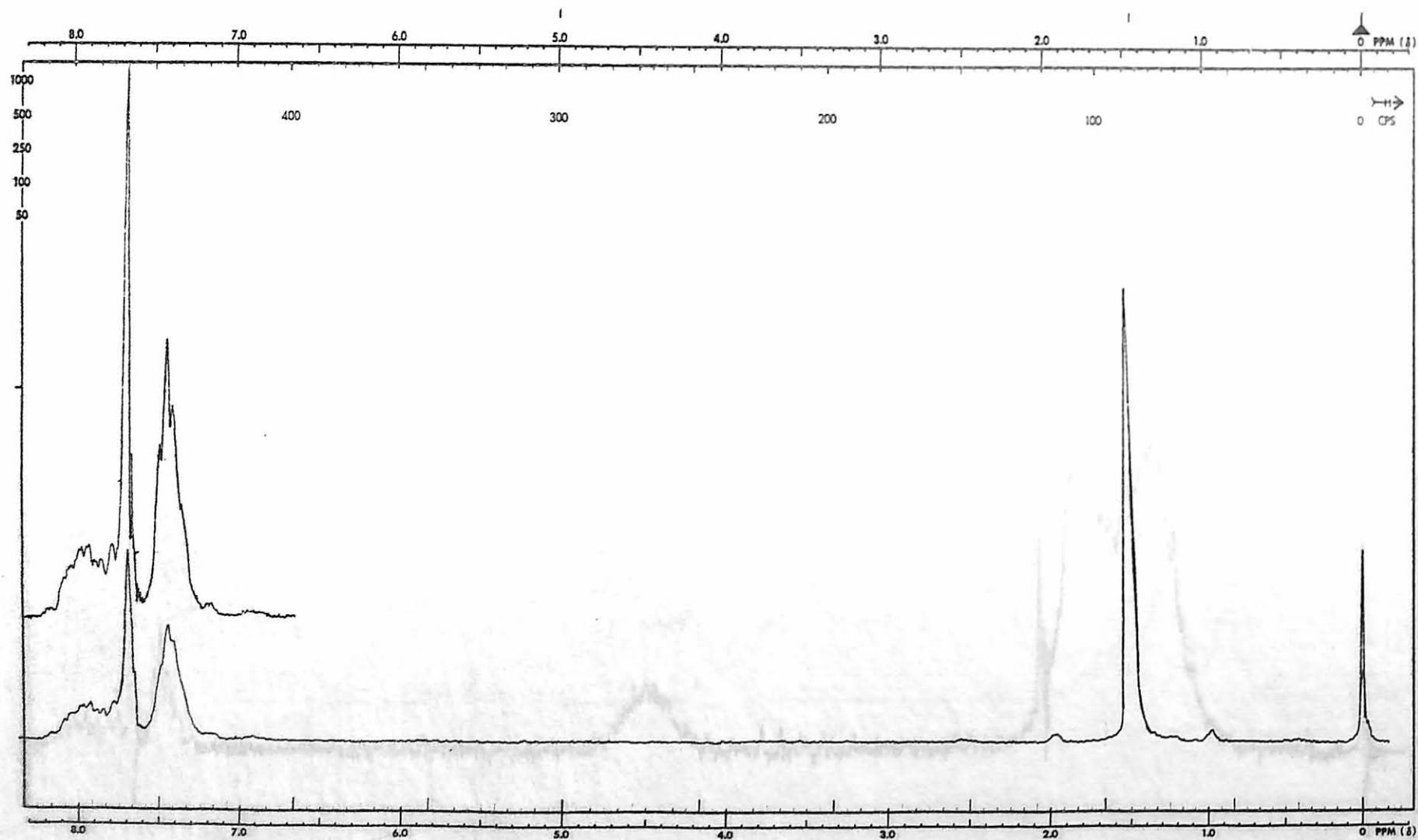
Plate XII



Isopropyl Diphenylphosphinate

Solvent	CHCl ₃	R.F. Field	0.2 mG	S.W.	500 cps	S.A.	1.6
F.B.	4.0 cps	S.T.250 sec	S.O.	000 cps	I.A.	off

