

- I. THE STEREOSPECIFICITY OF THE MICHAELIS-
ARBUZOV REARRANGEMENT IN 4-t-BUTYL-
CYCLOHEXYL DIPHENYLPHOSPHINITE
- II. NMR ANALYSIS OF SUBSTITUTED PHOSPHONATES

By

DALE MICHAEL HELLWEGE
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Bachelor of Arts

Oklahoma State University

Stillwater, Oklahoma

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Thesis Approved:

K. D. Berlin

Thesis Adviser

E. E. Eismann

W. J. J. J. J.

V. L. Pollak

J. H. B. B.

Dean of the Graduate College

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
Part	
I. THE STEREOSPECIFICITY OF THE MICHAELIS- ARBUZOV REARRANGEMENT IN 4- <i>t</i> -BUTYL- CYCLOHEXYL DIPHENYLPHOSPHINITE.	2
II. NMR ANALYSIS OF SUBSTITUTED PHOSPHONATES. .	66

INTRODUCTION

Because of the difference in the primary objectives of the two investigations recorded herein, this thesis has been divided into two parts. Each is complete and independent of the other, containing its own historical section, discussion and conclusions, experimental part, and bibliography.

The first part concerns the stereochemistry of the Michaelis-Arbuzov rearrangement in a conformationally homogeneous system. Conclusions are based on the similarity of the products detected in the reaction of three different compounds with trans-4-t-butylcyclohexyl diphenylphosphinite.

In the second part of the thesis, the preparation and the interpretation of the nuclear magnetic resonance spectra of a series of dialkyl acylphosphonates are discussed. The magnitudes of several coupling constants between hydrogen and phosphorus nuclei are utilized as a basis for conclusions regarding the spatial geometry of adjacent carbonyl and phosphoryl groups. This report is part of a continuing series of investigations of this unique system.

PART I

THE STEREOSPECIFICITY OF THE MICHAELIS-ARBUZOV
REARRANGEMENT IN 4-t-BUTYLCYCLOHEXYL DIPHENYL-
PHOSPHINITE

TABLE OF CONTENTS

Chapter	Page
I. HISTORICAL	6
The Michaelis-Arbuzov Rearrangement	6
Stereochemical Studies of the Decom- position of Quasiphosphonium Salts.	8
The Mechanism of the Reaction of Poly- halomethanes with Trivalent Phos- phorus Esters	10
The Reaction of Tosylate Esters with Trivalent Phosphorus Compounds.	13
The 4- <u>t</u> -Butylcyclohexyl Group	14
II. DISCUSSION OF RESULTS AND CONCLUSIONS.	18
III. EXPERIMENTAL	30
Preparation of Cyclohexyl Diphenyl- phosphinite	30
Preparation of <u>trans</u> -4- <u>t</u> -Butylcyclo- hexyl Diphenylphosphinite (VI).	31
Preparation of <u>cis</u> -4- <u>t</u> -Butylcyclo- hexanol (VII)	33
Preparation of <u>cis</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinate (X)	33
Preparation of <u>cis</u> - and <u>trans</u> -4- <u>t</u> - Butylcyclohexyl Chlorides (XII and XIII)	34
Reaction of Cyclohexyl Diphenylphos- phinite with Benzyl Chloride.	36
Reaction of <u>trans</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinite (VI) with Benzyl Chloride.	36
Thermal Decomposition of (<u>trans</u> -4- <u>t</u> - Butylcyclohexyloxy)benzylidiphenyl- phosphonium Chloride (XIV).	38
Attempted Dehydrochlorination of <u>cis</u> - and <u>trans</u> -4- <u>t</u> -Butylcyclohexyl Chlorides (XII) and (XIII).	38
Attempted Rearrangement of <u>trans</u> -4- <u>t</u> - Butylcyclohexyl Diphenylphosphinate (IX) with Benzyl Chloride ,	39
Reaction of <u>trans</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinite (VI) with Carbon Tetrachloride	39

TABLE OF CONTENTS

Chapter	Page
III. (Continued)	
Preparation of Cyclohexyl <u>p</u> -Toluene-sulfonate.	40
Preparation of <u>trans</u> -4- <u>t</u> -Butylcyclohexyl <u>p</u> -Toluenesulfonate (II).	41
Preparation of <u>cis</u> -4- <u>t</u> -Butylcyclohexyl <u>p</u> -Toluenesulfonate (I).	41
Reaction of Cyclohexyl Diphenylphosphinite with Methyl <u>p</u> -Toluenesulfonate	42
Reaction of <u>trans</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinite (VI) with Methyl <u>p</u> -Toluenesulfonate	42
BIBLIOGRAPHY	57

LIST OF ILLUSTRATIONS

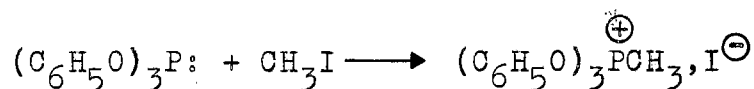
Plate	Infrared Spectra	Page
I.	<u>trans</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinite (VI), Film on NaCl Plates.	44
II.	<u>trans</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinate (IX), KBr Pellet	45
III.	<u>cis</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinate (X) Reaction Mixture, Film on NaCl Plates. .	46
IV.	<u>cis</u> - and <u>trans</u> -4- <u>t</u> -Butylcyclohexyl Chlorides (XII and XIII), Film on NaCl Plates.	47
V.	<u>trans</u> -4- <u>t</u> -Butylcyclohexyl Chloride (XIII) and 4- <u>t</u> -Butylcyclohexene (III), Film on NaCl Plates	48
VI.	(<u>trans</u> -4- <u>t</u> -Butylcyclohexyloxy)benzylidiphenylphosphonium Chloride (XIV), KBr Pellet . . .	49
VII.	1,2-Bis(Diphenylphosphinyl)-1,1,2,2-tetrachloroethane (XI), KBr Pellet.	50
Nuclear Magnetic Resonance Spectra		
VIII.	<u>trans</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinite (VI)	51
IX.	<u>trans</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinate (IX)	52
X.	<u>cis</u> -4- <u>t</u> -Butylcyclohexyl Diphenylphosphinate (X) Reaction Mixture	53
XI.	<u>cis</u> - and <u>trans</u> -4- <u>t</u> -Butylcyclohexyl Chlorides (XII and XIII)	54
XII.	<u>trans</u> -4- <u>t</u> -Butylcyclohexyl Chloride (XIII) and 4- <u>t</u> -Butylcyclohexene (III)	55
XIII.	<u>trans</u> -4- <u>t</u> -Butylcyclohexyl <u>p</u> -Toluenesulfonate (II)	56

CHAPTER I

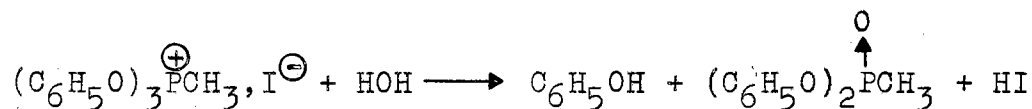
HISTORICAL

The Michaelis-Arbuzov Rearrangement

In 1898, Michaelis and Kaehne⁴⁰ recorded the first preparation of an "O-phosphonium" compound, methyltriphenoxyphosphonium iodide, via the reaction



between triphenyl phosphite and methyl iodide. It was shown that this compound and other salts derived from triaryl phosphites, later designated as quasiposphonium salts, decomposed in aqueous base to give hydroxy compounds, phosphonates,

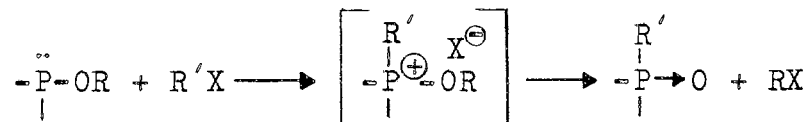


and hydrogen halides.

When trialkyl phosphites react with alkyl halides, the quasiposphonium salts formed are generally unstable and decompose under reaction conditions to yield alkyl halides and phosphonates. This reaction has become known as the Michaelis-Arbuzov rearrangement and has been extended to

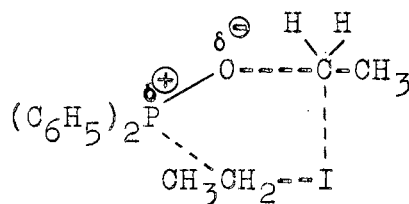
other types of phosphorus esters. The order of reactivity of trivalent-phosphorus esters towards attack by alkyl halides has been shown to be phosphite < phosphonite < phosphinite.⁴³ Thus the reactivity seems to be proportional to the number of carbon-phosphorus bonds.

A great deal of attention has been focused on the Michaelis-Arbuzov rearrangement since its discovery, largely owing to its synthetic utility as a convenient means of producing carbon-phosphorus bonds. Several reviews on the



scope and mechanism of this rearrangement and related reactions are available.^{26,35,36}

The two-step mechanism shown above was first proposed by Arbuzov.³ The presence of an addition compound as an intermediate seems well established,³⁴ although its degree of ionic character is subject to considerable speculation.²⁶ There is some recent evidence that a transition state, rather than an actual intermediate, is involved in the reaction between ethyl iodide and ethyl diphenylphosphinite. This

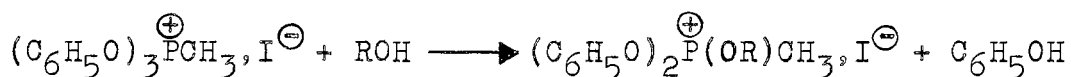


cyclic transition state is shown above, modified over the

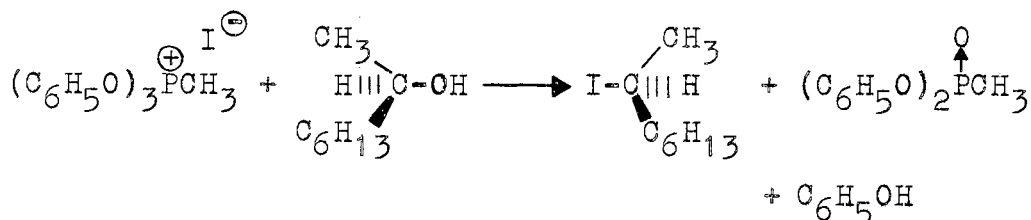
original representation¹ to exclude certain stereoelectronic ambiguities, such as two neutral carbon atoms with 4.5 bonds. Regardless of its representation, this species is improbable in view of the stereochemical studies of Gerrard and Green,^{2,20} since it would lead to retention of configuration. Furthermore, crystalline intermediates, which decompose to phosphine oxides upon warming, have been isolated from low-temperature reactions of alkyl dialkylphosphinites with alkyl halides.⁴⁴

Stereochemical Studies of the Decomposition of Quasiphosphonium Salts

Landauer and Rydon^{37,38} introduced a novel method of producing alkyl iodides via the decomposition of methyltriphenoxyphosphonium iodide by alcohols. Phenol and diphenyl



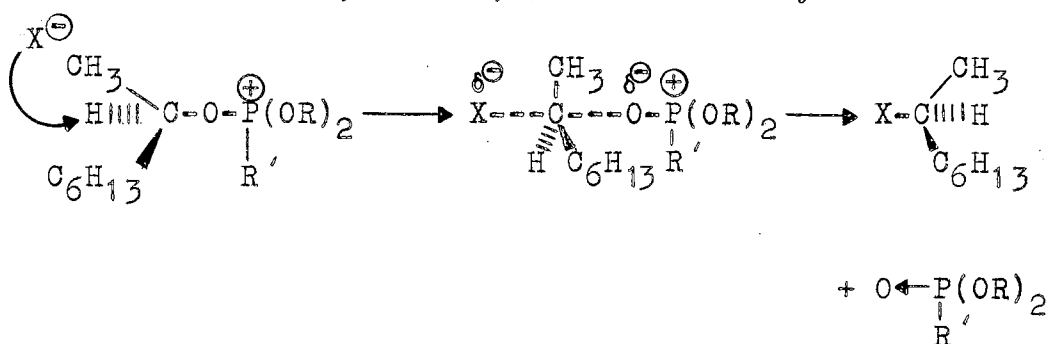
methylphosphonate were also isolated from the reaction mixture indicating that a transesterification had occurred first, followed by the usual type of decomposition of the less stable quasiphosphonium salt formed. The decomposition



step apparently occurred by an S_N2 route, as evidenced by the inversion of (+)-2-octanol to produce (-)-2-iodooctane and by the absence of rearrangement in the formation of neopentyl iodide.

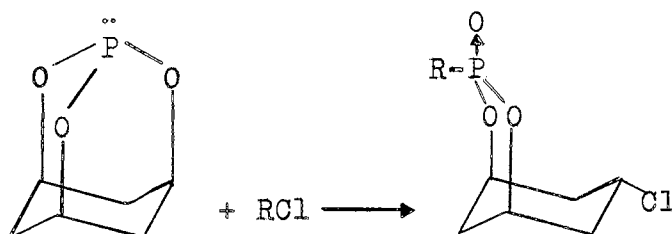
Likewise, tri-2-octyl phosphite, prepared from (+)-2-octanol,¹⁹ reacted with ethyl iodide to produce (-)-2-iodooctane²⁰ with inversion of configuration. Thus in a classical Michaelis-Arbuzov rearrangement, there is evidence for an S_N2 mechanism in the second stage of the reaction.

In these and other examples,^{21,22} the isolation of inverted 2-octyl halides was attributed to the occurrence of an intermolecular, end-on, 3-center dealkylation of the



quasiphosphonium ion by halide ion.

Berlin and co-workers^{6,7} treated 1-phospha-2,8,9-tri-oxadamantane with several alkyl halides to produce a series

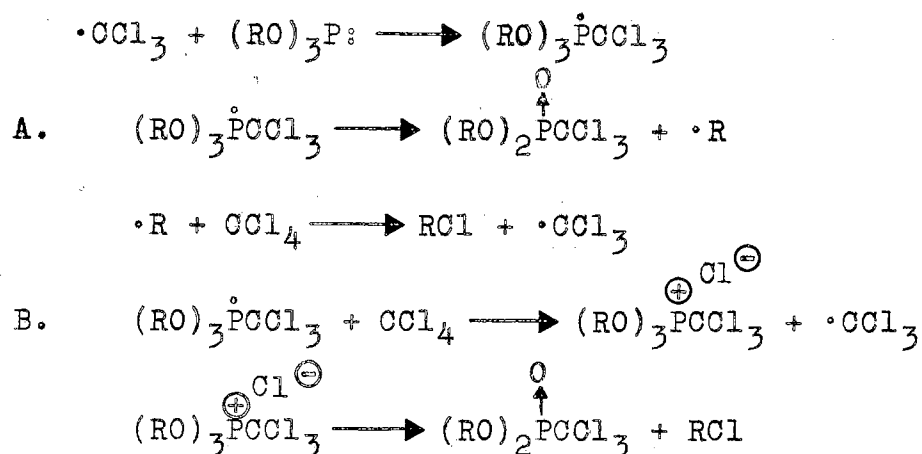


of bicyclic phosphonates. IR, NMR, and dipole moment studies

indicated that these products possessed an equatorial chlorine atom. This is in accord with an S_N2 displacement by chloride ion at one of the bridgehead atoms in a quasiphosphonium intermediate of the usual type. An extension of this work by Verkade⁴⁸ included a reaction with an alkyl tosylate, which gave comparable results.

The Mechanism of the Reaction of Polyhalomethanes
with Trivalent Phosphorus Esters

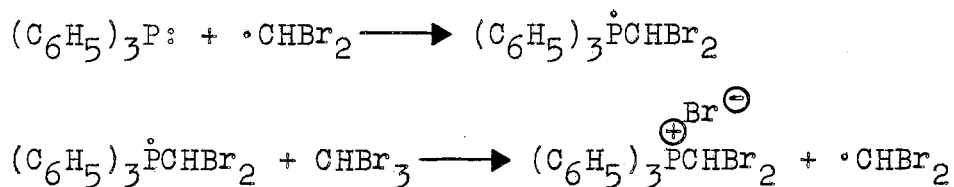
Kamai and Egorova³¹ first investigated the reaction between carbon tetrachloride and trialkyl phosphites. It was found that one of the four chlorine atoms reacted to give the usual Michaelis-Arbuzov products. Later this reaction was shown to be light- and peroxide-catalyzed,³² and thus a radical-chain process was suggested. Griffin²⁵



proposed two pathways, A and B, for the conversion of the phosphoranyl radical to phosphonate. The absence of hydrocarbon in his products led Griffin to express a preference for

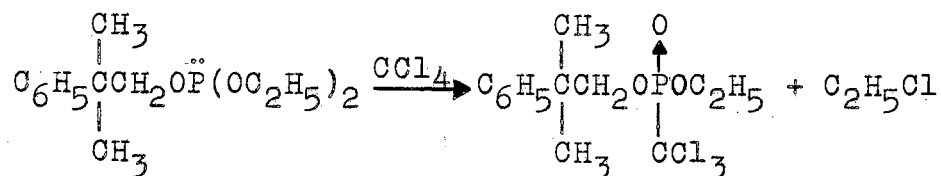
B. Walling,⁴⁹ however, pointed out that the reaction between $\cdot R$ and carbon tetrachloride is rapid enough to preclude the formation of hydrocarbons from this radical, and stated his preference for path A.

Ramirez and McKelvie⁴² showed that phosphonium salts were indeed obtainable by a free-radical route. From the



light-catalyzed reaction of carbon tetrabromide with triphenylphosphine, there was isolated a high-melting solid (80%), which was identified as triphenyl(dibromomethyl)phosphonium bromide. Unfortunately, aryl phosphorus esters are resistant to polyhalomethanes even at high temperatures,³³ and no case of a stable quasiphosphonium salt formed by a free-radical pathway has yet been isolated.

The most concrete evidence for scheme B was provided by Cadogan and Foster,¹² who treated β,β -dimethylphenethyl diethyl phosphite with carbon tetrachloride. A careful anal-



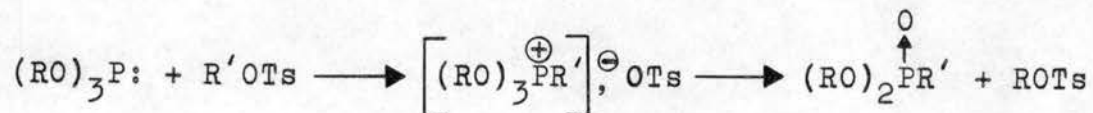
ysis of the products revealed only β,β -dimethylphenethyl ethyl trichloromethylphosphonate and ethyl chloride. It is apparent

The Reaction of Tosylate Esters with Trivalent
Phosphorus Compounds

In the synthesis of phosphonates and other phosphorus esters via the classical Michaelis-Arbuzov rearrangement, one of the difficulties frequently encountered has been the inconvenience of working with, or availability of alkyl halides. The need for a more convenient method of preparing phosphonates from simple alcohols led to the discovery by Myers and co-workers⁴¹ that the p-toluenesulfonate (tosylate) esters of these alcohols effected the necessary conversions under milder conditions than those necessary when halides were used.

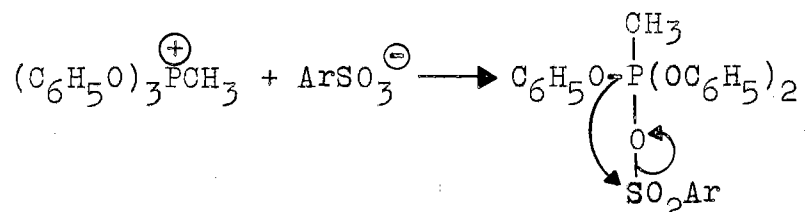
As noted previously, Verkade⁴⁸ successfully prepared a bicyclic phosphonate from the reaction of 1-phospha-2,8,9-trioxaadamantane with an alkyl tosylate. The presence of an equatorial tosylate group in the product suggests that an S_N2 pathway might be operative in this reaction, just as in the corresponding reaction with alkyl halides.

The only other published material found on this reaction was a note by Denney and Giacín.¹⁴ These workers treated tri-



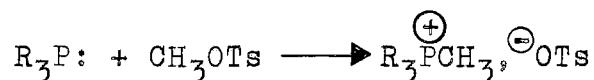
phenyl phosphite with methyl tosylate and obtained phenyl tosylate and diphenyl methylphosphonate. These same products were isolated from a mixture of methyltriphenoxyposphonium iodide and silver tosylate. Evidently a quasiposphonium

tosylate is formed but is too unstable to permit isolation. This instability is somewhat surprising in view of the weak nucleophilicity of the tosylate anion. The explanation provided was that the quasiphosponium ion and the tosylate anion united to produce an intermediate which could then decompose



intramolecularly as shown, or possibly by loss of phenoxide ion which subsequently attacked the sulfur atom.

Phosponium tosylates have been prepared³⁹ from tertiary phosphines and methyl tosylate. These salts were readily con-



verted to the corresponding iodides and picrates by which they were identified.