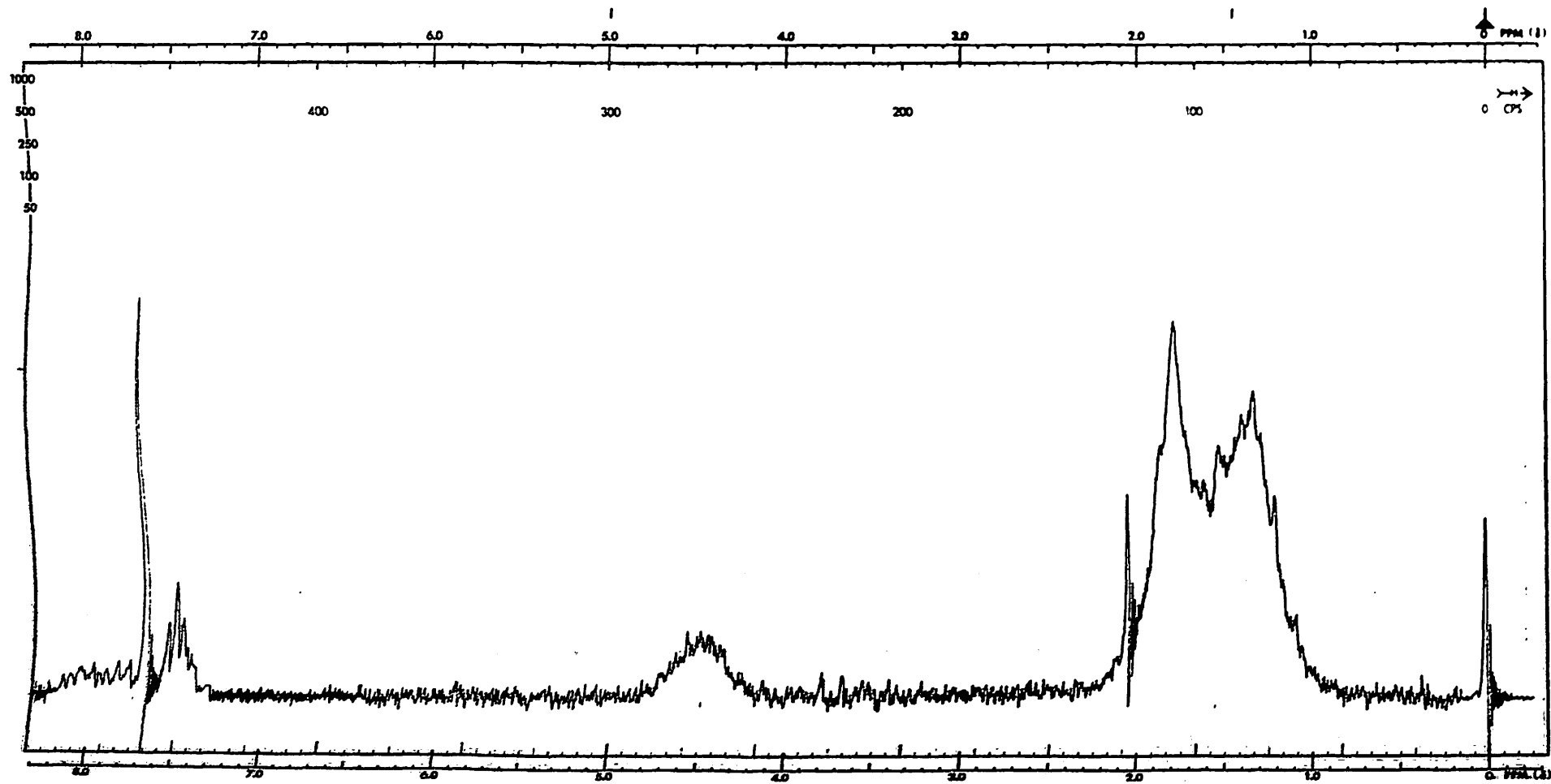
Plate XIII



t-Butyl Diphenylphosphinate

Solvent	CHCl ₃	R.F. Field	0.22 mG	S.W.	500 cps	S.A.	1.2
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

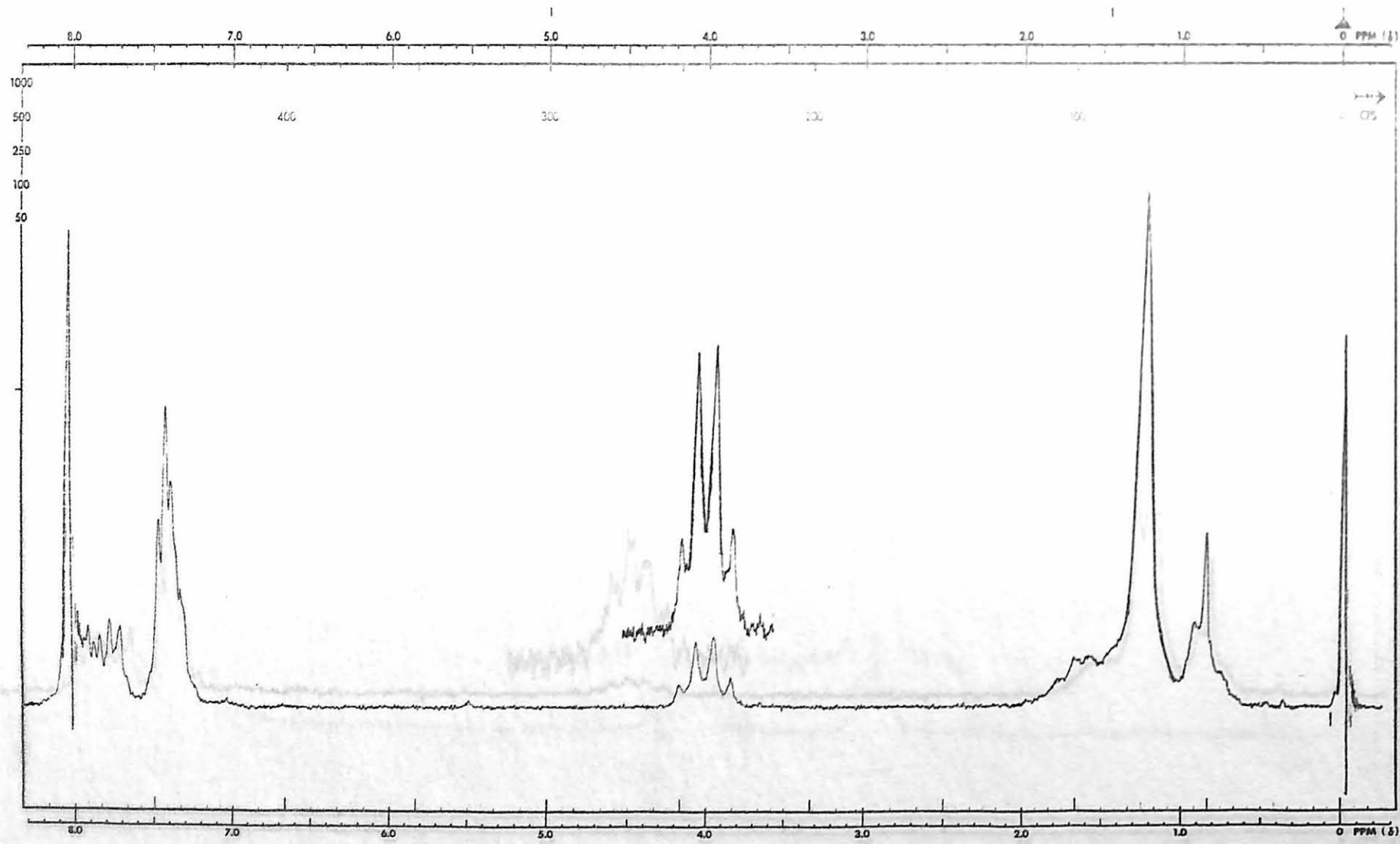
Plate XIV



Cyclohexyl Diphenylphosphinate

Solvent	CHCl ₃	R.F. Field	0.2 mG	S.W.	500 cps	S.A.	10
F.B.	2.0 cps	S.T.	250 sec	S.C.	000 sec	T.A.	000 sec