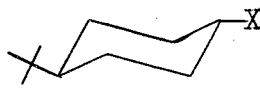
The 4-*t*-Butylcyclohexyl Group

The fact that 4-*t*-butylcyclohexyl compounds are conformationally homogeneous is rather well-established, although the reason for the so-called preference of the *t*-butyl group for an equatorial position is often misunderstood. The energy barrier toward ring inversion in such systems is not prohibitive; in fact, such "flipping" is believed to occur to a high degree. However, the equatorial conformers are so much

more stable ($\Delta F = 5.5$ kcal./mole) than the inverted, axial forms that the former predominate by a factor as high as 10,000 at room temperature. Consequently, substituents at



cis,axial

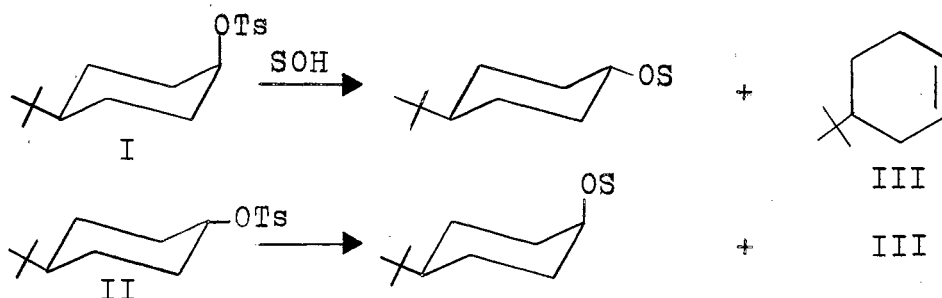


trans,equatorial

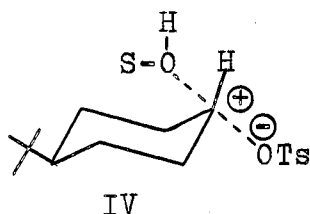
C-1 in cis-4-t-butylcyclohexyl compounds are directed almost exclusively to the axial position, whereas those in the corresponding trans-isomers prevail in the equatorial position, provided that such substituents are sufficiently smaller than the t-butyl group.¹⁵

The conformational homogeneity exhibited by these compounds has been used as a basis for stereochemical studies. Differentiation between the S_N1 and S_N2 mechanisms in displacements at C-1 can be accomplished by examination of the products obtained. Inversion should yield cis-isomers from trans-isomers, and vice versa.

Occasionally complications arise in using this method. Winstein and Holness⁵¹ described the solvolysis of cis- and trans-4-t-butylcyclohexyl tosylates (I and II, respectively). The ethanolysis of the trans-tosylate II was not accelerated

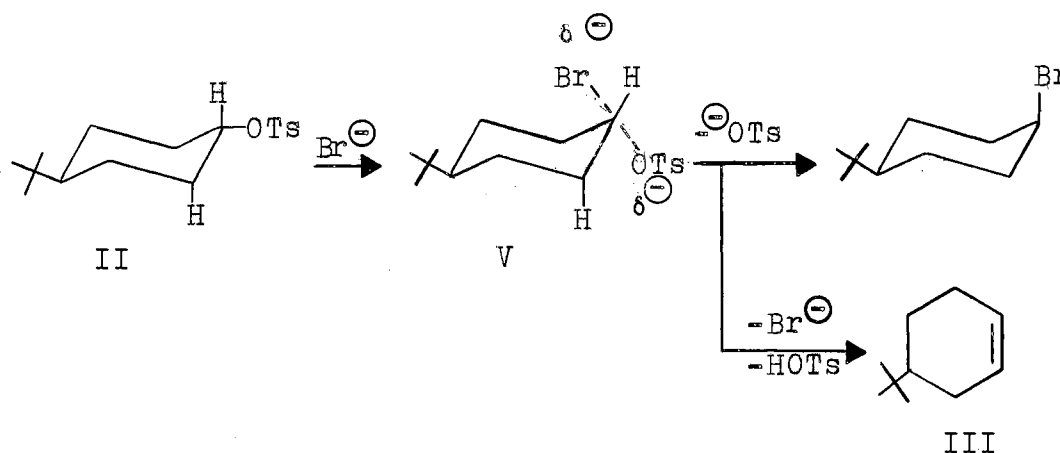


by addition of ethoxide ion, suggesting that an S_N1 reaction was occurring via the usual type of carbonium ion. However, only cis products and 4-*t*-butylcyclohexene (III) were isolated. To resolve this apparent contradiction, the authors proposed that, although a carbonium ion IV had formed, it remained closely associated with both the entering (SOH) and leaving ($^{\ominus}$ OTs) groups, through solvation and ion pair formation, respectively. Axial-side attack of solvent could



yield the stereospecific substitution product, or a β -proton could be eliminated, producing the olefin III. The cis-tosylate I also gave inverted products, and a slightly larger percentage of olefin III was found. The same mechanism was proposed for I as for II with possible limited intervention of E2 elimination, a highly favored reaction in some cases for axial substituents.³⁰

When treated with lithium bromide in acetone,⁵⁰ trans-tosylate II yielded cis-4-*t*-butylcyclohexyl bromide and olefin III. The occurrence of elimination simultaneously with S_N2 substitution was somewhat unusual and required further explanation. A novel mechanism was proposed, involving "merged substitution and elimination." An actual intermediate V, geometrically and electronically analogous to the usual



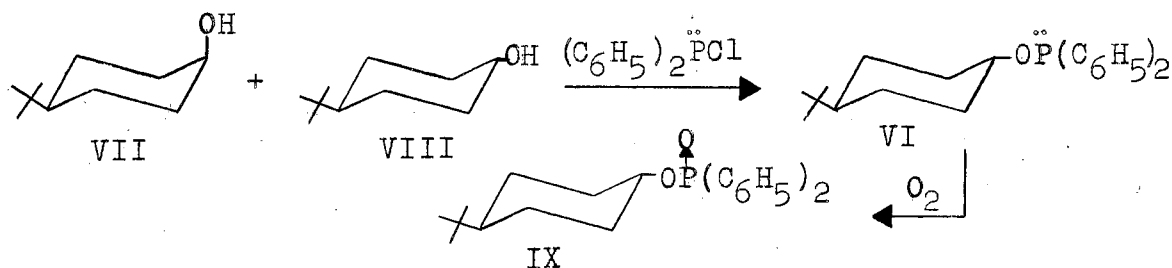
$\text{S}_{\text{N}}2$ transition state, was thought to appear just prior to the occurrence of both reactions. Completion of the usual $\text{S}_{\text{N}}2$ pathway could then produce the cis-bromide, or a non-stereospecific elimination could proceed with detachment of both nucleophiles, OTs^- and Br^- , along with a β -proton. The "merged" mechanism, as it is now designated, has received additional support from studies of displacements by thiophenolate ion at the C-1 atoms of cis- and trans-4-t-butylcyclohexyl bromides¹⁶ and 4,4-dimethylcyclohexyl tosylate.¹⁸ Some opposing evidence, which seems to favor an E2 mechanism for the elimination, has been described⁹ from free-energy considerations.

Other investigations of 4-t-butylcyclohexyl compounds include saponification rate studies of the ethyl 4-t-butylcyclohexanecarboxylates¹⁷ and 4-t-butylcyclohexyl terephthalates,⁵¹ oxidation rate-studies of the corresponding alcohols,⁴⁵ and reactions of the appropriate amines with nitrous acid.³⁰ Further information and references are available¹⁵ on this and other conformationally homogeneous cyclohexyl systems (decalins, steroids, menthyl compounds, etc.).

CHAPTER II

DISCUSSION OF RESULTS AND CONCLUSIONS

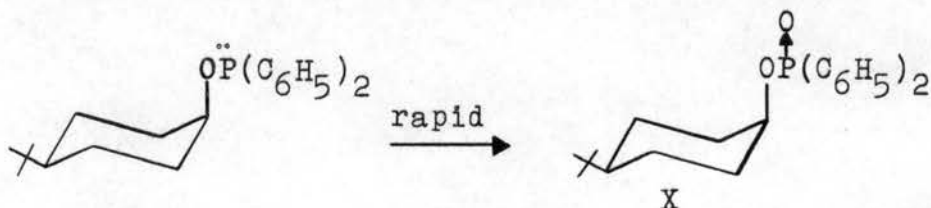
Three distinct but closely related reactions were studied from a stereochemical viewpoint, utilizing the conformationally homogeneous system of trans-4-t-butylcyclohexyl diphenylphosphinite (VI). This ester was prepared from a mixture of cis-



and trans-4-t-butylcyclohexanol (VII and VIII, respectively). The structure of VI was established by IR and NMR spectroscopy and by its oxidation in air to trans-4-t-butylcyclohexyl diphenyl phosphinate (IX), the structure of which has been established.⁵ The C-1 proton in VI (see Plate VIII) occupies a field position (ca. δ 4.0) very close to the corresponding absorption in IX (see Plate IX). Both peaks have half-widths greater than 20 c.p.s., indicating axial conformations for the protons represented.⁵ Equatorial protons generally display absorptions with half-widths less than 12 c.p.s., whereas those for axial protons are 15 c.p.s. or greater.²⁸ Examples of these two types of absorptions can be found in the NMR

spectra of the cis- and trans-chlorides, XII and XIII (Plates XI and XII). The equatorial proton in XII was displayed at δ 4.30, and the axial proton in XIII at δ 3.67 in carbon tetrachloride which clearly shows the large field separation of the two dissimilar protons. Thus it is concluded with a reasonable degree of certainty that VI is indeed conformationally homogeneous trans-4-t-butylcyclohexyl diphenylphosphinite.

Because the cis-isomer of VI would be an undesirable impurity, an attempt to prepare this cis-phosphinite was undertaken. Pure cis-alcohol VII was treated with diphenylphosphinous chloride under a steady stream of nitrogen. In spite of this precaution against air oxidation, the major components in the reaction mixture were VII and cis-4-t-butylcyclohexyl diphenylphosphate (X), as evidenced by the large absorptions for -OH (3360 cm.^{-1}) and $\text{P}\rightarrow\text{O}$ (1193 cm.^{-1}) displayed in the IR spectrum (Plate III). The facile oxidation of cis-4-t-butylcyclohexyl diphenylphosphinite to X is understandable in view of the vulnerable position of the

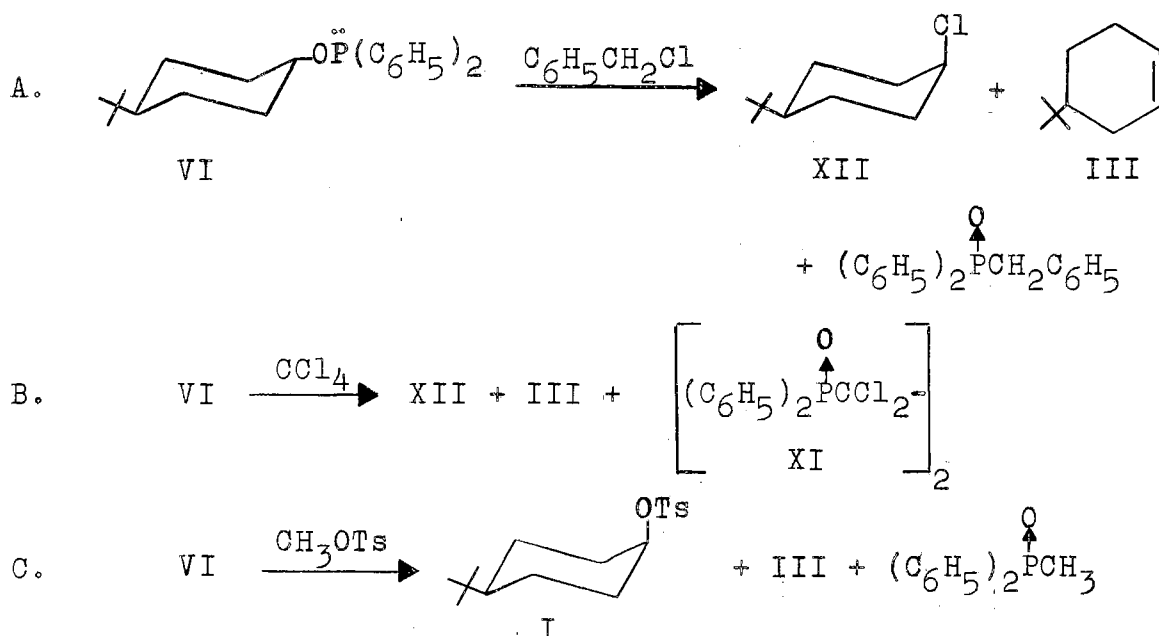


trivalent phosphorus atom above the ring. Molecular models indicate that the corresponding phosphorus atom in the equatorial conformer VI is somewhat protected by the equatorial β -hydrogen atoms. Thus the latter isomer should be less

readily oxidized, which indeed appears to be the case.

A small amount of cis-phosphinate X was detected in the trans-phosphinite VI reaction mixture by NMR. Subsequent distillations finally removed all detectable amounts of X, leaving trans-alcohol VIII as the only detectable impurity (ca. 20-30%).

The reactions A, B, and C of trans-phosphinite VI with benzyl chloride, carbon tetrachloride, and methyl tosylate

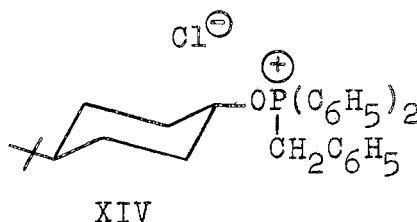


yielded the expected cis-products in each case, free of any detectable amounts of the corresponding trans-isomers, but contaminated with olefin III and unchanged trans-alcohol VIII. The phosphine oxides were also detected except in reaction B, which yielded 1,2-bis(diphenylphosphinyl)-1,1,2,2-tetrachloroethane (XI), rather than the expected product, diphenyl(trichloromethyl)phosphine oxide.

The first reaction, A, is a classical example of a Michaelis-Arbuzov rearrangement of a reactive phosphorus ester and a reactive halide. The stereochemistry of the resulting halide, cis-4-t-butylcyclohexyl chloride (XII), supports the evidence obtained by Gerrard and Green²⁰ for an S_N2 mechanism for the second step of rearrangements in this series.

Standard samples of XII and its isomer, trans-4-t-butylcyclohexyl chloride (XIII), were prepared by a published procedure.²⁴ It was not necessary to isolate the individual isomers by the time-consuming procedures described. The fortuitous ease of dehydrochlorination of the cis-isomer XII compared to that of the trans-isomer XIII provided a means of labeling these two compounds via TLC, which was all that was necessary in this study.

The occurrence of a salt-like material in reaction A at room temperature was not surprising. However, the high thermal stability of this material was quite unexpected. Nevertheless, the material was tentatively characterized as trans-(4-t-butylcyclohexyloxy)benzyl diphenylphosphonium chloride (XIV) on the basis of its high melting point, its IR spectrum, its reactions with aqueous silver nitrate, and its high-temperature decomposition to give cis-chloride XII and olefin III. The decomposition of XIV when it is dissolved in the reaction mixture A is evidently quite facile. Once XIV has precipitated from this medium, however, the chloride ions may be highly associated with the positively

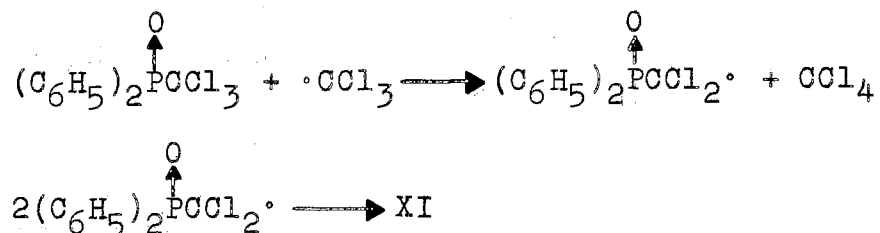


charged phosphorus atoms in a crystal lattice. These chloride ions would not be free to attack the C-1 position of the cyclohexyl ring until the lattice is broken up at or above the melting point of XIV (268-70°).

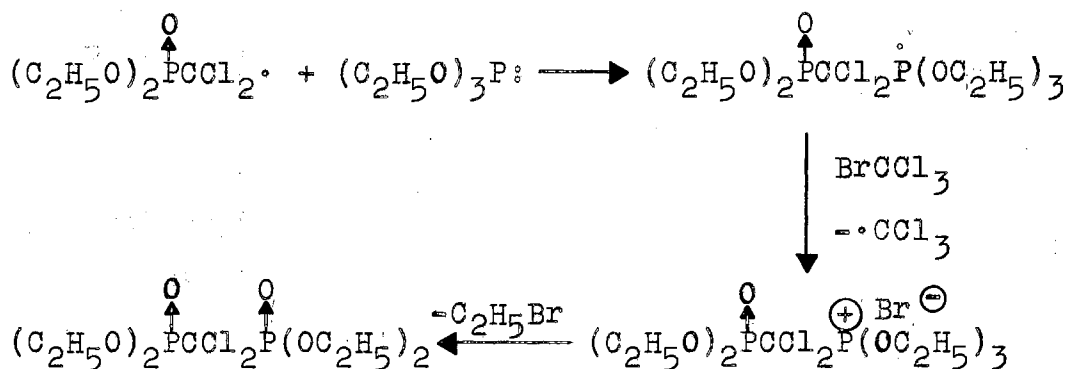
Further experiments will be necessary before the structure of XIV can be conclusively established. Very small yields (<2%) of this compound were obtained under the conditions employed, and the purification process proceeded slowly with significant loss of material. The IR spectrum indicates the presence of a hydroxylic impurity which is probably water or trans-alcohol VIII. Before the recrystallization from water, there was also evidence of the presence of benzyldiphenylphosphine oxide from comparison of the IR spectrum with a known standard. The presence of small amounts of this latter impurity could account for the low percentages of carbon and hydrogen and the high chlorine and phosphorus percentages in the elemental analysis of XIV (see Chapter III).

Reaction B may follow a radical-chain course similar to those described in Chapter I for the reactions of other phosphorus esters with carbon tetrachloride.^{12,25,31,32} The appearance of the coupling product XI seems to verify this

conclusion. A plausible mechanism for its formation from the



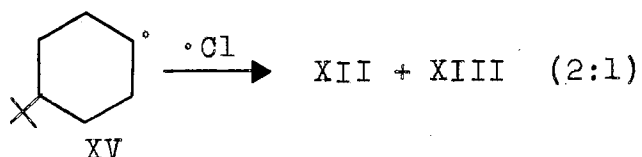
expected monomeric phosphine oxide is shown above. Bunyan and Cadogan¹⁰ have proposed a similar pathway for the reaction of bromotrichloromethane with triethyl phosphite. No coupling product was found in this reaction mixture. However, a radical analogous to the (diphenylphosphinyl)dichloromethyl



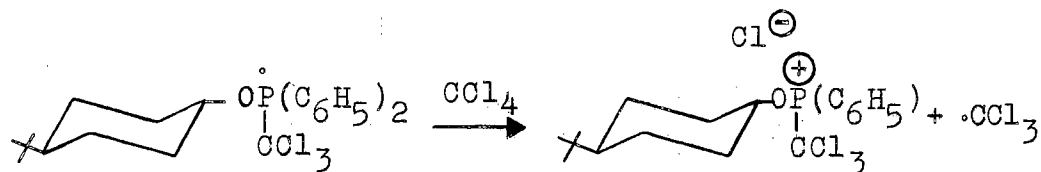
radical was proposed. Reaction of the latter with another molecule of triethyl phosphite evidently led to the production of bis(diethylphosphoryl)dichloromethane. Steric hinderance might have prevented the occurrence of this step in reaction B in our work.

The presence of cis-chloride XII and absence of the trans-isomer XIII shows reaction B to be stereospecific. Furthermore, the presence of olefin III suggests that the

intermediate in reaction B is analogous to that in reaction A, that is, a quasiphosphonium salt. This is also in accord with the conclusions expressed by most investigators (see Chapter I) regarding the fate of the initially formed phosphoranyl radical. The formation of 4-t-butylcyclohexyl radicals (XV) seems improbable in view of the behavior of XV



in the presence of a source of chlorine atoms, as reported by Greene and co-workers.²⁴ Both chlorides, XII and XIII, were obtained, but the detection of olefin III is not mentioned in their paper for a reaction involving the radical XV. Consequently, for reaction B, the most favorable mechanism appears to involve a disproportionation between a phos-

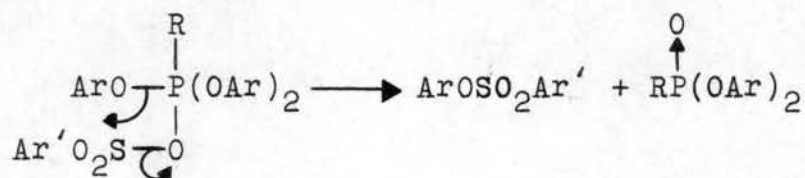


phoranyl radical and carbon tetrachloride to give the usual type of quasiphosphonium salt, which subsequently undergoes nucleophilic attack at C-1 by chloride ion to yield the observed products.