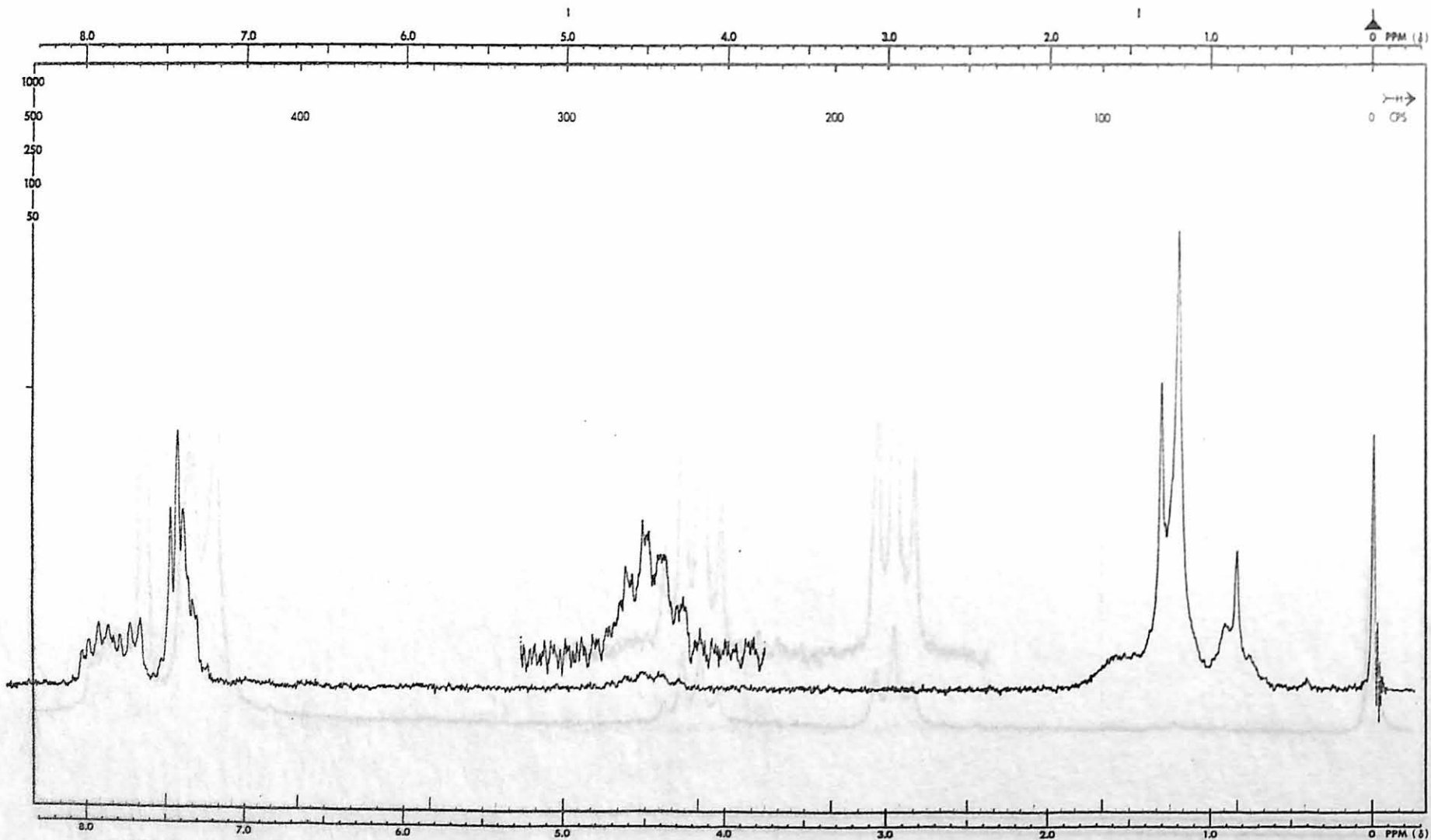
Plate XV



Octyl Diphenylphosphinate

Solvent	CHCl_3	R.F. Field	0.22 mG	S.W.	500 cps	S.A.	2.5
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

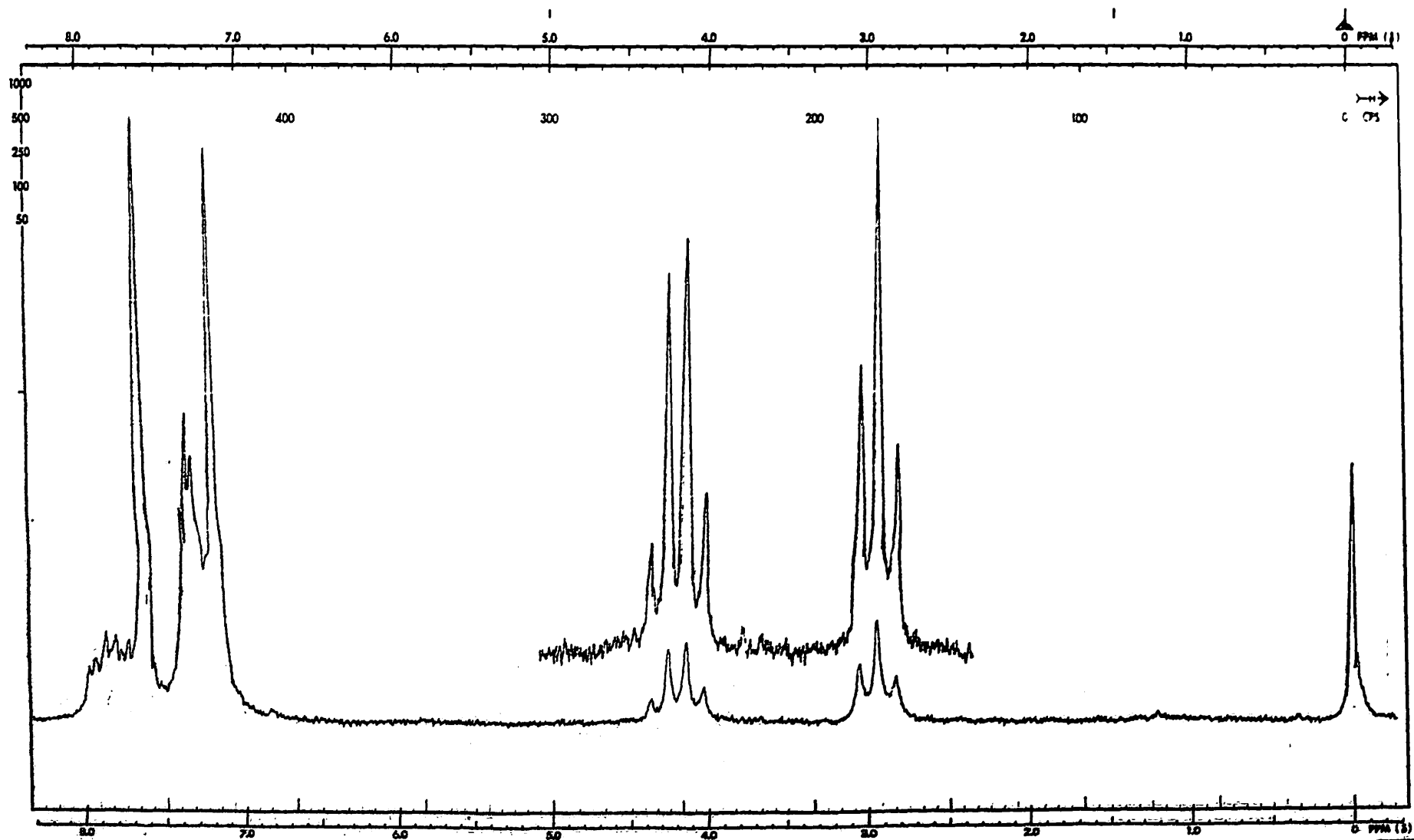
Plate XVI



2-Octyl Diphenylphosphinate

Solvent	CCl ₄	R.F. Field	0.2 mG	S.W.	500 cps	S.A.	3.2
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