Further studies of this reaction might include: (1) a conversion of an optically active 2-octyl phosphorus ester by carbon tetrachloride to verify the stereochemistry proposed

here, and (2) a low-temperature study which might allow isolation and identification of the elusive quasiphosphonium salt proposed but unverified for such free-radical reactions.

Reaction C belongs to a relatively unexplored area, the reactions of sulfonic esters with trivalent-phosphorus esters. In Chapter I, evidence is cited¹⁴ to indicate that a quasiphosphonium type of intermediate is involved but decomposes by a different pathway from the one generally accepted for Michaelis-Arbuzov rearrangements. This course would lead to



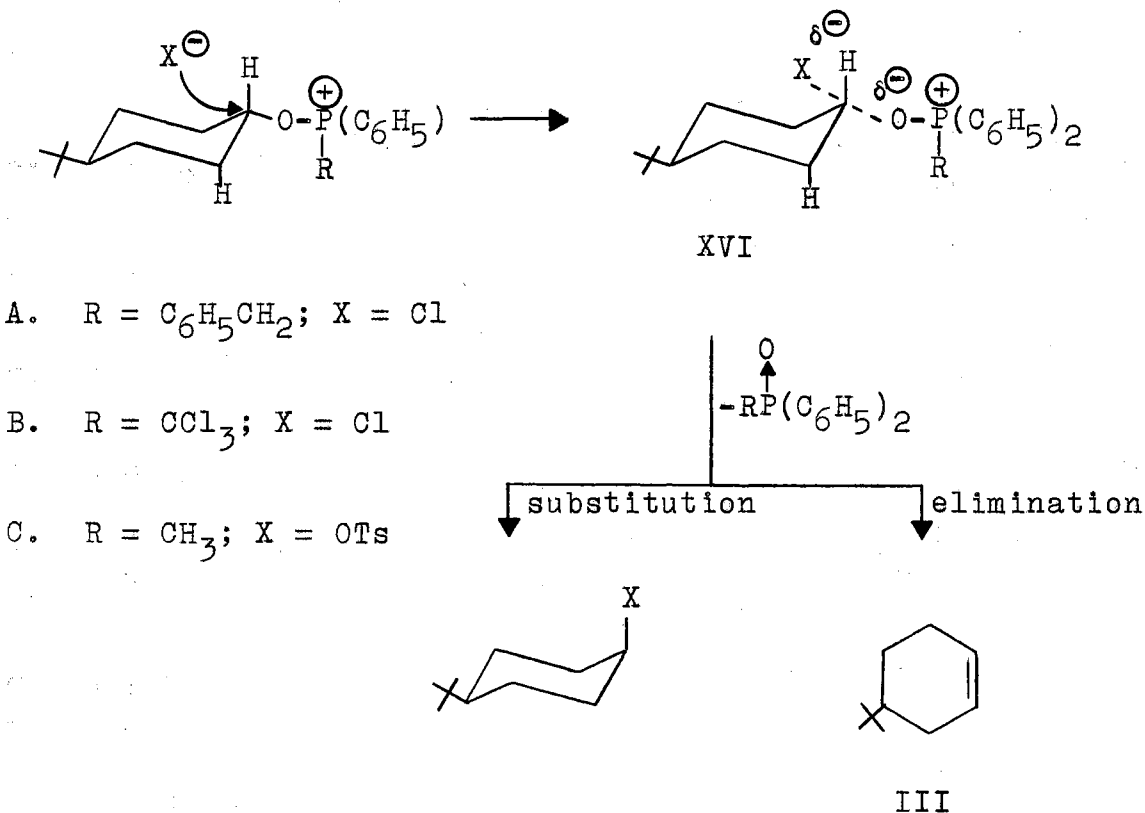
retention of configuration, however, and is thereby unsatisfactory for explaining the results described herein, although it may be valid for the rearrangement of aryl phosphorus esters.

The similarity of the products identified from C to those detected from A and B suggests that the same type of mechanism is operative in all three cases. Although the tosylate anion is a relatively weak nucleophile,²³ it now seems likely that the driving force for the production of compounds possessing a phosphoryl (P → O) group is sufficiently strong to overcome this obstacle. Thus it might be said that such tetrasubstituted phosphorus compounds are better "leaving groups" than even tosylate ion.

Further verification of the stereochemistry of this reaction could be attained from an investigation of the

products obtained from optically active tri-2-octyl phosphite and alkyl tosylate, as noted by Gerrard and Green²⁰ for alkyl halides.

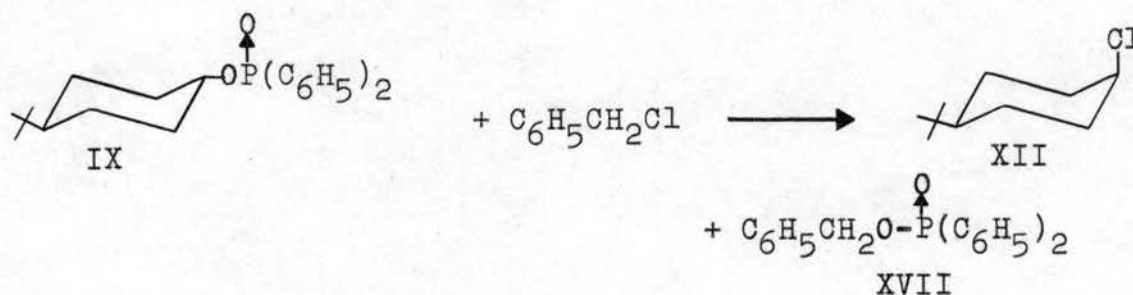
It is conceivable that all three reactions (A, B, and C) could proceed by a course resembling that proposed by Winstein and co-workers⁵⁰ for the reaction of trans-tosylate II with bromide ion. Whether or not the so-called "merged" mechanism is operative in either case, the analogy is quite close, and comparison of the two systems on this basis seems justified. The necessary assumptions are that a quasiphosphonium intermediate exists and that it is relatively ionic in character so that the halide or tosylate ion is free to attack the C-1 position. The resulting "intermediate", XVI, is a stereotype



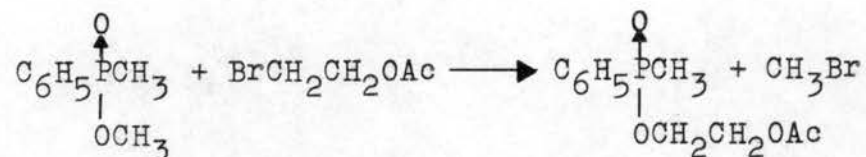
of V (see Chapter I), and loss of phosphine oxide could occur with simultaneous ("merged") substitution and elimination as described for loss of tosylate ion from V.

The production of olefin III by dehydrochlorination of cis-chloride XII in situ is unlikely in view of experiments (see Chapter III) designed to duplicate such an elimination under reaction conditions. In a like manner, it was shown that the absence of trans-chloride XIII could not be explained by such a dehydrochlorination. The latter experiment seemed particularly advisable in order to exclude the possibility of existence of XIII at any stage of the reaction, since its absence is the basis for the argument against a carbonium ion intermediate. Even so, the existence of a solvated ion-pair, such as IV (Chapter I), cannot be entirely discounted.

The production of cis-chloride XII in reaction A could conceivably have occurred via the trans-phosphinate IX as well as the trans-phosphinite VI. Harwood and Grisley²⁷ proposed such a conversion to account for an unexpected product



which they had encountered in a Michaelis-Arbuzov rearrangement with β -bromoethyl acetate. Since a trace of IX was thought to be present in all samples of VI, a control experiment was performed to see if an authentic sample of the



phosphinate IX would react with benzyl chloride. No trace of the expected products, XII and benzyl diphenylphosphinate (XVII), was found after 2 days at room temperature. Published evidence^{4,27} indicates that elevated temperatures are required for this type of reaction. Intuitively, one would not expect the phosphoryl group to be sufficiently nucleophilic to effect such a conversion via the usual quasiphosponium salt, but nucleophilicity is often dependent upon reaction conditions and other reagents involved.²³ If such conditions could be conveniently attained, the utility of the Michaelis-Arbuzov rearrangement might be improved markedly by the use of tetravalent phosphorus esters instead of the easily oxidized trivalent esters.

In summary, the reactions of conformationally homogeneous trans-4-t-butylcyclohexyl diphenylphosphinite (VI) with benzyl chloride, carbon tetrachloride, and methyl tosylate each yielded cis-4-t-butylcyclohexyl compounds. It has been proposed that, in each case, a quasiphosponium salt is formed and subsequently decomposes via an S_N2 mechanism, giving inverted products. Also identified were 4-t-butylcyclohexene (III) and the expected phosphine oxide, except in the case of the reaction of carbon tetrachloride with VI. Evidently

the phosphine oxide produced in this latter reaction underwent free-radical coupling.

CHAPTER III

EXPERIMENTAL^{a-f}

Preparation of Cyclohexyl Diphenylphosphinite. A solution of 25.0 g. (0.250 mole) of cyclohexanol and 25.2 g. (0.250 mole) of triethylamine in 200 ml. of benzene was prepared in a 500-ml. three-necked flask fitted with a mechanical stirrer, a condenser with drying tube, an immersion thermometer, and a pressure-equalizing addition funnel with a

^a All melting points are corrected; all boiling points are uncorrected.

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

^c The 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. Unless otherwise stated, the solvent employed was carbon tetrachloride.

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

^e Thin-layer chromatography was performed using 5-cm. x 20-cm. glass plates coated with a 250- μ layer of activated silica gel G obtained from Research Specialties Company, Richmond, California. The plates were eluted with chloroform containing a trace of acetone and were developed in iodine vapors.

^f The microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

nitrogen inlet. A solution of 55.1 g. (0.250 mole) of diphenylphosphinous chloride in 50 ml. of benzene was added dropwise with stirring under dry nitrogen. The reaction was exothermic, the temperature of the solution rising to 45° during the 40-minute addition period. The mixture was stirred for 4 hours at room temperature, after which it was heated at reflux for 2 hours and then cooled to 4°. Triethylamine hydrochloride was removed by filtration under nitrogen. Removal of the solvent gave an oil which was distilled, b.p. 160-2°/0.3 mm.; yield 56.5 g. (79.6%). The infrared (IR) spectrum showed P-phenyl absorption at 1440 cm.⁻¹. The nuclear magnetic resonance (NMR) spectrum showed two broad multiplets covering ranges in delta (δ) values of 1.0-2.2 (cyclohexyl protons) and 7.2-8.3 (phenyl protons).

Anal. Calcd. for C₁₈H₂₁OP: C, 76.06; H, 7.39; P, 10.92

Found: C, 75.89; H, 7.19; P, 11.04.

Preparation of trans-4-t-Butylcyclohexyl Diphenylphosphinite (VI). A solution of 39.0 g. (0.250 mole) of 4-t-butylcyclohexanol^g and 25.2 g. (0.250 mole) of triethylamine in 200 ml. of benzene was prepared in an apparatus similar to that described for the preparation of the cyclohexyl ester in the previous experiment. A solution of 55.1 g. (0.250 mole) of diphenylphosphinous chloride in 100 ml. of anhydrous benzene was added dropwise with stirring under dry nitrogen. The flask was kept over an ice bath during the 30-minute

^g Columbia Organic Chemicals, Columbia, South Carolina, m.p. 66-8°, containing approximately 65% trans-isomer.

addition period to keep the contents below 55° . The mixture was allowed to stir overnight at room temperature and was then heated at reflux ($83-4^{\circ}$) for 2 hours. The mixture was filtered under nitrogen, supplied through an inverted funnel, to remove the triethylamine hydrochloride, and the filtrate was stripped of benzene under aspirator pressure. Distillation was accomplished using a short-path system without a condenser since previous attempts had resulted in clogging of narrow passageways in the system with condensed solid material. A clear, viscous liquid, 30.5 g. (35%), was obtained, b.p. $174-84^{\circ}/0.1$ mm. This material solidified upon standing, m.p. $30-55^{\circ}$. A second and a third distillation, b.p. $175-78^{\circ}/0.1$ mm., gave material of higher purity with each successive distillation as evidenced by the reduction and final disappearance of absorption at 52 c.p.s. in the NMR spectrum of the mixture. This peak was assigned to the t-butyl protons in cis-4-t-butylcyclohexyl diphenylphosphate, (X) based on the spectra obtained with mixed samples. As shown in Plate VIII, there is a sharp singlet at 47 c.p.s. (t-butyl protons) and a smaller singlet at 53.5 c.p.s.. The smaller absorption was assigned to t-butyl protons in trans-4-t-butylcyclohexanol (VII) based on results obtained with mixed samples with cis-4-t-butylcyclohexanol (VIII) and with the cis-trans mixture of the alcohols. The solvent employed for these spectra was benzene, since carbon tetrachloride reacts with the trivalent-phosphorus ester. The IR spectrum (Plate I) further supports the structure assigned.

Anal. Calcd. for $C_{22}H_{29}OP$: C, 77.62; H, 8.59; P, 9.10

Found: C, 78.26; H, 8.72; P, 8.90.

Preparation of cis-4-t-Butylcyclohexanol (VII). This sample was prepared in a manner similar to Winstein's method.⁵¹ A 7.5 g. portion of cis- and trans-4-t-butylcyclohexanol was chromatographed through 250 g. of acid-washed alumina in a 72-cm. x 3-cm. column, using petroleum ether (b.p. 30-60°) as the eluant. The first fraction melted at 49-50° and appeared to be 4-t-butylcyclohexanone, reported m.p. 49-50°. The second fraction collected melted at 81-2°. Only a small amount (0.4 g.) of pure cis-alcohol VII was obtained from this fraction. The NMR spectrum of this material supported the structure, displaying an absorption at δ 4.10 with a half width of ca. 10 c.p.s.. Half-widths of less than 12 c.p.s. are characteristic of equatorial protons.²⁸

Preparation of cis-4-t-Butylcyclohexyl Diphenylphosphate (X). A solution of 0.16 g. (0.0010 mole) of cis-alcohol VII and 0.10 g. (0.0010 mole) of triethylamine in 8 ml. of benzene was prepared in a 25-ml. four-necked flask fitted with a condenser and drying tube, an addition funnel, an immersion thermometer, a nitrogen inlet, and a magnetic stirring bar. A solution of 0.22 g. (0.0010 mole) of diphenylphosphinous chloride in 4 ml. of benzene was added to the contents of the flask. The addition was accomplished in less than 1 minute with no more than 10° rise in temperature and a small amount of precipitation of amine hydrochloride.

The precipitate and solvent were removed in the usual manner, but distillation was not attempted in view of the very small quantity of crude material obtained. IR absorption (see Plate III) of this material indicates the presence of the functional groups -OH (3360 cm.^{-1}) and $\text{P} \rightarrow \text{O}$ (1195 cm.^{-1}). The NMR spectrum of a benzene solution of this material is shown in Plate X. The largest peak at 55 c.p.s. was shown by mixed standard samples to be due to cis-alcohol VII. The smaller peak at 52 c.p.s. was identified as arising from the cis-phosphinate X. Mixed samples showed the presence of both of these compounds in trace amounts in the reaction mixture obtained in the preparation trans-phosphinite VI.

Preparation of cis- and trans-4-t-Butylcyclohexyl Chlorides. (XII) and (XIII). The procedure used here is a modification of that described by Greene and co-workers.²⁴ A solution of 60.5 g. (0.388 mole) of 4-t-butylcyclohexanol and 71.6 g. (0.388 mole) of tri-n-butylamine in 750 ml. of anhydrous ether was prepared in a 2-l. three-necked flask fitted with a mechanical stirrer, a condenser with drying tube, an immersion thermometer, and a pressure-equalizing addition funnel. A solution of 76 ml. (46.1 g., 0.388 mole) of thionyl chloride in 150 ml. of anhydrous ether was added dropwise with stirring during 1 hour to the contents of the flask. Shortly after the addition was started, it became necessary to utilize an ice bath in order to maintain the contents of the flask below 40° . The mixture was stirred at room temperature overnight and then poured over ice-water.

The ether layer was separated and washed with 250 ml. of 10% sodium bicarbonate solution, then with three 250-ml. portions of distilled water. The ether solution was then dried (MgSO_4), stripped of ether at aspirator pressure, and vacuum distilled. One simple distillation gave material boiling at $53-8^\circ/0.4$ mm. Three spots were observed on the TLC, at R_f values of 0.32, 0.47, and 0.78. A 4.3 g. (ca. 0.025 mole) sample of this material was treated with 4.0 g. (0.7 mole) of potassium hydroxide in 20 ml. of 95% ethanol under gentle reflux for 1 day. To this mixture was then added 100 ml. of distilled water, and the resulting liquid was extracted twice with 100-ml. portions of petroleum ether. The ether layer was dried (MgSO_4), and the solvent was removed under aspirator pressure. The resulting liquid showed only two TLC spots, at R_f 0.47 and 0.77. A forerun from the vacuum distillation of the original mixture, which had boiled at $32-40^\circ/0.6$ mm., was found to contain only the material of R_f 0.77, identified as 4-t-butylcyclohexene (III) by its NMR spectrum, which showed a vinyl proton absorption at δ 5.58. The three-component sample (Plate XI) showed a multiplet centered at δ 4.30 (equatorial tertiary proton). After treatment of the mixture with ethanolic potassium hydroxide, this peak had disappeared (Plate XII), and the vinyl protons were clearly visible along with a very broad multiplet centered at δ 3.67 (axial tertiary protons in the trans-chloride). The IR spectra of these samples (Plates IV and V, respectively) lend additional support to these data. Thus R_f values were assigned as

follows: 0.32, cis-chloride XII; 0.47, trans-chloride XIII; and 0.77, olefin III.

Reaction of Cyclohexyl Diphenylphosphinite with Benzyl Chloride. A solution of 5.78 g. (0.0200 mole) of cyclohexyl diphenylphosphinite in 10.12 g. (0.0800 mole) of benzyl chloride was heated for 24 hours under nitrogen over boiling o-dichlorobenzene (180°) in a 1.5-cm. x 7.5-cm. tube fitted with a nitrogen inlet, a condenser, and a drying tube. The sample was allowed to stand at room temperature overnight, and the white solid which had formed was then removed by filtration. Washing this solid material with benzene separated two components. The benzene-soluble material, yield 2.2 g. (38%), was identified as benzyldiphenylphosphine oxide by its melting point ($192-3^{\circ}$ from benzene), IR, and NMR data. The benzene-insoluble material, m.p. $267-8^{\circ}$, was tentatively labeled as (cyclohexyloxy)benzyldiphenylphosphonium chloride. The IR spectrum showed peaks at 1439, 1158, 1114, 868, 797, 751, and 698 cm.^{-1} .

From the mother liquors, benzyl chloride and chlorocyclohexane were identified by gas-liquid chromatography (GLC) using a 6-ft. x 1/8-in. column packed with 5% Silicone 30 on acid-washed Chromosorb G. Retention times at 110° were: chlorocyclohexane, 1.5 minutes; benzyl chloride, 3.5 minutes.

Reaction of trans-4-t-Butylcyclohexyl Diphenylphosphinite (VI) with Benzyl Chloride. Essentially the same procedure was utilized here as in the previous experiment. Thus from a mixture of 5.1 g. (0.015 mole) of trans-phosphinite

VI and 1.9 g. (0.015 mole) of benzyl chloride was obtained 4.3 g. (98%) of benzyldiphenylphosphine oxide. A benzene-insoluble material, m.p. 268-70° from water, was isolated in very small quantity. This material was slightly soluble in cold water, giving a solution which reacted with aqueous silver nitrate to give a white precipitate which darkened upon exposure to light. From these properties and from the IR spectrum (Plate VI), the material was assigned the structure of (trans-4-t-butylcyclohexyloxy)benzyldiphenylphosphonium chloride (XIV), although a good elemental analysis was difficult to achieve.

Anal. Calcd. for $C_{29}H_{36}ClOP$: C, 74.58; H, 7.77;

Cl, 7.59; P, 6.63.

Found: C, 73.91; H, 6.16;

Cl, 8.43; P, 7.45.

The mother liquors were examined by TLC for the presence of cis-chloride XII, trans-chloride XIII, and olefin III. Of the three, only the olefin III was identified.

When this reaction was performed at room temperature, however, the cis-chloride XII was also found along with the olefin III in the mother liquors. When the trans-phosphinite VI was dissolved in a minimum of acetonitrile before addition of benzyl chloride, the same results were obtained except that the TLC spot for cis-chloride XII was greatly magnified, indicating a much better yield of this compound. Both reactions were carried out in a 150-mm. x 18-mm. tube fitted with a nitrogen inlet and a magnetic stirring bar, using 3.0 g.

(0.0088 mole) of the trans-phosphinite VI and 1.3 g. (0.010 mole) of benzyl chloride. In no instance was trans-chloride XIII detected, but further examination revealed the presence of unchanged trans-alcohol VIII.