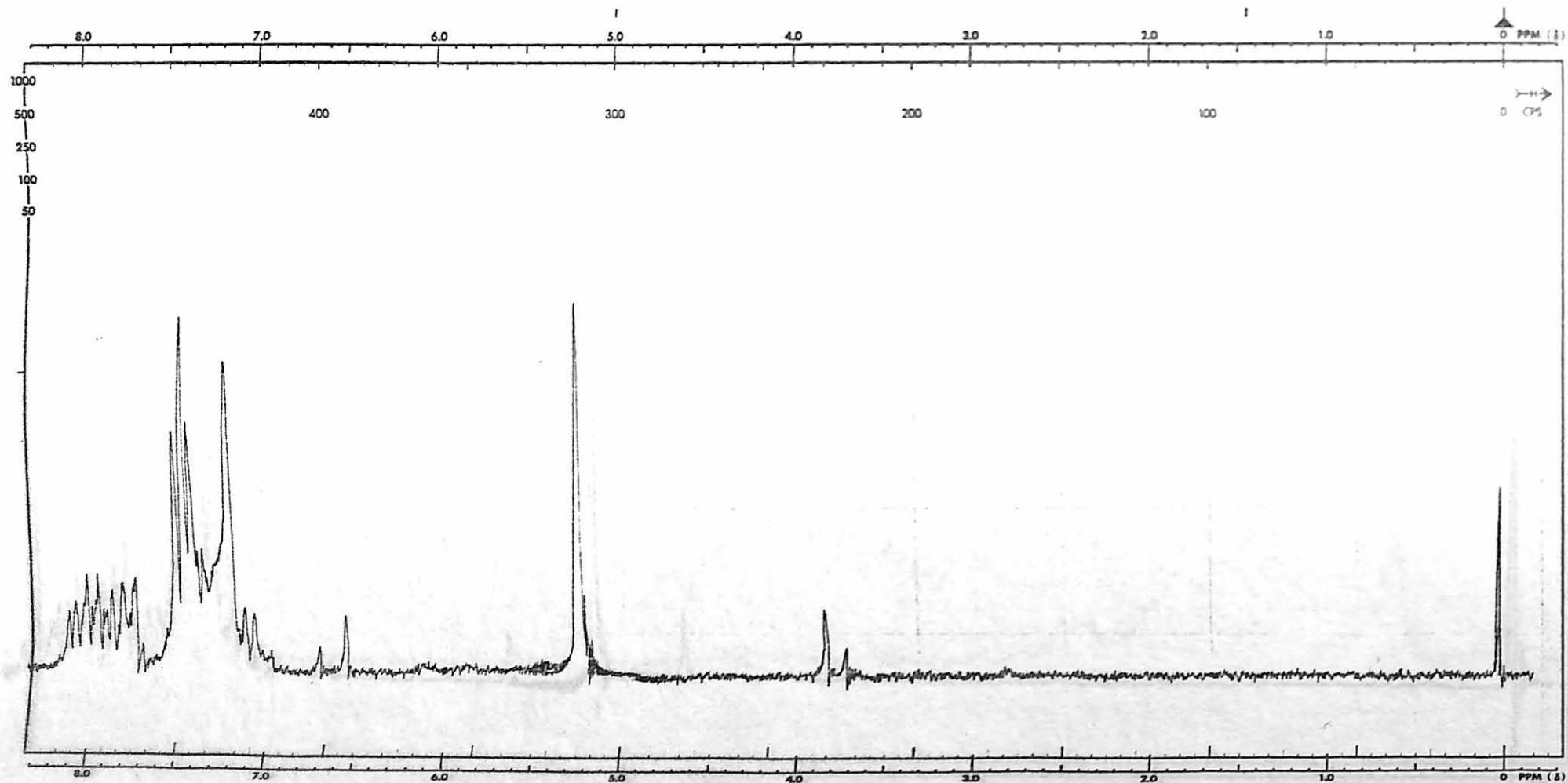
Plate XVII



β -Phenethyl Diphenylphosphinate

Solvent	CHCl_3	R.F. Field	0.22 mG	S.W.	500 cps	S.A.	3.2
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