Thermal Decomposition of (trans-4-t-Butylcyclohexyloxy) benzyldiphenylphosphonium Chloride (XIV). A 150-mm. x 18-mm. tube was charged with 0.3 g. (0.64 mmole) of the quasiposphonium chloride XIV and was heated over an oil bath at 150° for 6 hours. A slight charring was observed, but TLC analysis of a petroleum ether extract of the material revealed no products. The tube was then heated for 1 minute over a sand bath at 290°. TLC examination of a methylene chloride extract revealed olefin III and a trace of cis-chloride XII.

Attempted Dehydrochlorination of cis- and trans-4-t-Butylcyclohexyl Chlorides (XII) and (XIII). Five 75-mm. x 10-mm. tubes were charged with two drops each of cis-chloride XII. To one of the tubes was added a crystal of the phosphonium salt XIV; to another tube was added benzyldiphenylphosphine oxide, to a third tube was added phosphinite VI, and to a fourth tube was added phosphinate IX. The fifth tube served as a fixed standard. Each tube was immersed in an oil bath at 175° for 5 minutes. TLC analysis of each heated sample still showed the presence of cis-chloride XII. Repeating the procedure with trans-chloride XIII at room temperature gave comparable results.

Attempted Rearrangement of trans-4-t-Butylcyclohexyl Diphenylphosphinate (IX) with Benzyl Chloride. A mixture of 3.56 g. (0.0100 mole) of the trans-phosphinate IX and 1.27 g. (0.0100 mole) of benzyl chloride was stirred at room temperature for 2 days in a 10-ml. flask. The only product detected by TLC was starting material. The absence of cis-chloride XII and benzyl diphenylphosphinate XVII was verified by this same method.

Reaction of trans-4-t-Butylcyclohexyl Diphenylphosphinite (VI) with Carbon Tetrachloride. Into a 10-ml. one-necked flask fitted with a nitrogen inlet and a magnetic stirring bar was placed 3.9 ml. (6.2 g., 0.040 mole) of carbon tetrachloride. A sample of trans-phosphinite VI (2.5 g., 0.0074 mole) was added and the mixture was stirred under nitrogen. Soon after the solid material had dissolved, an exothermic reaction began, and white solid material began to collect on the sides of the flask. After 0.5 hr., the solid material was recovered by filtration and recrystallized, first from methylene chloride-petroleum ether and then from methanol, giving 0.15 g. of crystals melting at 197-8°. The IR spectrum (Plate VII) and elemental analysis support the structure XI proposed.

Anal. Calcd. for $C_{26}H_{20}Cl_4O_2P_2$: C, 54.96; H, 3.55;
Cl, 24.96; P, 10.90.

Found: C, 54.45; H, 3.86;
Cl, 24.66; P, 10.64.

The cis-chloride XII and olefin III were detected via TLC in the mother liquors. When the reaction was carried out in an NMR tube, the characteristic multiplets for these two components were observed at δ 4.48 and δ 5.78, respectively. However, no signal was observed near δ 3.7 for the C-1 axial proton in the trans-chloride XIII.

Preparation of Cyclohexyl p-Toluenesulfonate. This ester was prepared by a modification of Tipson's method.⁴⁷ A mixture of 21.0 g. (0.110 mole) of tosyl chloride and 10.0 g. (0.100 mole) of cyclohexanol in 100 ml. (98.3 g., 1.24 mole) of pyridine was swirled in a 500-ml. flask until the solid chloride had dissolved. The mixture was allowed to stand overnight, and then 100 ml. of chloroform was used to wash the material into a separatory funnel. The solution was washed successively with 100 ml. of water, with 250 ml. of 8 N sulfuric acid, with 100 ml. of 10% sodium bicarbonate solution, and finally with another 100 ml. of water. The organic layer was dried (MgSO_4), and the solvent was removed. After 3 days, the liquid solidified to yield crystals (15.7 g., 61.8%) melting at $41-5^\circ$ (reported m.p. $44.5-5.0^\circ$).⁸ The IR spectrum of this material showed absorption for sulfonic ester (1362 and 1180 cm^{-1}), the S-O-C linkage (939 cm^{-1}), and p-disubstituted benzene (816 cm^{-1}). The NMR spectrum showed a broad multiplet for cyclohexyl protons at δ 1.5, a sharp singlet for methyl protons at δ 2.42, a broad multiplet for the tertiary ring proton at δ 4.5, and an A_2B_2 quartet for the aryl protons at δ 7.55 ($J_{AB} = 8 \text{ c.p.s.}$,

$\nu_o (= \nu_A - \nu_B) = 26$ c.p.s.). Relative intensities of these peaks were 11:3:1:4, respectively.

Preparation of trans-4-t-Butylcyclohexyl p-Toluene-sulfonate (II). This compound was prepared by essentially the same procedure as described for the corresponding cyclohexyl ester. A mixture of 15.6 g. (0.100 mole) of 4-t-butylcyclohexanol and 21.0 g. (0.110 mole) of tosyl chloride in 100 ml. of pyridine yielded 22.9 g. (76.3%) of crude material. Recrystallization from petroleum ether containing a trace of ethyl acetate gave white crystals, m.p. $87-9^{\circ}$ (m.p. pure trans-isomer II, $89.4-90^{\circ}$).⁵¹ The IR spectrum showed absorption for sulfonic ester (1348 and 1180 cm^{-1}), the S-O-C linkage (952 cm^{-1}), and p-disubstituted benzene (820 cm^{-1}). The NMR spectrum (Plate XIII) confirms the structure.

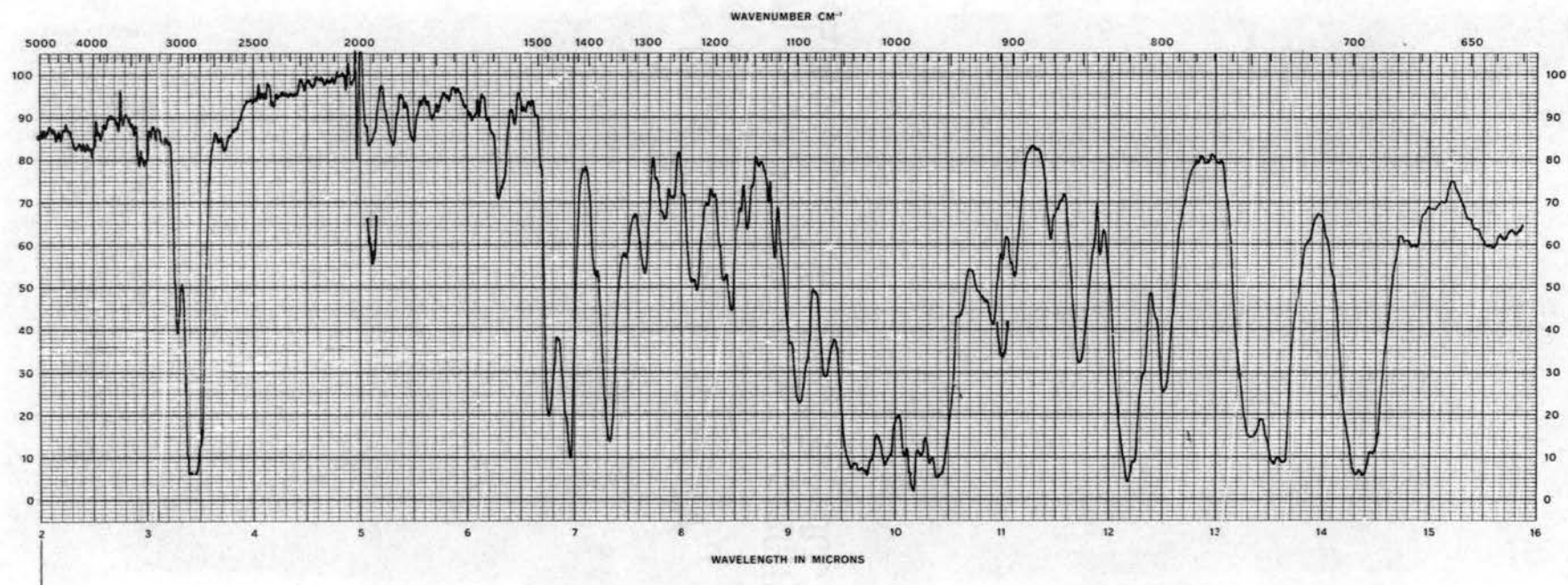
Preparation of cis-4-t-Butylcyclohexyl p-Toluenesulfonate (I). This compound was prepared by a procedure similar to that described for the corresponding cyclohexyl ester. Thus from 0.20 g. (1.3 mmole) of cis-alcohol VII and 0.36 g. (1.9 mmole) of tosyl chloride in 2 ml. of pyridine was isolated a white solid which was recrystallized from a mixture of petroleum ether and ethyl acetate to give crystals melting at $79-80^{\circ}$ (reported m.p. $79-80^{\circ}$).⁵¹ The IR spectrum showed peaks for sulfonic ester (1348 and 1171 cm^{-1}), the S-O-C linkage (914 cm^{-1}), and p-disubstituted benzene (815 cm^{-1}).

Reaction of Cyclohexyl Diphenylphosphinite with Methyl p-Toluenesulfonate. A 1.5 cm. x 7.5 cm. tube was fitted with a condenser, a drying tube, and a nitrogen inlet. The tube was charged with 2.9 g. (0.010 mole) of cyclohexyl diphenylphosphinite and 1.9 g. (0.010 mole) of methyl tosylate. The mixture was heated under nitrogen over boiling xylene (135°) for 72 hours. The product was allowed to cool and dissolved in methylene chloride. TLC examination showed the major products to be cyclohexyl tosylate ($R_f = 0.50$) and methyldiphenylphosphine oxide ($R_f = 0.10$).

Reaction of trans-4-t-Butylcyclohexyl Diphenylphosphinite (VI) with Methyl p-Toluenesulfonate. In a similar apparatus to that used in the previous experiment, a mixture of 3.4 g. (0.010 mole) of trans-phosphinite VI and 1.9 g. (0.010 mole) of methyl tosylate was heated under nitrogen over boiling xylene for 17 hours. At the end of this time the mixture had separated into two layers. As the mixture cooled, the bottom layer became semi-solid. The top layer was removed and was found to consist chiefly of olefin III from its IR spectrum. The bottom layer was examined by TLC, which showed the presence of methyldiphenylphosphine oxide and the absence of the trans-sulfonate II. Identification of the cis-sulfonate I by this method was inconclusive because of interference by an excess of methyl tosylate. However, GLC was used successfully in this identification. A 6-ft. x 1/8-in. column packed with 5% Silicone 30 on 80/100 mesh, acid-washed, DMCS-treated Chromosorb G was utilized.

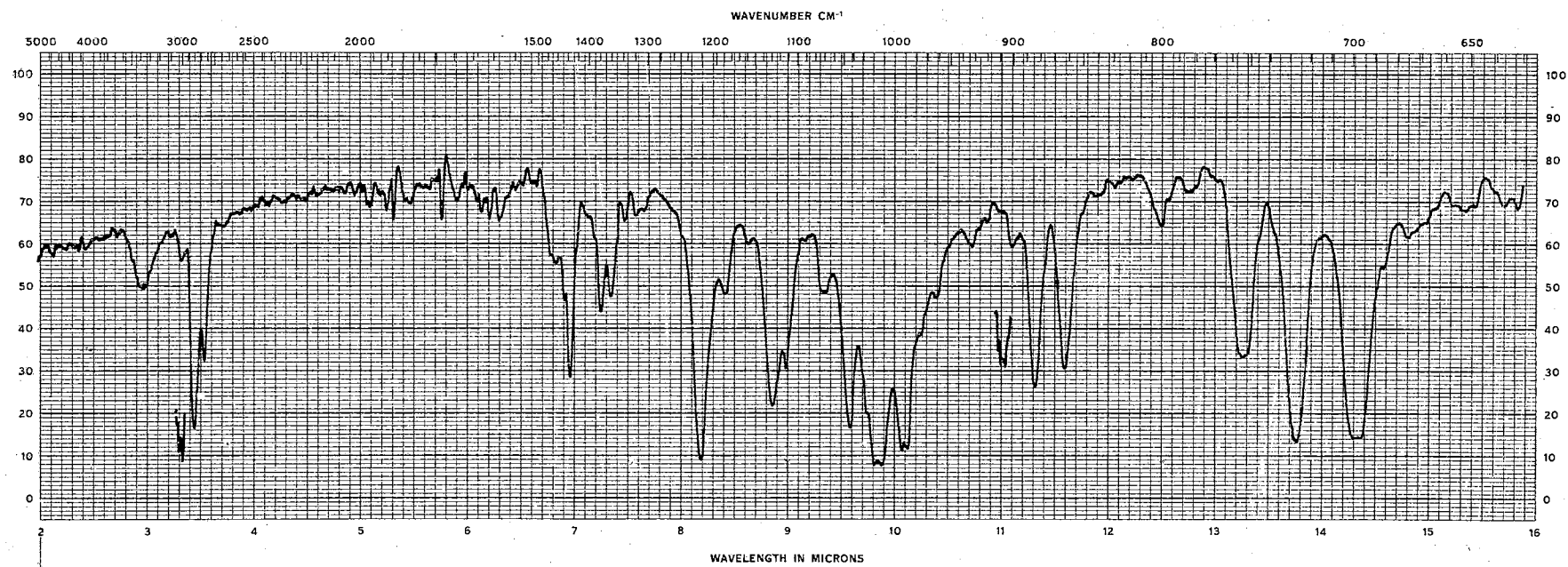
Retention times at 145⁰ were: cis-sulfonate I, 2 minutes;
methyl tosylate, 12 minutes.

Plate I



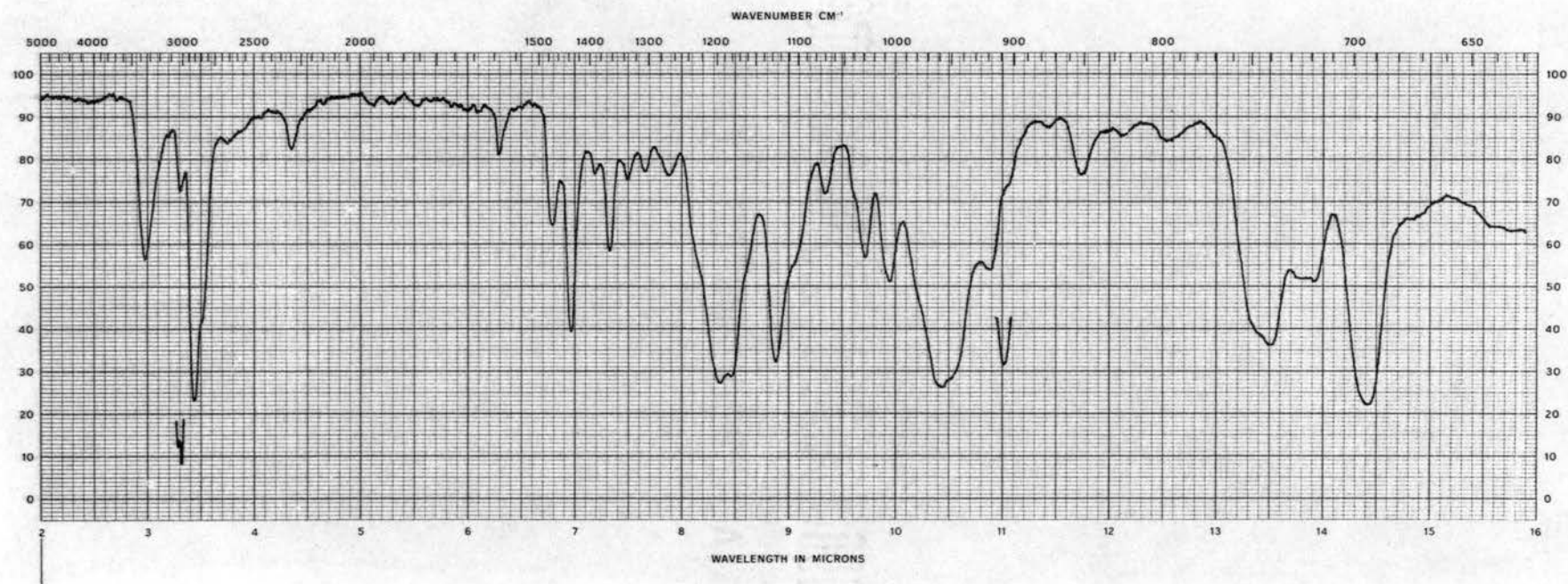
trans-4-t-Butylcyclohexyl Diphenylphosphinite (VI), Film on NaCl Plates

Plate II



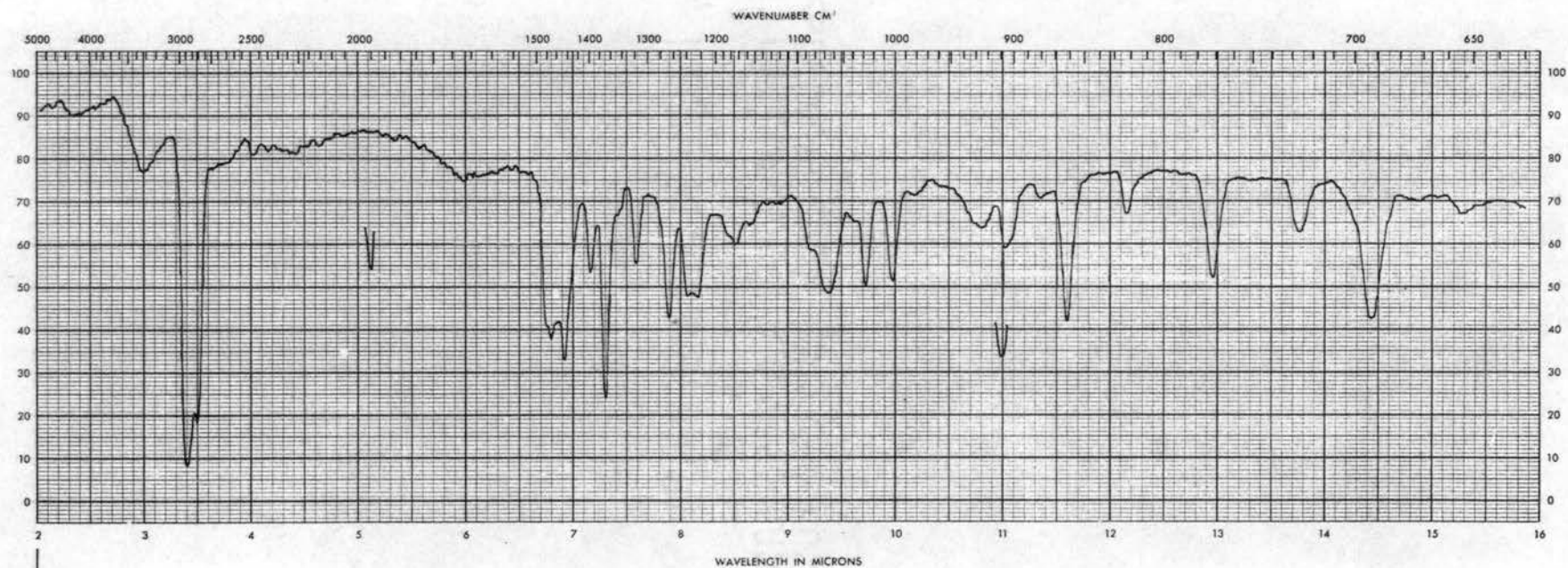
trans-4-t-Butylcyclohexyl Diphenylphosphinate (IX), KBr Pellet

Plate III



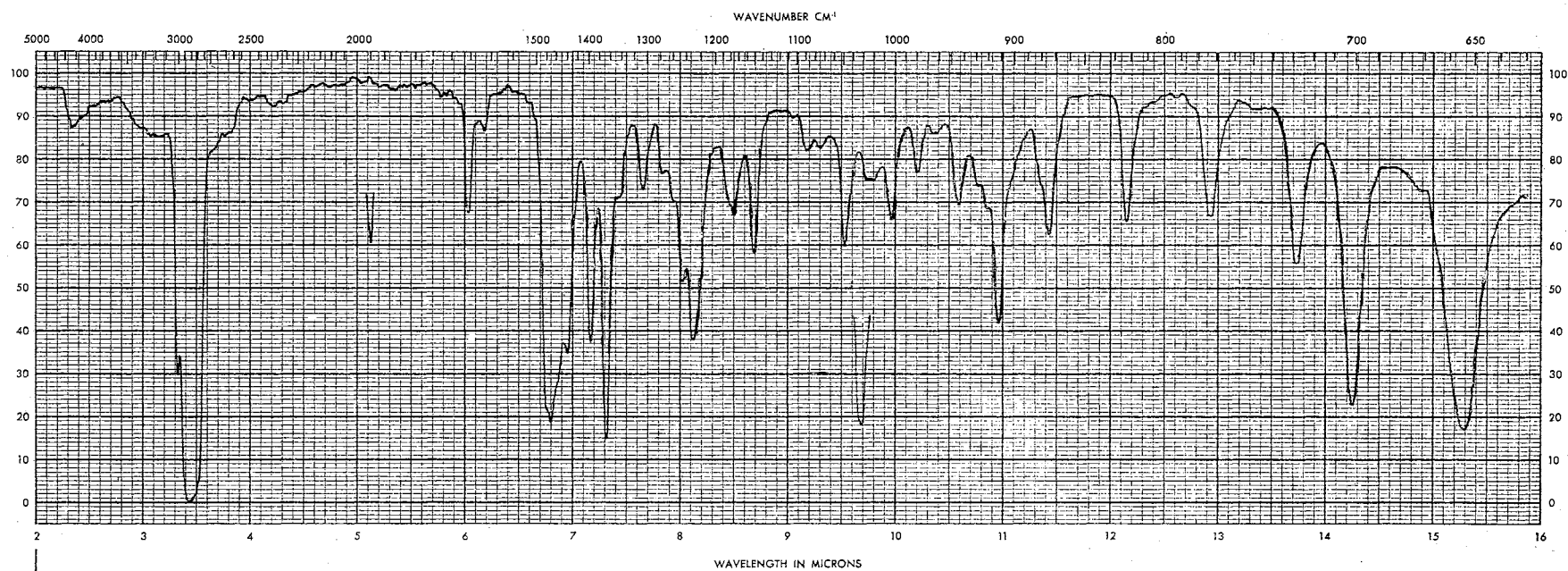
cis-4-t-Butylcyclohexyl Diphenylphosphinate (X) Reaction Mixture, Film on NaCl Plates

Plate IV



cis- and trans-4-t-Butylcyclohexyl Chlorides (XII and XIII), Film on NaCl Plates

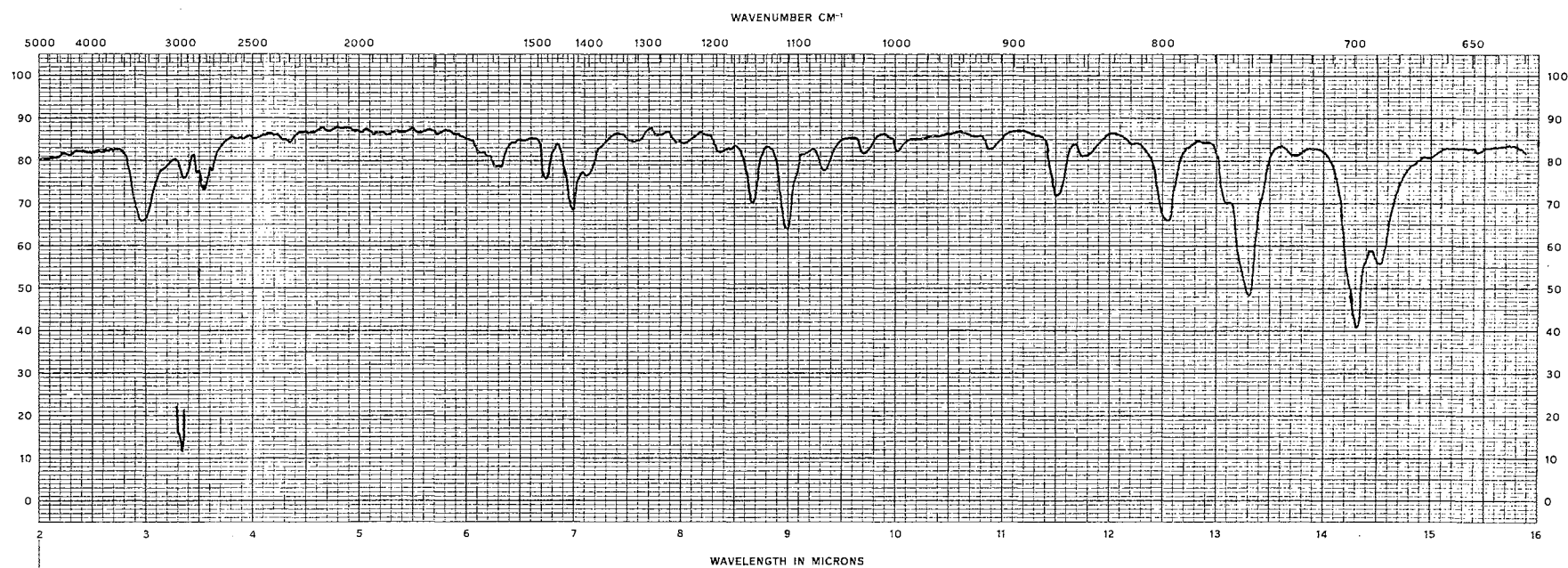
Plate V



trans-4-t-Butylcyclohexyl Chloride (XIII) and 4-t-Butylcyclohexene (III),

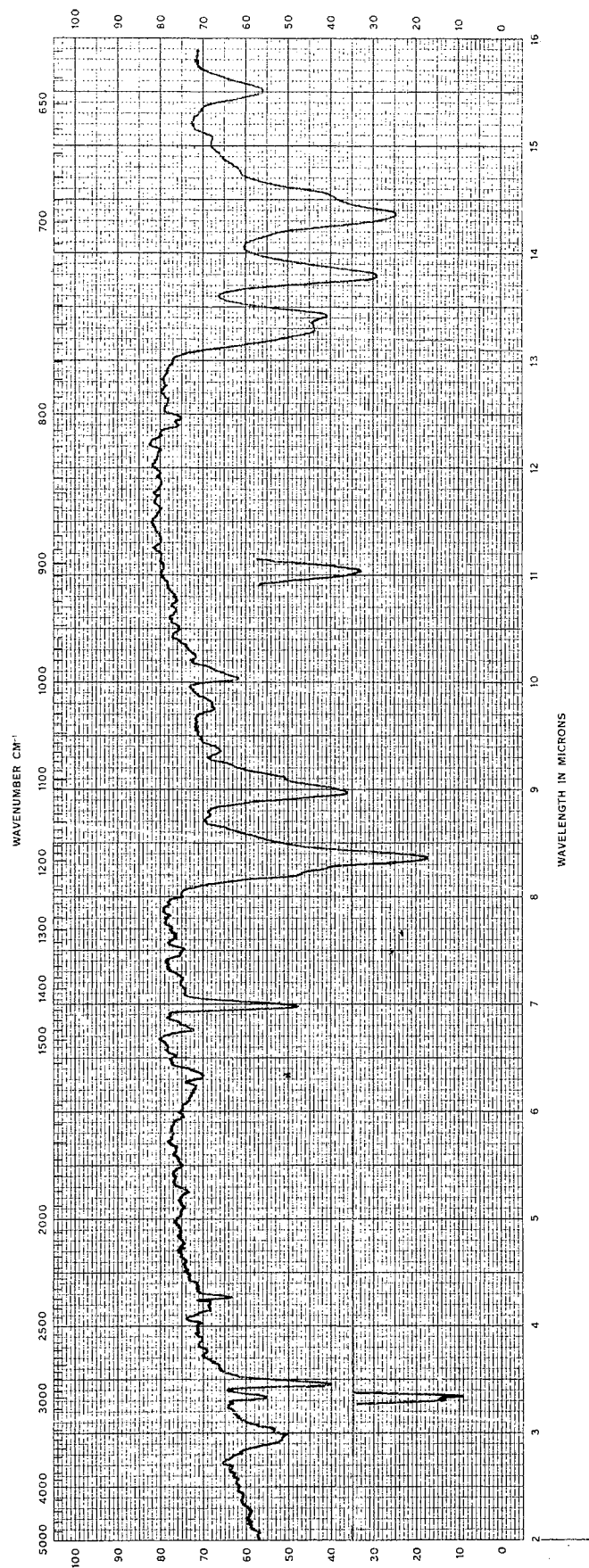
Film on NaCl Plates

Plate VI



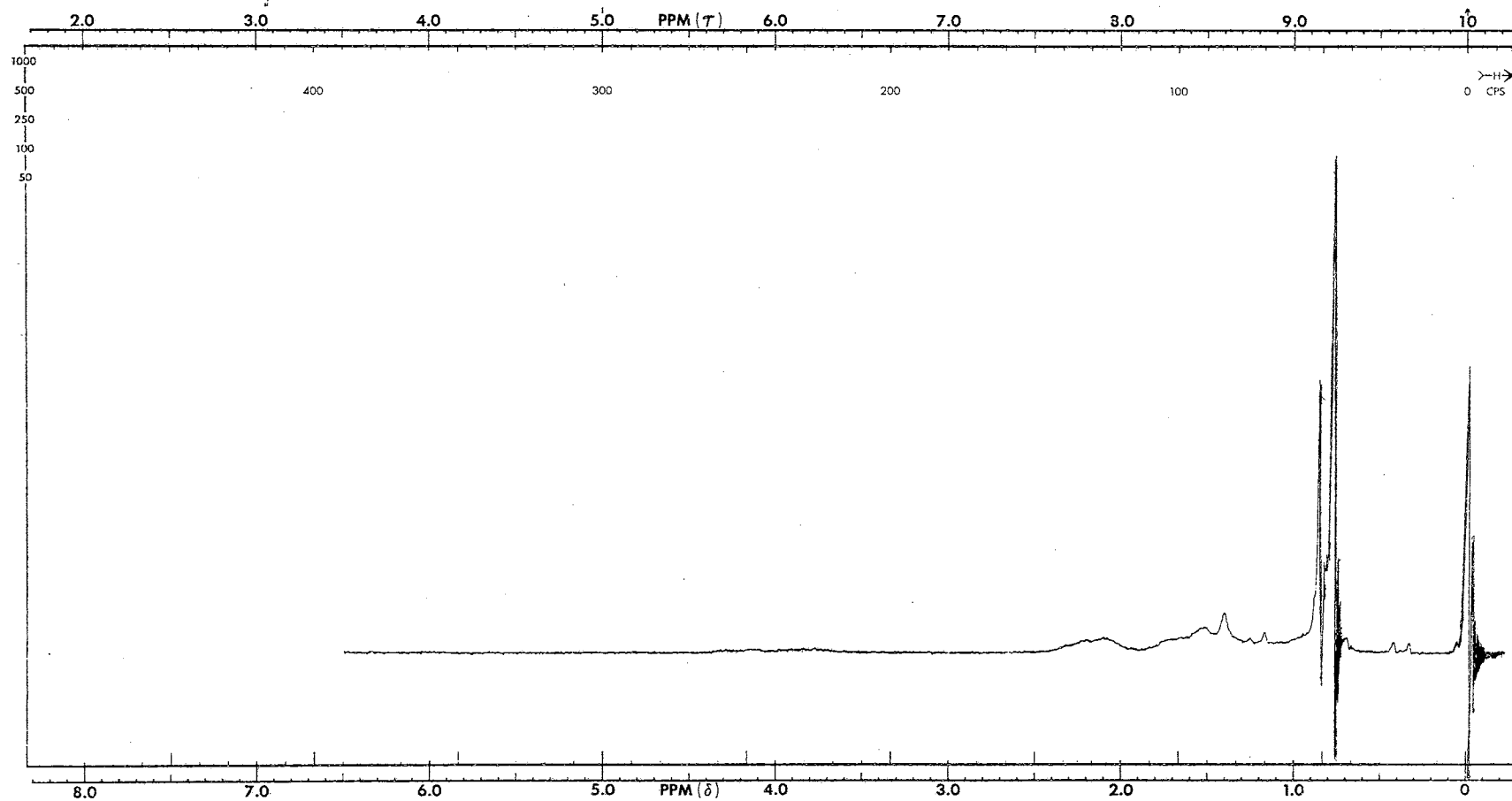
(trans-4-t-Butylcyclohexyloxy)benzyl diphenylphosphonium Chloride (XIV), KBr Pellet

Plate VII



1,2-Bis(Diphenylphosphinyl)-1,1,2,2-Tetrachloroethane (XI), KBr Pellet

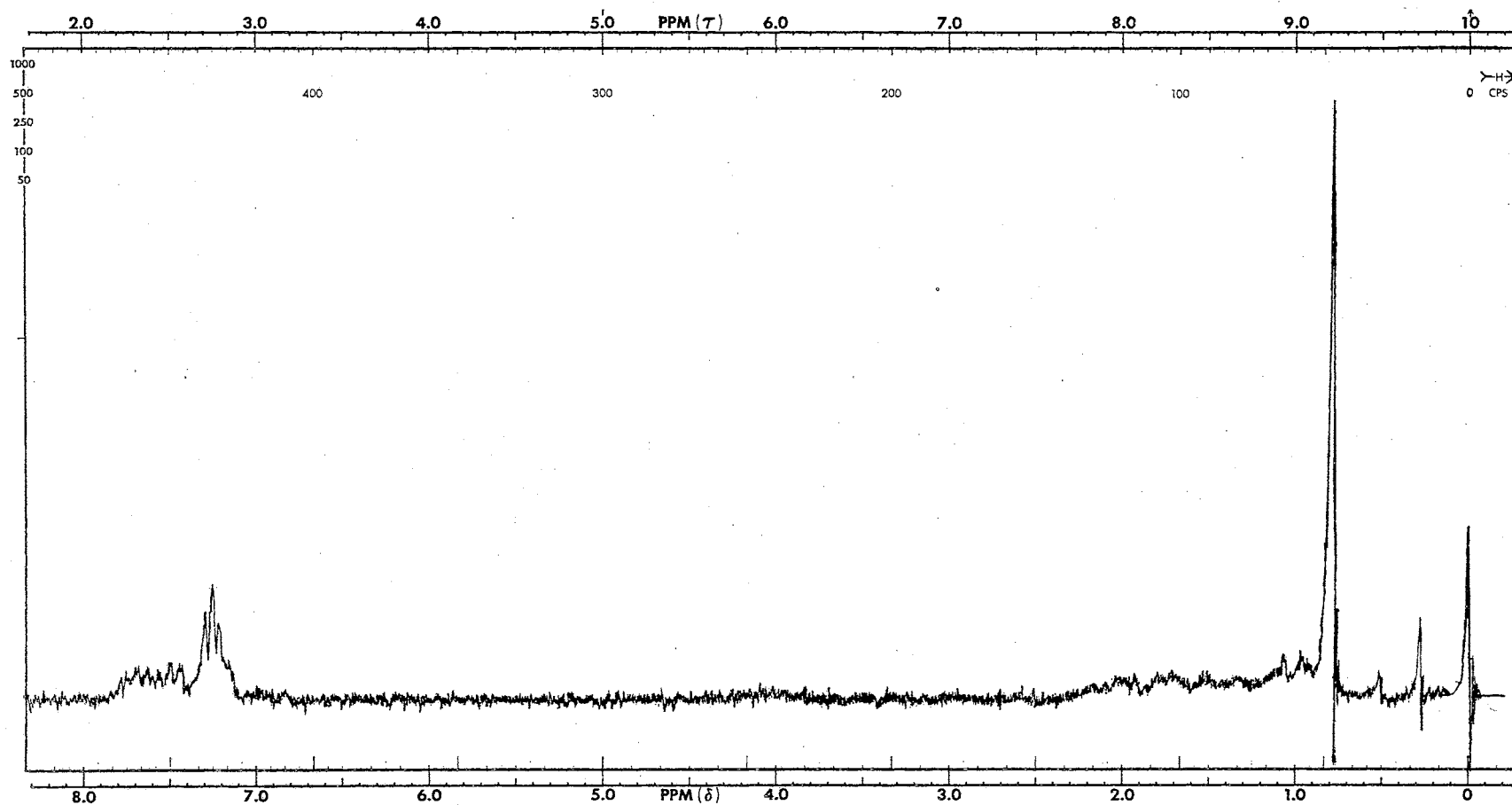
Plate VIII



trans-4-t-Butylcyclohexyl Diphenylphosphinite (VI)

Solvent	C ₆ H ₆	R.F. Field	0.05 mG	S.W.	500 cps	S.A.	1.0
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

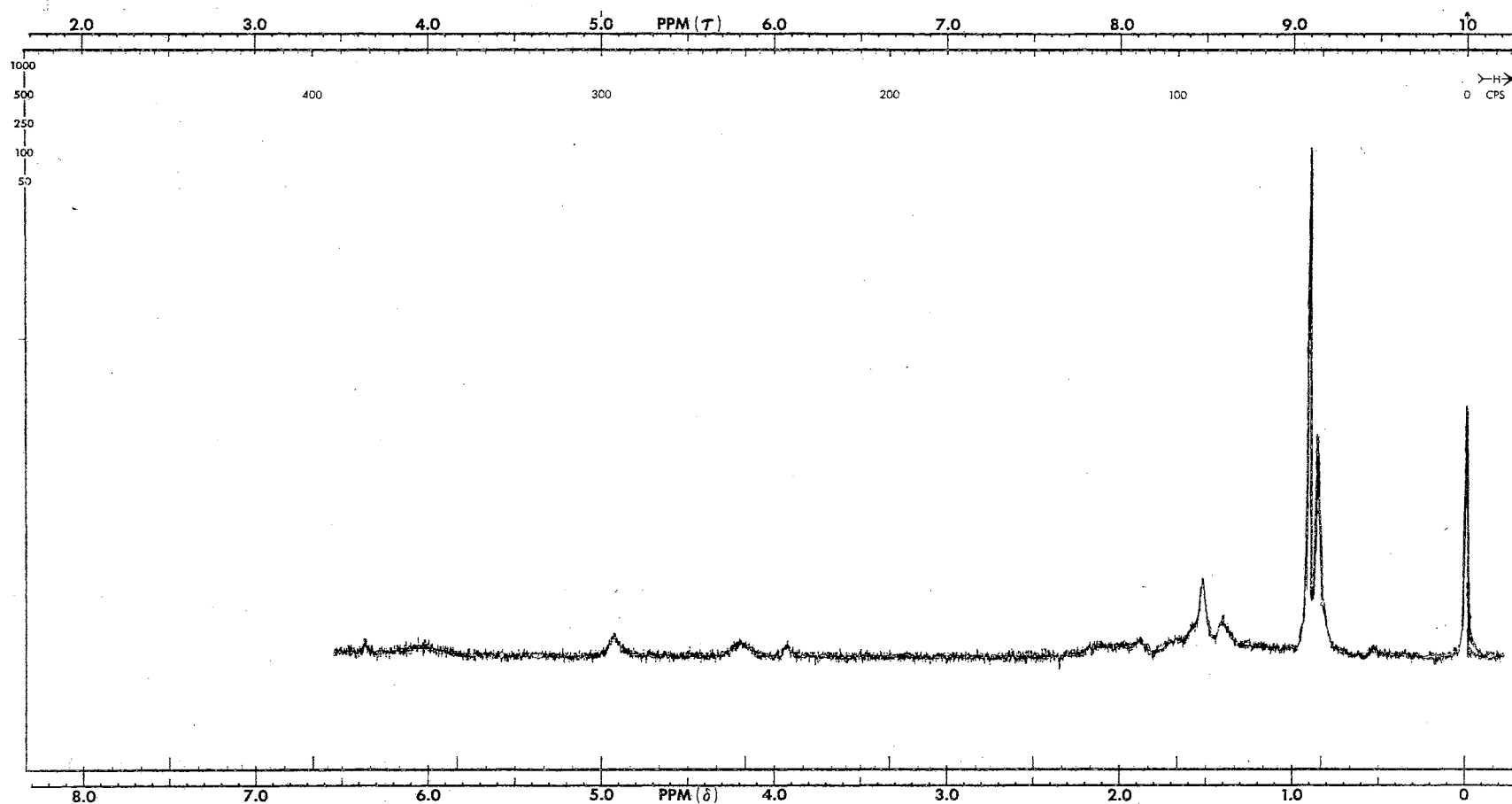
Plate IX



trans-4-t-Butylcyclohexyl Diphenylphosphinate (IX)

Solvent.	CCl ₄	R.F. Field	0.05 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