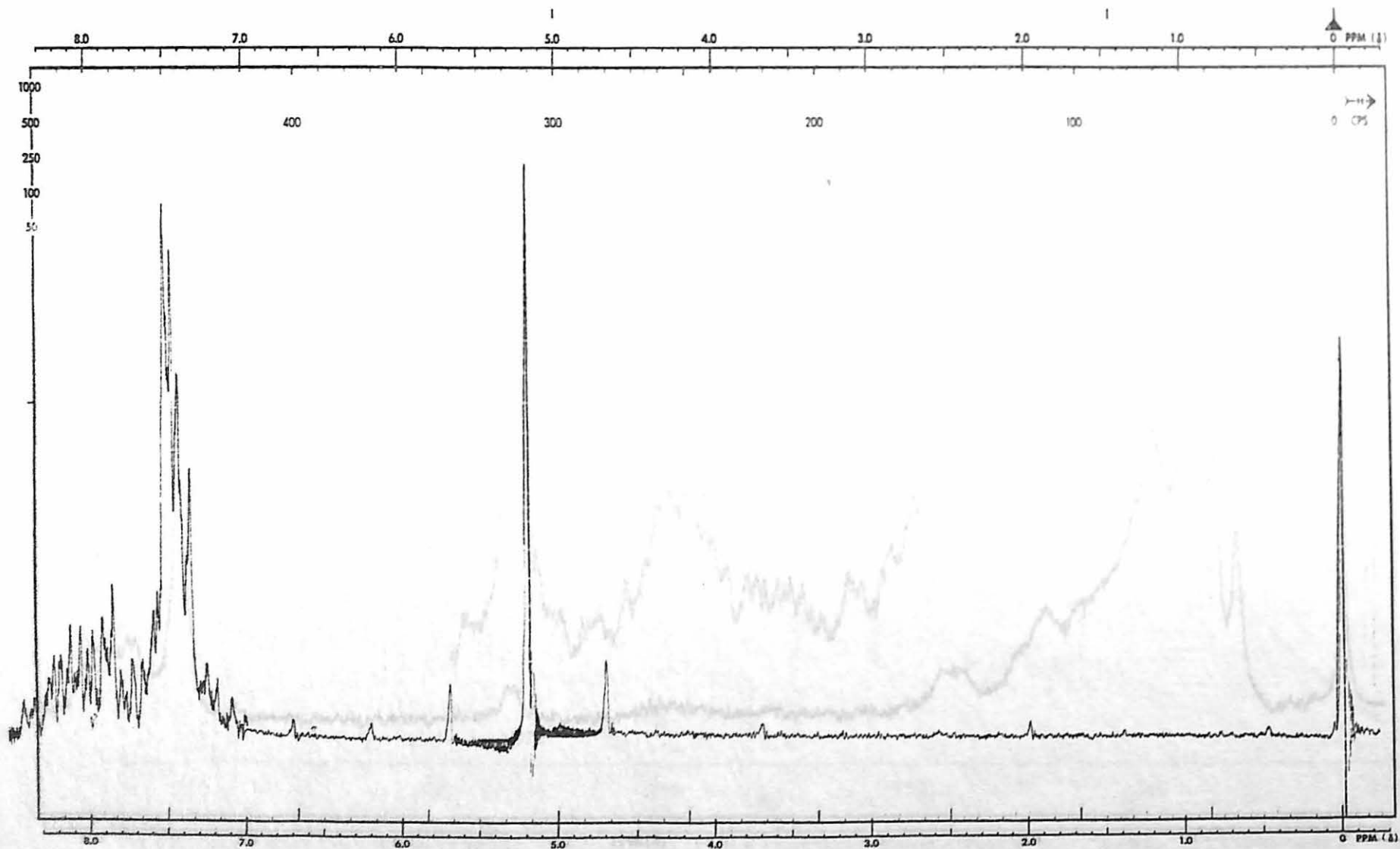
Plate XVIII



Phenyl Diphenylphosphinate

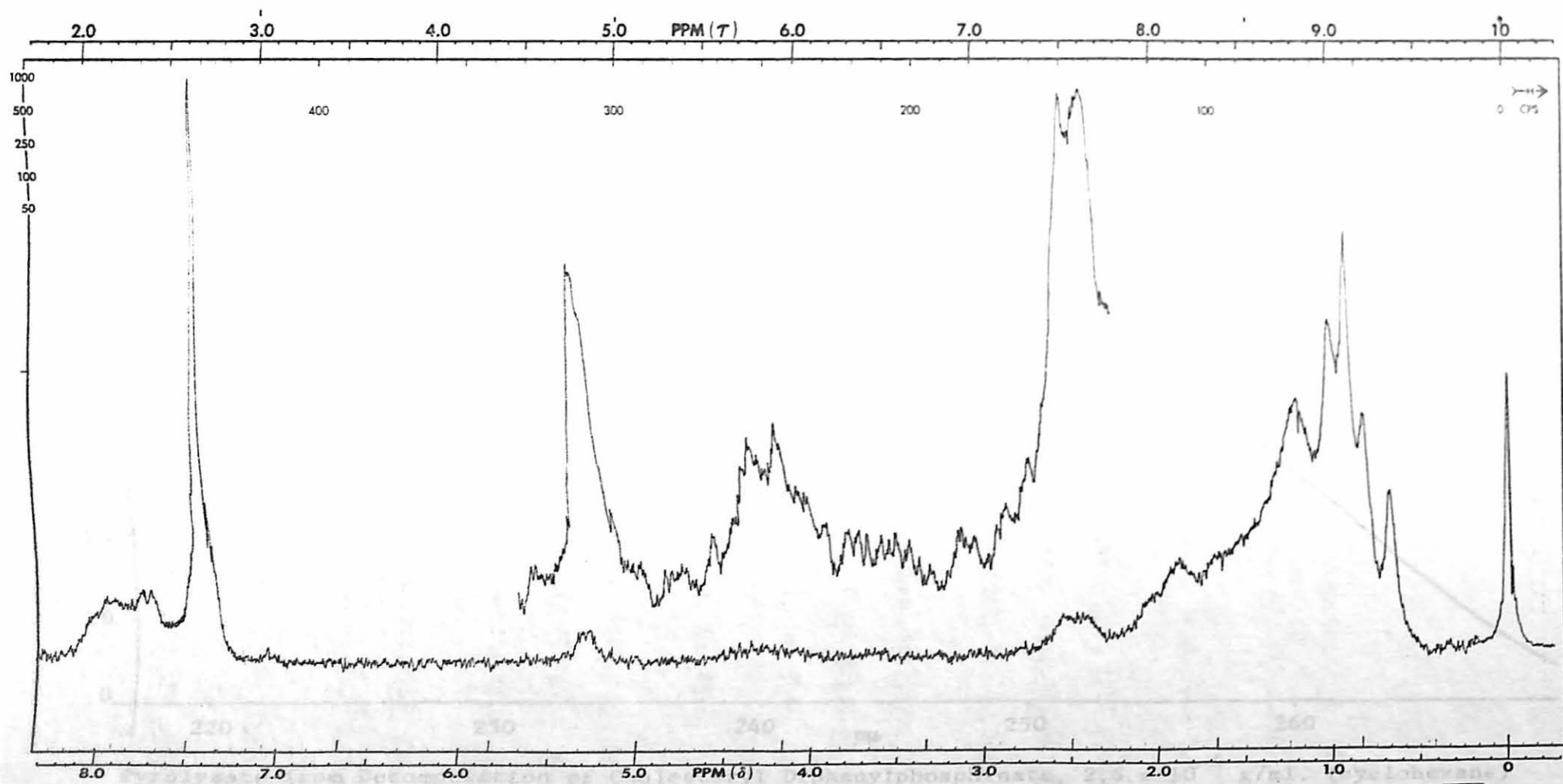
Solvent	CH_2Cl_2	R.F. Field	0.2 mG	S.W.	500 cps	S.A.	4
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