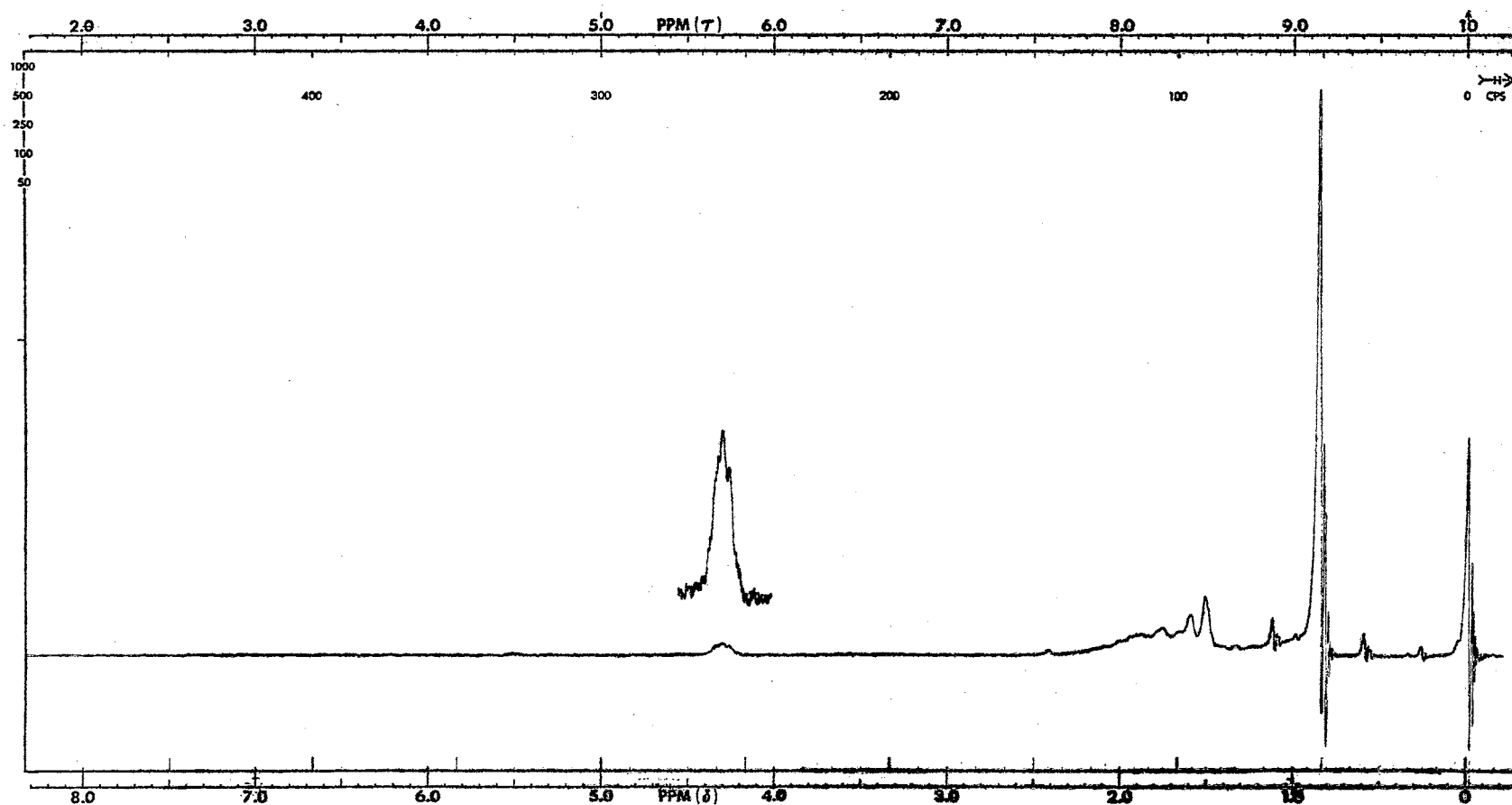
Plate X



cis-4-t-Butylcyclohexyl Diphenylphosphinate (X) Reaction Mixture

Solvent. . . C ₆ H ₆	R.F. Field . . . 0.05 mG	S.W. . . . 500 cps	S.A. 4.0
F.B. . . .4.0 cps	S.T. 500 cps	S.O. 000 cps	I.A. off

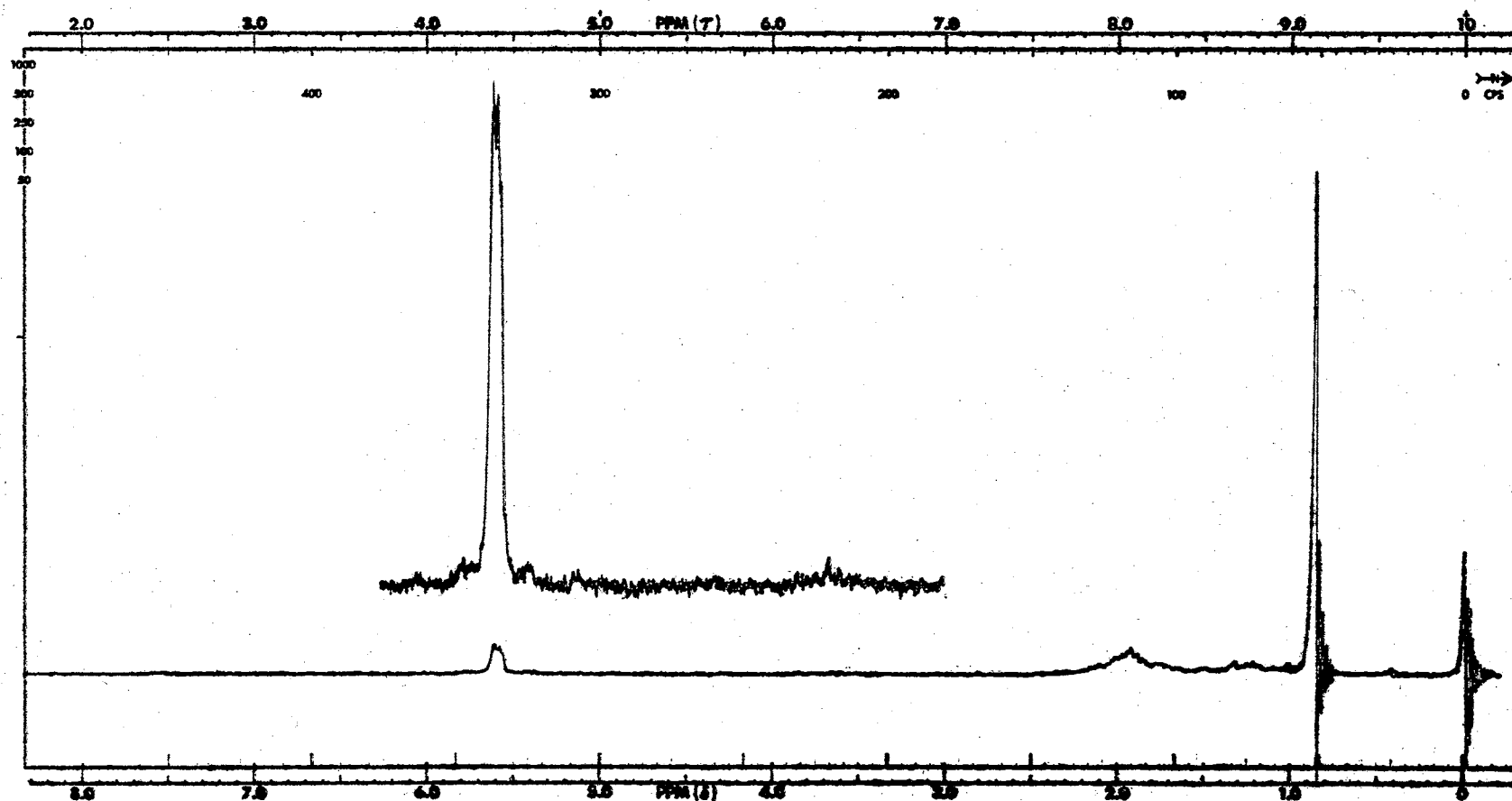
Plate XI



cis- and trans-4-t-Butylcyclohexyl Chlorides (XII and XIII)

Solvent. CCl ₄	R.F. Field 0.05 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

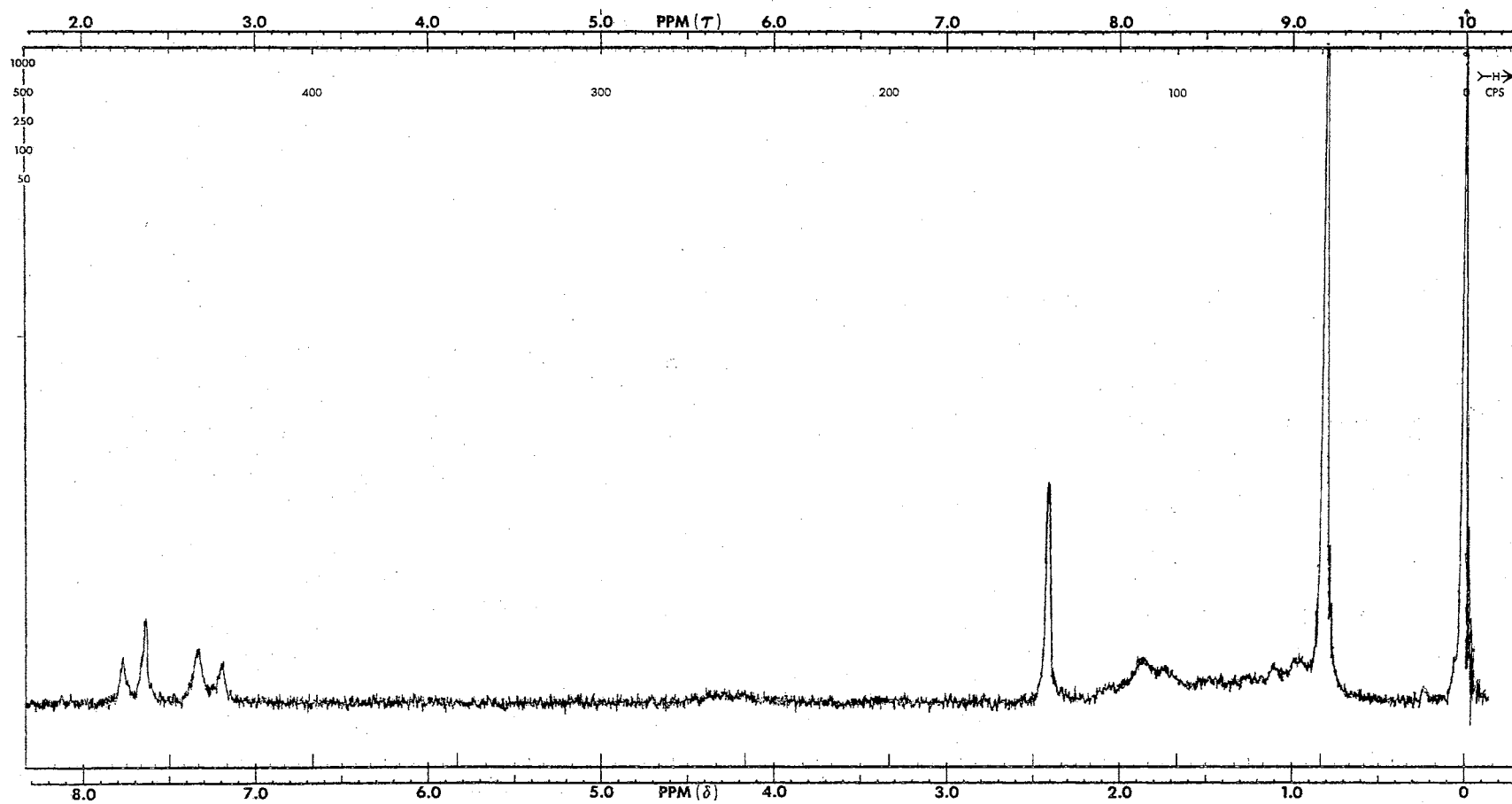
Plate XII



trans-4-t-Butylcyclohexyl Chloride (XIII) and 4-t-Butylcyclohexene (III)

Solvent. . .CCl ₄	R.F. Field . . . 0.05 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 XIII



trans-4-t-Butylcyclohexyl p-Toluenesulfonate (II)

Solvent. . . CCl ₄	R.F. Field . . . 0.05 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

BIBLIOGRAPHY

1. Aksnes, G. and Aksnes, D., Acta Chem. Scand., 18, 38 (1964).
2. Aksnes, G. and Aksnes, D., Acta Chem. Scand., 19, 898 (1965).
3. Arbuzov, A. E., J. Russ. Phys. Chem. Soc., 42, 395 (1910); Chem. Abstr., 5, 1397 (1911).
4. Arbuzov, B. A., Fuzhenkova, A. V., Vinogradova, V. S., and Tolkacheva, T. G., Khim. i Primenenie Fosfororgan. Soedinenii, Akad. Nauk SSSR, Trudy 1-oj Konferents., 62 (1955); Chem. Abstr., 52, 239 (1958).
5. Berlin, K. D., Austin, T. H., and Nagabhushanam, M., J. Org. Chem., 30, 1267 (1965).
6. Berlin, K. D., Hildebrand, C., South, A., Hellwege, D. M., Peterson, M., Pier, E. A., and Verkade, J. G., Tetrahedron, 20, 323 (1964).
7. Berlin, K. D., Hildebrand, C., Verkade, J. G., and Dermer, O. C., Chem. & Ind., 291 (1963).
8. Brown, H. C. and Ham, G., J. Am. Chem. Soc., 78, 2735, (1956).
9. Bunnett, J. F., Angew. Chem. Internat. Ed., 1, 225 (1962).
10. Bunyan, P. J. and Cadogan, J. I. G., J. Chem. Soc., 2953 (1962).
11. Burn, A. J. and Cadogan, J. I. G., Chem. & Ind., 736 (1963).
12. Cadogan, J. I. G. and Foster, W. R., J. Chem. Soc., 3071 (1961).
13. Crofts, P. C. and Downie, I. M., J. Chem. Soc., 2559 (1963).

14. Denney, D. B. and Giacin, J., Tetrahedron Letters, 1747 (1964).
15. Eliel, E. L., Allinger, N. L., Angyal, S. J., and Morrison, G. A., "Conformational Analysis," Ch. 2, Interscience Publishers, New York, N. Y., 1965.
16. Eliel, E. L. and Haber, R. G., J. Am. Chem. Soc., 81, 1249 (1959).
17. Eliel, E. L., Haubenstock, H., and Acharya, R. V., J. Am. Chem. Soc., 83, 2351 (1961).
18. Eliel, E. L. and Ro, R. S., Tetrahedron, 2, 353 (1958).
19. Gerrard, W., J. Chem. Soc., 85 (1944).
20. Gerrard, W. and Green, W. J., J. Chem. Soc., 2550 (1951).
21. Gerrard, W. and Jeacocke, G. J., J. Chem. Soc., 3647 (1954).
22. Gerrard, W. and Philip, N. H., Research, 1, 477 (1948).
23. Gould, E. S., "Mechanism and Structure in Organic Chemistry," Ch. 8, Holt, Rinehart, and Winston, Inc., New York, N. Y., 1959.
24. Greene, F. D., Chu, C., and Wallia, J., J. Org. Chem., 29, 1285 (1964).
25. Griffin, C. E., Chem. & Ind., 415 (1958).
26. Harvey, R. G. and De Sombre, E. R., "Topics in Phosphorus Chemistry," I, 57, Interscience Publishers, New York, N. Y., 1964.
27. Harwood, H. J. and Grisley, D. W., Jr., J. Am. Chem. Soc., 82, 423 (1960).
28. Hassner, A. and Heathcock, C., J. Org. Chem., 29, 1350 (1964).
29. Heck, R. and Winstein, S., J. Am. Chem. Soc., 79, 3432 (1957).
30. Hückel, W. and Heyder, K., Chem. Ber., 96, 220 (1963).
31. Kamaï, G. and Egorova, L. P., Zh. Obshch. Khim., 16, 1521 (1946); Chem Abstr., 41, 5439 (1947).

32. Kamaĭ, G. and Kharrasova, F. M., Zh. Obshch. Khim., 27, 953 (1957); Chem. Abstr., 52, 3666 (1958).
33. Khisamova, Z. L. and Kamaĭ, G., Zh. Obshch. Khim., 20, 1162 (1950); Chem. Abstr., 45, 1531 (1951).
34. Kosolapoff, G. M., J. Am. Chem. Soc., 66, 109 (1944).
35. Kosolapoff, G. M., "Organic Reactions," VI, 273, J. Wiley and Sons, New York, N. Y., 1951.
36. Kosolapoff, G. M., "Organophosphorus Compounds," J. Wiley and Sons, New York, N. Y., 1950.
37. Landauer, S. R. and Rydon, H. N., Chem. & Ind., 313 (1951).
38. Landauer, S. R. and Rydon, H. N., J. Chem. Soc., 2224 (1953).
39. Mallion, K. B. and Mann, F. G., J. Chem. Soc., 5716 (1964).
40. Michaelis, A. and Kaehne, R., Ber., 31, 1048 (1898).
41. Myers, T. C., Preis, S., and Jensen, E. V., J. Am. Chem. Soc., 76, 4172 (1954).
42. Ramirez, F., and McKelvie, N., J. Am. Chem. Soc., 79, 5829 (1957).
43. Razumov, A. I., J. Gen. Chem. USSR, 29, 1609 (1959); Chem. Abstr., 54, 8608 (1960).
44. Razumov, A. I., and Bankovskaya, N. N., Doklady Akad. Nauk SSSR, 116, 241 (1957); Chem. Abstr., 52, 6164 (1958).
45. Richer, J. C., Pilato, L. A., and Eliel, E. L., Chem. & Ind., 2007 (1961).
46. Schmerling, L., J. Am. Chem. Soc., 69, 1121 (1947).
47. Tipson, R. S., J. Org. Chem., 9, 235 (1944).
48. Verkade, J. G., Huttemann, T. J., Fung, M. K., and King, R. W., Inorg. Chem., 4, 83 (1965).
49. Walling, C., and Rabinowitz, R., J. Am. Chem. Soc., 81, 1243 (1959).
50. Winstein, S., Darwish, D., and Holness, N. J., J. Am. Chem. Soc., 78, 2915 (1956).

51. Winstein, S., and Holness, N. J., J. Am. Chem. Soc.,
77, 5562 (1955).

PART II

NMR ANALYSIS OF SUBSTITUTED PHOSPHONATES

TABLE OF CONTENTS

Chapter	Page
I. HISTORICAL	66
Esters of α -Keto Phosphonic Acids	66
Phosphorus-Proton Spin-Spin Coupling Constants	69
II. DISCUSSION OF RESULTS AND CONCLUSIONS.	83
III. EXPERIMENTAL	96
Preparation of Pivalyl Chloride	96
Preparation of Diethyl Acetylphos- phonate (Ia).	97
Preparation of Diethyl Acetylphos- phonate (2,4-Dinitrophenyl)hydrazone. .	98
Attempted Preparation of Dimethyl Phenylacetylphosphonate	98
Attempted Preparation of Diethyl Phenylacetylphosphonate	99
Preparation of Diethyl (α -Hydroxy- benzyl) phosphonate	99
IV. BIBLIOGRAPHY	126

LIST OF TABLES

Table		Page
I.	P-C-C-H Coupling Constants	70
II.	P-O-C-H Coupling Constants	77
III.	Preparation and Properties of Dialkyl Acylphosphonates	84
IV.	Properties of 2,4-Dinitrophenylhydrazones. . .	86
V.	NMR Chemical Shift Parameters and Coupling Constants of Dialkyl Acylphosphonates. . . .	89
VI.	Preparation and Properties of Acyl Chlorides .	97

LIST OF ILLUSTRATIONS

Plate		Page
Infrared Spectra		
I.	Diethyl Acetylphosphonate (Ia), Film on NaCl Plates	101
II.	Diethyl Propionylphosphonate (Ib), Film on NaCl Plates	102
III.	Diethyl Isobutyrylphosphonate (Ic), Film on NaCl Plates	103
IV.	Diethyl Pivalylphosphonate (Id), Film on NaCl Plates	104
V.	Diethyl Cyclopropanecarbonylphosphonate (Ie), Film on NaCl Plates	105
VI.	Diethyl Cyclobutanecarbonylphosphonate (If), Film on NaCl Plates	106
VII.	Diethyl Cyclopentanecarbonylphosphonate (Ig), Film on NaCl Plates	107
VIII.	Diethyl Cycloheptanecarbonylphosphonate (Ik), Film on NaCl Plates	108
IX.	Diethyl <u>trans</u> -2-Phenylcyclopropanecarbonylphosphonate (Il), Film on NaCl Plates	109
X.	Dimethyl <u>trans</u> -2-Phenylcyclopropanecarbonylphosphonate (Im), Film on NaCl Plates	110
XI.	Dimethyl Cinnamoylphosphonate (In), Film on NaCl Plates	111
XII.	Dimethyl Crotonylphosphonate (Io), Film on NaCl Plates	112
Nuclear Magnetic Resonance Spectra		
XIII.	Diethyl Acetylphosphonate (Ia).	113
XIV.	Diethyl Propionylphosphonate (Ib)	114
XV.	Diethyl Isobutyrylphosphonate (Ic).	115
XVI.	Diethyl Pivalylphosphonate (Id)	116
XVII.	Diethyl Cyclopropanecarbonylphosphonate (Ie).	117
XVIII.	Diethyl Cyclobutanecarbonylphosphonate (If).	118

LIST OF ILLUSTRATIONS

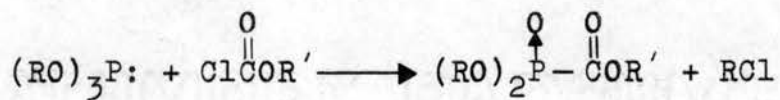
Plate		Page
	Nuclear Magnetic Resonance Spectra	
XIX.	Diethyl Cyclopentanecarbonylphosphonate (Ig)	119
XX.	Diethyl Cycloheptanecarbonylphosphonate (Ik)	120
XXI.	Diethyl <u>trans</u> -2-Phenylcyclopropanecar- bonylphosphonate (Il)	121
XXII.	Dimethyl <u>trans</u> -2-Phenylcyclopropanecar- bonylphosphonate (Im)	122
XXIII.	Dimethyl Cinnamoylphosphonate (In)	123
XXIV.	Dimethyl Crotonylphosphonate (Io)	124
XXV.	Diethyl (α -Hydroxybenzyl)phosphonate (IV)	125

CHAPTER I

HISTORICAL

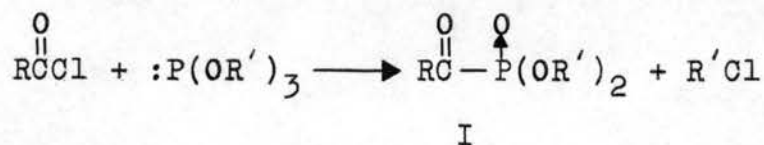
Esters of α -Keto Phosphonic Acids

In the early stages of the development of the Michaelis-Arbuzov rearrangement, it was shown^{9,30} that chloroformic esters, as well as other halogen-bearing carbonyl compounds, would react with trialkyl phosphites in a manner analogous



to that of alkyl halides. Following these initial investigations of compounds with adjacent carbonyl and phosphoryl functions, no further published material appeared on the subject during the period 1927-45.

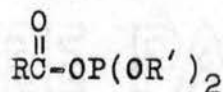
Kabachnik and Rossiiskaya reopened this area of investigation in 1945 with a series of publications²⁹⁻³¹ concerning the reactions of a series of carboxylic acid chlorides



with phosphites. Shortly afterwards, Arbuzov^{4,5,8} resumed his studies of this system, extending the reaction to bromides and cyclic phosphites. In these early studies the resulting

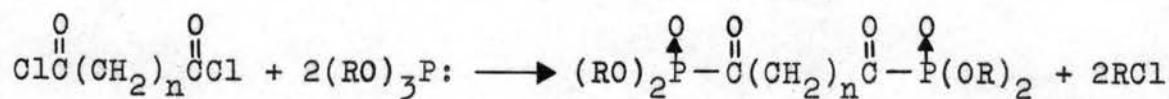
phosphonates I were characterized by chemical means, including identification of hydrolysis products, reduction to α -hydroxy phosphonic esters, evaluation of saponification equivalents, and preparation of various carbonyl derivatives such as phenylhydrazones and cyanohydrins.

Ackerman and co-workers¹ provided additional support for the structure I in the form of instrumental data. A series of fatty acids with an even number of carbon atoms (C_4 to C_{18}) and oleic acid were converted to their acid chlorides which reacted with triethyl phosphite in the usual manner. It was proposed that the only structure possible, other than I, was that of a mixed anhydride, which was feasible in view of the



ease of hydrolysis of these compounds. The structure I was favored, however, from molar refraction studies, the presence of polarographic waves and UV absorption, and finally the presence of a phosphoryl ($\text{P} \rightarrow \text{O}$) absorption in the IR spectrum at 1258 cm.^{-1} , along with another absorption at 1698 cm.^{-1} for carbonyl ($\text{C}=\text{O}$) conjugated with a phosphoryl group.

Acyl diphosphonates have been prepared from several diacid chlorides, including phosgene³² and a series of acid chlorides derived from long-chain aliphatic dibasic acids.⁴¹



Although the reaction appears to be a straightforward extension of the work with monobasic acid chlorides, some contradictory evidence has been found in which other types of products were isolated.⁴⁴

Other interesting variations of this rearrangement include the use of α -halo acid halides,³² carbamoyl chlorides,⁴⁹ and acid anhydrides.³³

In their stereochemical study of the Michaelis-Arbuzov rearrangement, Gerrard and Green (see Part I, Chapter I) obtained inverted 2-chlorooctane from the reaction of acetyl chloride with optically active tri-2-octyl phosphite. This was in accord with the results obtained with alkyl halides, and it was suggested that the two reactions may proceed by a similar pathway.

Recently a series of aroylphosphonates has been synthesized by Berlin and co-workers.¹⁵ This work was followed by a similar study of acylphosphonates,¹⁴ including a series of cycloalkanecarbonylphosphonates. In both investigations, the compounds were well characterized by NMR, and it was suggested that an evaluation of P-H coupling constants would be instructive, particularly if proton-proton spin decoupling could be utilized.

A more detailed description of the chemistry of α -keto phosphonic esters is available.⁶⁰ This work includes further examples of preparations of these compounds as well as some of the reactions that they will undergo.

Phosphorus-Proton Spin-Spin Coupling Constants

Although there is little recorded discussion of directly-bonded P-H coupling constants, a few general statements can be made about them. It has been suggested that these constants are large and positive,³⁶ as predicted for B-H, N-H, and ^{13}C -H constants on the basis of theoretical calculations.^{34,42} In these studies it was also proposed that the magnitude of these coupling constants was proportional to the s character of the bonds between the two atoms. This correlation has now been extended to P-H coupling constants,²⁶ and it was further suggested that P-C-H coupling constants followed a similar trend except that the s-character of the P-C bond contributed to a more negative coupling constant whereas the reverse was true for the C-H bond. Owing to a lack of sufficient bond angle data for such systems, no significant correlations have yet been made between P-C-H coupling and the PCH angle.

A variety of data is available for P-C-C-H coupling, although fewer compounds have been found to display such splitting than those which show geminal (P-C-H) coupling. A large portion of the available data on $J_{\text{P-C-C-H}}$ is summarized in Table I. Discussion and interpretation of this data is postponed until the Discussion section.

TABLE I

P-C-C-H COUPLING CONSTANTS

Compound	$J_{\text{P-C-C-H}}$ (c.p.s.)	References
$(\text{CH}_3\text{CH}_2)_3\text{P}$	13.7	26, 28, 43
$\text{CH}_3\text{CH}_2\text{PCl}_2$	15.5	26, 35
$(\text{CH}_3\text{CH}_2)_3\text{PO}$	16.3	26, 28
$(\text{CH}_3\text{CH}_2)_3\text{PS}$	18.1	26, 28
$(\text{CH}_3\text{CH}_2)_4\text{P}^{\oplus}, \text{I}^{\ominus}$	18.3	26, 28
$\text{CH}_3\text{CH}_2\text{P}(\text{C}_6\text{H}_5)_3^{\oplus}, \text{Br}^{\ominus}$	20.0	26, 28
$\text{CH}_3\text{CH}_2\text{P}(\text{O})(\text{C}_6\text{H}_5)(\text{Cl})$	22.1	26, 56
$(\text{CH}_3\text{CH}_2)_3\text{PBr}^{\oplus}, \text{Br}^{\ominus}$	23.0	26, 28
$\text{CH}_3\text{CH}_2\text{P}(\text{O})\text{Cl}_2$	30.0	26, 38, 56
$\text{CH}_3\text{CH}_2\text{P}(\text{S})\text{Cl}_2$	31.4	26, 38
$(\text{CH}_3)_2\text{CHP}(\text{O})(\text{C}_6\text{H}_5)(\text{OC}_2\text{H}_5)$	17.1	56
$(\text{CH}_3)_2\text{CHP}(\text{O})(\text{C}_6\text{H}_5)(\text{OCH}_3)$	17.3	56
$(\text{CH}_3)_2\text{CHP}(\text{O})(\text{C}_6\text{H}_5)(\text{OH})$	17.6	56
$(\text{CH}_3)_2\text{CHP}(\text{O})(\text{OH})_2$	18.4	26
$(\text{CH}_3)_2\text{CHP}(\text{C}_6\text{H}_5)_3^{\oplus}, \text{Br}^{\ominus}$	18.7	26, 28
$(\text{CH}_3)_2\text{CHP}(\text{O})(\text{C}_6\text{H}_5)\text{Cl}$	20.6	26, 56
$(\text{CH}_3)_2\text{CHP}(\text{O})\text{Cl}_2$	27.6	26, 56
$(\text{C}_6\text{H}_5)(\text{CH}_3)\text{CHP}(\text{O})(\text{C}_6\text{H}_5)(\text{OH})$	16.8	56

TABLE I (Continued)

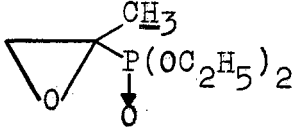
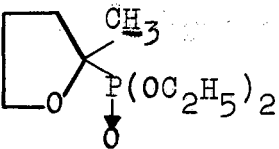
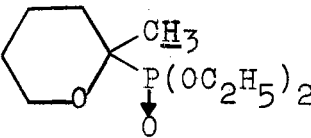
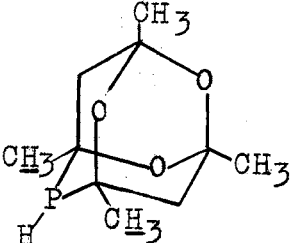
Compound	$J_{\text{P-C-C-H}}$ (c.p.s.)	References
$(\text{C}_6\text{H}_5)(\text{CH}_3)\text{CHP}(\text{O})(\text{C}_6\text{H}_5)(\text{OCH}_3)$	17.1	56
$(\text{C}_2\text{H}_5)(\text{CH}_3)\text{CHP}(\text{O})(\text{C}_6\text{H}_5)\text{Cl}$	20.0	56
$(\text{CH}_3)_3\text{CP}(\text{O})(\text{C}_6\text{H}_5)(\text{OH})$	15.7	25
$[(\text{CH}_3)_3\text{C}]_2\text{P}(\text{O})\text{Cl}$	17	3,26
$(\text{CH}_3)_3\text{CP}(\text{C}_6\text{H}_5)_3^{\oplus}, \text{Br}^-$	17.2	26,52
$(\text{CH}_3)_3\text{CP}(\text{O})(\text{C}_6\text{H}_5)(\text{Cl})$	17.7	26,56
$(\text{CH}_3)_3\text{CP}(\text{O})\text{Cl}_2$	24.8	56
	11.1	59
	14.6	26,59
	14.4	26,59
	13.5	22,26

TABLE I (Continued)

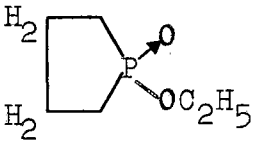
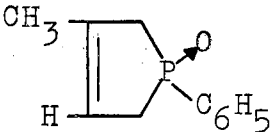
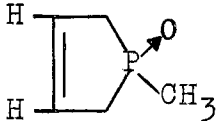
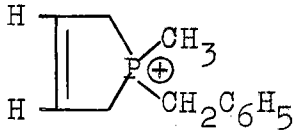
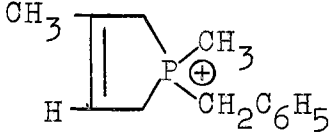
Compound	$J_{\text{P-C-O-H}}$ (c.p.s.)	References
	33.0	62
$(\text{CH}_3)_2\text{C}=\text{CHCH}_2\text{P}(\text{O})(\text{OR})_2$	7.7	26
	24.9	26
	27.2	26, 45
	28.0	26, 45
	30.0	26

TABLE I (Continued)

Compound	$J_{\text{P-C-C-H}}$ (c.p.s.)	References
	32.25	26,62
	33.25	62
	35.50	26,62
	39.0	62
	42.3	26,62
$(\text{CH}_2=\text{CH})_3\text{P}$	13.62 (cis) 30.21 (trans)	2,26
$\text{CH}_2=\text{C}(\text{Cl})\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	13.6 (cis) 35.9 (trans)	26

TABLE I (continued)

Compound	$J_{P-C-C-H}$ (c.p.s.)	References
$ClCH=CHP(O)(OC_2H_5)_2$	13.6 (cis) 40.3 (trans)	26
$p\text{-NO}_2C_6H_4CH=CHP(O)(OC_2H_5)_2$	22.3 (cis)	26
$p\text{-CH}_3OC_6H_4CH=CHP(O)(OC_2H_5)_2$	22.6 (cis)	26
$p\text{-ClC}_6H_4CH=CHP(O)(OC_2H_5)_2$	22.7 (cis)	26
$C_6H_5CH=CHP(O)(OC_2H_5)_2$	19.5 (cis) 40.3 (trans)	26
	39.7	26
	47.70	26,62
	47.75	62
	48.0	62

TABLE I (Continued)

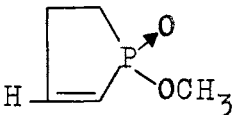
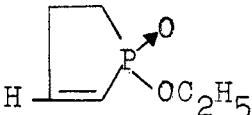
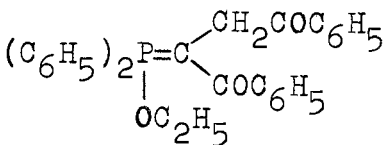
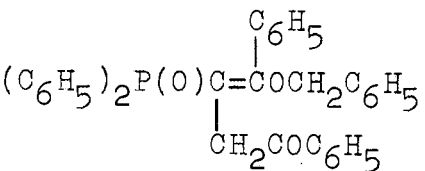
Compound	$J_{\text{P-C-C-H}}$ (c.p.s.)	References
	48.0	62
	48.8	62
$\text{HC}\equiv\text{CP}(\text{O}) [\text{OCH}(\text{CH}_3)_2]_2$	11	26,50
$\text{HC}\equiv\text{CP}(\text{O})(\text{C}_6\text{H}_5)_2$	9.7	17,26
	21	26,46,47
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{CHO})\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	16.1	26
$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)(\text{CHO})\text{P}(\text{O})(\text{OC}_2\text{H}_5)_2$	1.0	26
$\text{CH}_3\text{CH}(\text{COOH})\text{P}(\text{O})(\text{C}_6\text{H}_5)_2$	16.0	26,53
	16	46

TABLE I (Continued)

Compound	$J_{\text{P-C-C-H}}$	References
$\text{CH}_3\text{COP}(\text{O})(\text{OC}_2\text{H}_5)_2$	5.0	14,26
$\text{CH}_3\text{COP}(\text{O})[\text{OCH}(\text{CH}_3)_2]_2$	5.8	26,50

In Table II, a list of P-O-C-H coupling constants for selected compounds is presented. Although such a list is useful empirically, there is no theoretical explanation yet available that successfully accounts for the effect of various substituents on this type of coupling. A few limited generalities are evident from these data, however. Electron-donating groups attached to the carbon atom produce a decrease in $J_{\text{P-O-C-H}}$ although the expected opposite effect for electron-withdrawing groups is not observed.²¹ The presence of P-H²⁶ or P-S⁵⁸ bonds increases the coupling constant significantly in all cases observed, but no other substituents attached to the phosphorus atom affect $J_{\text{P-O-C-H}}$ consistently. An interesting exception to this is found in the bicyclic and tricyclic esters studied by Verkade and co-workers,⁶¹ in which the P-O-C-H coupling increased markedly with electronegativity of the attached ligand for each of the adducts studied. The rigidity of these polycyclic systems probably accounts for their unusual behavior compared to acyclic esters.

No correlation of P-S-C-H coupling constants has been

TABLE II

P-O-C-H COUPLING CONSTANTS

Compound	$J_{\text{P-O-C-H}}$ (c.p.s.)	References
$(\text{CH}_3\text{O})_3\text{P}$	11.8	26,27
	10.8	58
$(\text{CH}_3\text{O})_3\text{PBH}_3$	11.00	26,61
$(\text{CH}_3\text{O})_3\text{PB}(\text{CH}_3)_3$	9.60	26,61
$(\text{CH}_3\text{O})_3\text{PO}$	10.65	26,61
	10.19	10,26,55
	11.4	26,27
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{H}$	13	26,65
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CH}_3$	11.0	26,37
$(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{CH}_3$	13.5	26,37
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{COC}_6\text{H}_5$	11	15,26,60
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CO}-\underline{\text{p}}-\text{C}_6\text{H}_4\text{OCH}_3$	11	15,60
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CO}-\underline{\text{p}}-\text{C}_6\text{H}_4\text{Cl}$	11	15,60
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CO}-\underline{\text{o}}-\text{C}_6\text{H}_4\text{Cl}$	11	15,60
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{CO}-\underline{\text{p}}-\text{C}_6\text{H}_4\text{C}(\text{CH}_3)_3$	11	15,60
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{C}_6\text{H}_5$	11	26,51
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{OC}_6\text{Cl}_5$	12.0	58
$(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{SC}_6\text{Cl}_5$	13.2	58
$(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{OC}_6\text{Cl}_5$	14.3	58
$(\text{CH}_3\text{O})_2\text{P}(\text{S})\text{SC}_6\text{Cl}_5$	15.6	58
$\text{CH}_3\text{OP}(\text{O})\text{H}_2$	13	24,26
$\text{CH}_3\text{OP}(\text{O})(\text{C}_6\text{H}_5)_2$	11.0	12,26

TABLE II (Continued)

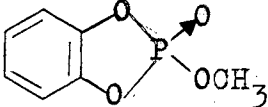
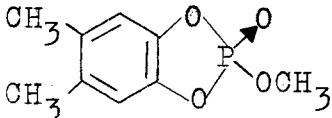
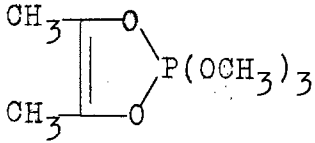
Compound	$J_{\text{P-O-C-H}}$	References
	12.0	16
	11.5	16
$(\text{CH}_3\text{O})_4\text{P}^{\oplus}$	11.2	18
$(\text{CH}_3\text{O})_5\text{P}$	12	19,26
	13	26,48
$(\text{CH}_3\text{CH}_2\text{O})_3\text{P}$	7.90	11,26
	8.0	58
$\text{CH}_3\text{CH}_2\text{OP}(\text{C}_6\text{H}_5)_2$	9.8	26
$(\text{CH}_3\text{CH}_2\text{O})_3\text{POCH}_2\text{CH}_3^{\oplus}, \text{BF}_4^-$	7.45	61
$(\text{CH}_3\text{CH}_2\text{O})_3\text{PC}(\text{C}_6\text{H}_5)_3^{\oplus}, \text{BF}_4^-$	6.70	26,61
$(\text{CH}_3\text{CH}_2\text{O})_3\text{PO}$	6.84	26,61
	8.38	10,26,55
$(\text{CH}_3\text{CH}_2\text{O})_3\text{PS}$	10.18	55

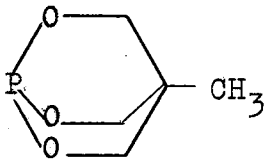
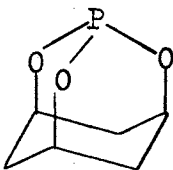
TABLE II (Continued)

Compound	$J_{\text{P-O-C-H}}$	References
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{H}$	9.3	26
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{CH}_3$	8.4	26, 37
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{S})\text{CH}_3$	10.2	26, 37
	10.3, 10.7	26, 54
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{Cl}$	9.5	26
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{S})\text{Cl}$	11.0	26
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OC}_6\text{H}_5$	8.7	57
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{OC}_6\text{Cl}_5$	8.0	58
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{SC}_6\text{Cl}_5$	8.8	58
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{S})\text{OC}_6\text{Cl}_5$	9.5	58
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{S})\text{SC}_6\text{Cl}_5$	9.8	58
$(\text{CH}_3\text{CH}_2\text{O})_2\text{PC}_6\text{H}_5$	8.3	57
$(\text{CH}_3\text{CH}_2\text{O})_2\text{P}(\text{O})\text{C}_6\text{H}_5$	8.2	57
$(\text{CHCl}_2\text{CH}_2\text{O})_3\text{PO}$	8.4	21
$(\text{CCl}_3\text{CH}_2\text{O})_3\text{PO}$	7.05	21, 26
$(\text{CF}_3\text{CH}_2\text{O})_3\text{PO}$	8.34	21, 26
$[\text{CH}_3(\text{CH}_2)_2\text{O}]_3\text{PO}$	7.70	10, 26, 55
$[\text{CH}_3(\text{CH}_2)_2\text{O}]_2\text{P}(\text{O})\text{CH}_3$	7.7	26, 37
$[\text{CH}_3(\text{CH}_2)_2\text{O}]_2\text{P}(\text{S})\text{CH}_3$	9.9	26, 37

TABLE II (Continued)