Plate XIX



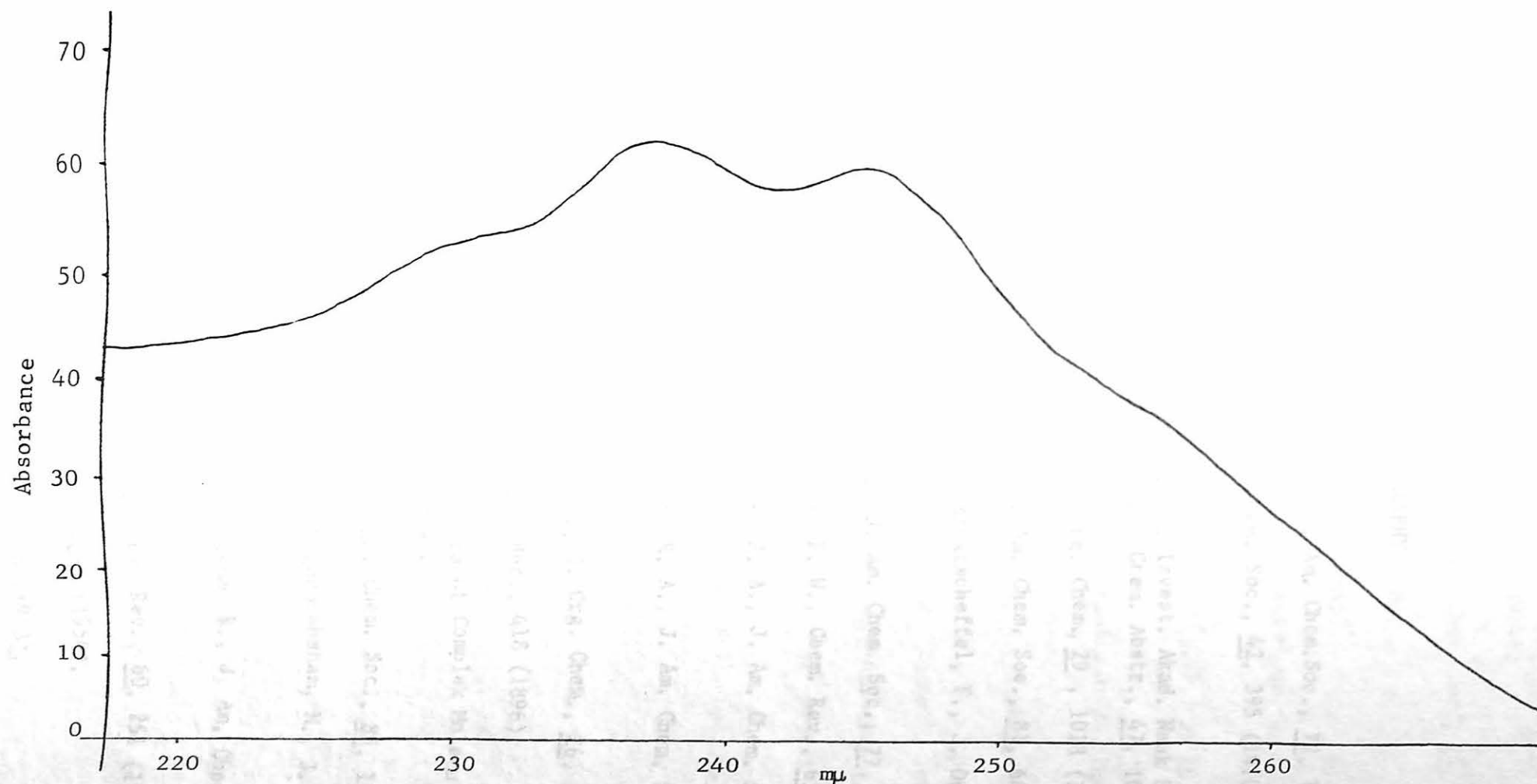
α-Naphthyl Diphenylphosphinate

Solvent	CH ₂ Cl ₂	R.F. Field	0.22 mG	S.W.	500 cps	S.A.	2.5
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off



Cholesteryl Diphenylphosphinate

Solvent	CHCl ₃	R.F. Field	0.22 mG	S.W.	500 cps	S.A.	8
F.B.	2.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off



Pyrolyzate from Decomposition of Cholesteryl Diphenylphosphinate, 2.6×10^{-4} g/ml. (cyclohexane)

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VITA

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- Thesis: I. A STUDY OF THE NUCLEOPHILIC DISPLACEMENT REACTION ON
TRIMETHYL PHOSPHITE BY PHENYL GRIGNARD REAGENT
II. THE PYROLYTIC DECOMPOSITION OF ALKYL DIPHENYLPHOSPHINATES --
AN OLEFIN FORMING ELIMINATION REACTION

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