Compound	$J_{P-O-C-H}$	References
$[\text{CH}_3(\text{CH}_2)_3\text{O}]_3\text{P}$	7.47	55
$[\text{CH}_3(\text{CH}_2)_3\text{O}]_3\text{PO}$	7.65	10,55
$[\text{CH}_3(\text{CH}_2)_3\text{O}]_2\text{P(O)CH}_3$	7.1	37
$[\text{CH}_3(\text{CH}_2)_3\text{O}]_2\text{P(S)CH}_3$	9.4	37
$[\text{CH}_3(\text{CH}_2)_4\text{O}]_3\text{PO}$	7.62	10,55
$[\text{CH}_3(\text{CH}_2)_5\text{O}]_3\text{PO}$	7.32	55
$[(\text{CH}_3)_2\text{CHCH}_2\text{O}]_3\text{PO}$	6.60	10,55
$[(\text{CH}_3)_3\text{CCH}_2\text{O}]_3\text{P}$	6.1	26
$[(\text{CH}_3)_3\text{CCH}_2\text{O}]_3\text{PO}$	4.8	20,26
$[(\text{CH}_3)_3\text{CCH}_2\text{O}]_4\text{P}^{\oplus}, \text{OTs}^{\ominus}$	4.8	20
$(\text{CH}_2=\text{CHCH}_2\text{O})_3\text{PO}$	8.3	21,26
$(\text{C}_6\text{H}_5\text{CH}_2\text{O})_3\text{PO}$	9.07	21,26
$(\text{C}_6\text{H}_5\text{CH}_2\text{O})_4\text{P}_2\text{O}_3$	8.62	21
$(\text{C}_6\text{H}_5\text{CH}_2\text{O})_2\text{P(O)OCH}_3$	8.68	21
$[(\text{CH}_3)_2\text{CHO}]_3\text{P}$	8.5	57
$[(\text{CH}_3)_2\text{CHO}]_3\text{PO}$	7.4	57
$[(\text{CH}_3)_2\text{CHO}]_2\text{P(O)C}_6\text{H}_5$	7.8	57
$[(\text{CH}_3\text{CH}_2)_2\text{CHO}]_3\text{PO}$	7.7	57
$[(\text{CH}_3\text{CH}_2)_2\text{CHO}]_2\text{P(O)C}_6\text{H}_5$	7.5	57

TABLE II (Continued)

Compound	$J_{\text{P-O-C-H}}$	References
 $(\text{C}_5\text{H}_9\text{O}_3\text{P})$	1.8	61
$\text{C}_5\text{H}_9\text{O}_3\text{PB}(\text{CH}_3)_3$	2.2	61
$\text{C}_5\text{H}_9\text{O}_3\text{PBH}_3$	4.2	61
$\text{C}_5\text{H}_9\text{O}_3\text{PCH}_2\text{CH}_3^{\oplus}, \text{BF}_4^{\ominus}$	5.2	61
$\text{C}_5\text{H}_9\text{O}_3\text{PC}(\text{C}_6\text{H}_5)_3^{\oplus}, \text{BF}_4^{\ominus}$	5.8	61
$\text{C}_5\text{H}_9\text{O}_3\text{PO}$	7.0	61
 $(\text{C}_6\text{H}_9\text{O}_3\text{P})$	6.3	61
$\text{C}_6\text{H}_9\text{O}_3\text{PB}(\text{CH}_3)_3$	6.7	61
$\text{C}_6\text{H}_9\text{O}_3\text{PBH}_3$	12.5	61
$\text{C}_6\text{H}_9\text{O}_3\text{PCH}_2\text{CH}_3^{\oplus}, \text{BF}_4^{\ominus}$	15.7	61
$\text{C}_6\text{H}_9\text{O}_3\text{PC}(\text{C}_6\text{H}_5)_3^{\oplus}, \text{BF}_4^{\ominus}$	18.0	61
$\text{C}_6\text{H}_9\text{O}_3\text{PO}$	20.0	61

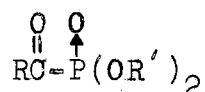
attempted, owing to the lack of sufficient data. Likewise, $J_{\text{P-N-C-H}}$ values are seldom reported, and most of those which are available lie within a very narrow range (10 ± 1.5 c.p.s.).²⁶ The only noteworthy exceptions are for compounds with P-Cl linkages for which many coupling constants of this type are significantly larger [e.g. $(\text{CH}_3)_2\text{NP}(\text{O})\text{Cl}_2$, for which $J_{\text{P-N-C-H}} = 15.87^{39}$], but no explanation has been offered for this anomalous behavior.

Other P-H coupling constants recorded include those in which the phosphorus and hydrogen atoms are separated by more than three bonds. For ethyl esters of phosphorus acids, $J_{\text{P-O-C-C-H}}$ values are generally small (1.1 c.p.s. or less), as are many of these "long range" coupling constants. In allylic and homoallylic systems, the values are usually larger, particularly if the phosphorus atom is bonded to an sp^3 hybridized carbon atom. Further discussions of these phenomena and other aspects of proton NMR spectra in phosphorus chemistry are available.²⁶

CHAPTER II

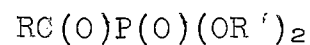
DISCUSSION OF RESULTS AND CONCLUSIONS

A series of acylphosphonic esters I was prepared by a procedure similar to that of Kabachnik,³⁰ except that the order of addition was reversed, the acid chloride being added to the phosphite. The yields (see Table III) were fairly high, indicating that the presence of excess phos-

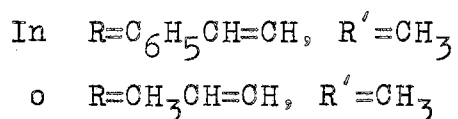


- Ia $\text{R}=\text{CH}_3$, $\text{R}'=\text{CH}_3\text{CH}_2$
- b $\text{R}=\text{CH}_3\text{CH}_2$, $\text{R}'=\text{CH}_3\text{CH}_2$
- c $\text{R}=(\text{CH}_3)_2\text{CH}$, $\text{R}'=\text{CH}_3\text{CH}_2$
- d $\text{R}=(\text{CH}_3)_3\text{C}$, $\text{R}'=\text{CH}_3\text{CH}_2$
- e $\text{R}=\text{cyclopropyl}$, $\text{R}'=\text{CH}_3\text{CH}_2$
- f $\text{R}=\text{cyclobutyl}$, $\text{R}'=\text{CH}_3\text{CH}_2$
- g $\text{R}=\text{cyclopentyl}$, $\text{R}'=\text{CH}_3\text{CH}_2$
- h $\text{R}=\text{cyclohexyl}$, $\text{R}'=\text{CH}_3$
- i $\text{R}=\text{cyclohexyl}$, $\text{R}'=\text{CH}_3\text{CH}_2$
- j $\text{R}=\text{cyclohexyl}$, $\text{R}'=(\text{CH}_3)_2\text{CH}$
- k $\text{R}=\text{cycloheptyl}$, $\text{R}'=\text{CH}_3\text{CH}_2$
- l $\text{R}=\text{trans-2-phenylcyclopropyl}$, $\text{R}'=\text{CH}_3\text{CH}_2$
- m $\text{R}=\text{trans-2-phenylcyclopropyl}$, $\text{R}'=\text{CH}_3$

TABLE III
PREPARATION AND PROPERTIES OF DIALKYL ACYLPHOSPHONATES



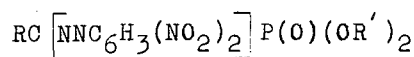
Compound	R	R'	Moles of Reactants	Yield (per cent)	B.p. °C (mm)	Analysis (per cent)			Found			Reference
						Calculated			C	H	P	
Ia	CH ₃	C ₂ H ₅	0.0903	73.6	181-6(3-4)							30,40,14
Ib	C ₂ H ₅	C ₂ H ₅	0.216	85.7	105(7)							9,14
Ic	(CH ₃) ₂ CH	C ₂ H ₅	0.235	85.5	99-100(4)							40,14
Id	(CH ₃) ₃ C	C ₂ H ₅	0.0307	65	97-100(5)							14
Ie	Cyclopropyl	C ₂ H ₅	0.100	69	119-20(5)	46.60	7.33	15.02	46.47	7.28	15.08	14
If	Cyclobutyl	C ₂ H ₅	0.0843	64.5	120-4(5-6)	49.09	7.78	14.07	48.85	7.86	14.07	14
Ig	Cyclopentyl	C ₂ H ₅	0.189	81.5	121-6(3-4)	51.28	8.18	13.22	51.43	8.30	13.33	14
Ih	Cyclohexyl	CH ₃	0.10	82	98-9(0.5)	49.09	7.72	14.09	49.47	7.59	13.77	14
Ii	Cyclohexyl	C ₂ H ₅	0.050	88	89-90(0.2)	53.22	8.46	12.50	53.45	8.71	12.18	14
Ij	Cyclohexyl	(CH ₃) ₂ CH	0.050	83	100-2(0.4)	56.52	9.06	11.23	56.58	9.21	10.95	14
Ik	Cycloheptyl	C ₂ H ₅	0.0435	61.4	127-31(0.8)	54.95	8.84	11.81	54.78	8.91	11.69	14
Il	<u>trans</u> -2- Phenyl- cyclopropyl	C ₂ H ₅	0.100	65.3	153-6(0.5)	59.57	6.79	10.97	60.13	7.02	10.69	
Im	<u>trans</u> -2- Phenyl- cyclopropyl	CH ₃	0.033	61	180-2(1.2)							
In	C ₆ H ₅ CH=CH	CH ₃	0.100	28.8	90°(3)	55.00	5.46	12.90	48.54	5.76	12.34	
Io	CH ₃ CH=CH	CH ₃	0.100	23	78-82(0.075)							



phite during most of the reaction did not lead to the excessive formation of by-products, probably because of the high reactivity of the acyl halides compared to that of the alkyl halide products.

The reactions were highly exothermic but could be controlled by adjusting the rate of addition of halide. The resulting products were nearly colorless except for the cinnamoyl and crotonyl derivatives, In and Io, which were greenish-yellow. The 2,4-dinitrophenylhydrazones (DNP) derivatives were light yellow, again with exception of those of In and Io which were orange. Diethyl trans-2-phenylcyclopropanecarbonylphosphonate Ie yielded an orange DNP which melted over a wide range. Slow recrystallization from methanol produced two types of crystals (see Table IV) which were large enough to be separated with a forceps. One type was in the form of yellow needles, similar to those of the other DNP's, but the other was isolated as large, reddish-orange, monoclinic crystals. Differences in color, melting point, and IR absorptions emphasized the fact that two different compounds were being dealt with, but the closeness of the two elemental analyses seemed to indicate the same molecular formula for both compounds. One might speculate on the occurrence of syn-anti isomers, isolable azo-hydrazone tautomers, dimerization, and other possibilities, but further

TABLE IV
PROPERTIES OF 2,4-DINITROPHENYLHYDRAZONES



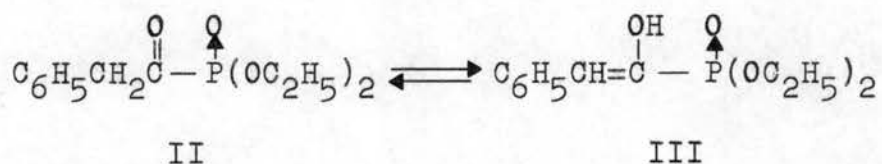
Parent Compound	R	R'	M.p. °C	Analysis (per cent)			
				Calculated N	P	Found N	P
Ia	CH ₃	C ₂ H ₅	130-2				
Ib	C ₂ H ₅	C ₂ H ₅	93-4	14.97	8.28	15.37	8.10
Ic	(CH ₃) ₂ CH	C ₂ H ₅	126-7				
Id	(CH ₃) ₃ C	C ₂ H ₅	140-1	13.89	7.68	13.44	7.41
Ie	Cyclopropyl	C ₂ H ₅	114-5	14.50	8.02	14.33	7.95
If	Cyclobutyl	C ₂ H ₅	136-6.5	14.00	7.74	14.20	7.82
Ig	Cyclopentyl	C ₂ H ₅	123-5	13.52	7.48	13.32	7.26
Ih	Cyclohexyl	CH ₃	125-6	13.94	7.75	14.00	7.75
Ii	Cyclohexyl	C ₂ H ₅	113.5-5.0	13.07	7.22	13.08	7.24
Ij	Cyclohexyl	(CH ₃) ₂ CH	84-6	12.43	6.83	12.28	6.80
Ik	Cycloheptyl	C ₂ H ₅	147-8	12.67	7.00	12.63	6.91
Il	<u>trans</u> -2-Phenylcyclopropyl	C ₂ H ₅	137-8 ^a	12.12	6.70	12.10	6.74
			116-7 ^b			12.42	6.75
Im	<u>trans</u> -2-Phenylcyclopropyl	CH ₃	180-2				
In	Cinnamoyl	CH ₃	219-20				
Io	Crotonyl	CH ₃	124-5				

^a Long, yellow needles similar to other derivatives.

^b Reddish-orange monoclinic crystals.

investigation is obviously required in order to favor any of these suppositions.

It was anticipated that an NMR analysis of dimethyl phenylacetylphosphonate (II) would be instructive in the evaluation of ^{31}P - ^1H coupling constants in systems with intervening carbonyl groups. However, the spectral properties of the solid material isolated from the triethyl phosphite-phenylacetyl chloride reaction mixture are inconsistent with structure II. A tautomeric structure III is indicated

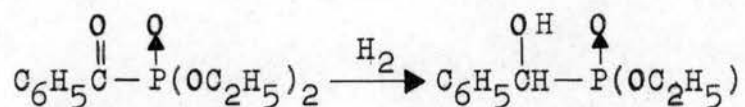


instead (see Chapter III), although the formation of a DNP seems to indicate the presence of II, at least to a limited extent. The stability of the enolic structure III would probably be enhanced both by hydrogen bonding of the hydroxy and phosphoryl groups and extension of conjugation, the latter factor being absent in similar tautomers of the structures I where such tautomerism is possible. This extended conjugation might be expected to produce a colored compound. Although the original compound is white, the unusual greenish tinge of the DNP suggests that a similar type of tautomerism is operative here.

If the foregoing assumptions are correct, the residual liquid from the filtration of III, and perhaps the entire products in the attempted synthesis of the corresponding

ethyl ester, might consist of the phenylacetic ester of the enolic compound as well as the suggested condensation products (see Chapter III).

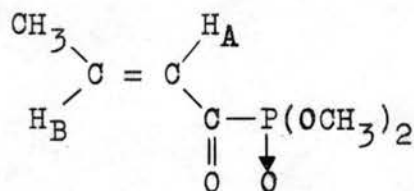
A straightforward synthesis of α -hydroxyphosphonates is illustrated in the preparation of diethyl α -hydroxybenzylphosphonate (IV) from the corresponding α -ketophosphonate. The physical and spectral properties of IV (see Plate XXV)



IV

are consistent with the structure assigned and with preliminary reports.²⁵ Further investigations of this system are forthcoming.

The NMR spectra (see Table V) of the compounds I support the assigned structures. The OR' groups follow the usual trends for P-O-C-H coupling constants; i.e., 10-12 c.p.s. for POCH_3 and 6-8 c.p.s. for POCH_2CH_3 and $\text{POCH}(\text{CH}_3)_2$. The only observed P-C-C-H couplings were for the acetyl Ia and crotonyl Io derivatives, which were 5 c.p.s. and 16 c.p.s., respectively. The latter value was deduced from the appearance of three quartets for H_A , presumably due to equal values



Io

TABLE V
NMR CHEMICAL SHIFT PARAMETERS AND COUPLING CONSTANTS
OF DIALKYL ACYLPHOSPHINATES

RC(O)P(O)(OR') ₂						
Compound	Plate	R	R'	δ value (p.p.m.) ^a	J(c.p.s.)	Assignment
Ia	XIII	CH ₃	C ₂ H ₅	2.43 d	5	R CH ₃
				1.37 t	7.5	R' CH ₃
				4.22 qt	7	R' CH ₂
Ib	XIV	C ₂ H ₅	C ₂ H ₅	1.05 t	7.5	R CH ₃
				2.80 q	7	R CH ₂
				1.32 t	7.5	R' CH ₃
				4.16 qt	7	R' CH ₂
Ic	XV	(CH ₃) ₂ CH	C ₂ H ₅	1.14 d	7	R CH ₃
				3.10 m	7	R CH
				1.35 t	7.5	R' CH ₃
				4.16 qt	7	R' CH ₂
Id	XVI	(CH ₃) ₃ C	C ₂ H ₅	1.23 s		R CH ₃
				1.33 t	7.5	R' CH ₃
				4.14 g	7	R' CH ₂
Ie	XVII	Cyclopropyl	C ₂ H ₅	ca. 1.15 m		R CH ₂
				2.58 m	6	R CH
				1.22 t	7.5	R' CH ₃
				4.10 qt	7	R' CH ₂
If	XVIII	Cyclobutyl	C ₂ H ₅	ca. 2.16 m		R CH ₂
				3.70 m		R CH
				1.33 t	7.5	R' CH ₃
				4.19 qt	7	R' CH ₂

TABLE V (Continued)

Compound	Plate	R	R'	δ value (p.p.m.) ^a	J(c.p.s.)	Assignment
Ig	XIX	Cyclopentyl	C ₂ H ₅	ca. 1.67 m		R CH ₂
				ca. 3.40 m		R CH
				1.30 t	7.5	R' CH ₃
				4.05 qt	7	R' CH ₂
Ih		Cyclohexyl	CH ₃	ca. 1.65 m		R CH ₂
				3.81 d	11	R' CH ₃
Ii		Cyclohexyl	C ₂ H ₅	ca. 1.65 m		R CH ₂
				1.35 t	7.5	R' CH ₃
				4.18 qt	7	R' CH ₂
Ij		Cyclohexyl	(CH ₃) ₂ CH	ca. 1.65 m		R CH ₂
				1.43 d	6.5	R' CH ₃
				4.85 m	7.5	R' CH
Ik	XX	Cycloheptyl	C ₂ H ₅	ca. $\begin{bmatrix} 1.58 \\ 2.40 \\ 3.00 \end{bmatrix}$ m		R $\begin{bmatrix} \text{CH}_2 \\ \text{CH} \end{bmatrix}$
				1.35 t	6.5	R' CH ₃
				4.18 qt	7.5	R' CH ₂
Il	XXI	<u>trans</u> -2- Phenylcyclo- propyl	C ₂ H ₅	7.20 s		R C ₆ H ₅
				ca. $\begin{bmatrix} 1.70 \\ 2.75 \end{bmatrix}$ m		R $\begin{bmatrix} \text{CH}_2 \\ \text{CH} \end{bmatrix}$
				$\begin{bmatrix} 1.27 \\ 1.32 \end{bmatrix}$ t	7	R' CH ₃
				4.17 qt	7	R' CH ₂

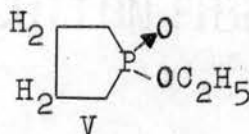
TABLE V (Continued)

Compound	Plate	R	R'	δ value (p.p.m.) ^a	J(c.p.s.)	Assignment	
Im	XXII	<u>trans</u> -2- Phenylcyclo- propyl	CH ₃	<div><div>7.20</div><div>7.34</div><div>ca. 1.65</div><div>2.75</div><div>3.74</div><div>3.78</div></div> <div><div>s</div><div>m</div><div>d</div></div>	10.5	<div>R C₆H₅</div> <div>R <div>CH₂ CH</div></div> <div>R' CH₃</div>	
In	XXIII	C ₆ H ₅ CH=CH	CH ₃	<div>6.19</div> <div>5.15</div> <div>6.89</div> <div>3.88</div>	<div>m</div> <div>d</div> <div>d</div>	<div>17</div> <div>12</div>	<div>R C₆H₅</div> <div>R <div>HC=CH </div></div> <div>R' CH₃</div>
Io	XXIV	CH ₃ CH=CH	CH ₃	<div>2.02</div> <div>2.13</div> <div>6.25</div> <div>6.52</div> <div>6.79</div> <div>7.57</div> <div>7.84</div> <div>3.90</div>	<div>d</div> <div>g</div> <div>g</div> <div>d</div>	<div>1.5</div> <div>7</div> <div>11</div>	<div>R CH₃</div> <div>R <div>HC=CH </div></div> <div>R' CH₃</div>

^a The multiplicity of each peak is indicated as follows: singlet, s; doublet, d; triplet, t; quartet, q; and multiplet, m.

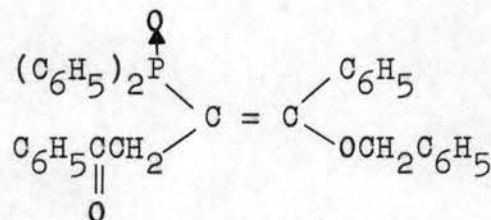
for J_{H_A-P} and $J_{H_A-H_B}$. The middle quartet is largest and is probably actually two quartets perfectly overlapped. The J values must be taken as approximate since second order effects are obviously operative (see Plate XXIV).

The absence of P-C-C-H coupling in the propionyl derivative Ib was confirmed by spin-decoupling. When the α methylene protons were decoupled from the adjacent methyl protons the quartet collapsed to a singlet with no indication of splitting from another source. Thus β -substitution of electron-donating alkyl groups appears to decrease or eliminate $J_{P-C-C-H}$ in this system in contrast to the increase of $J_{P-O-C-H}$ due to alkyl substitution. Since there are no previous reports of $J_{P-C-C-H}$ values for acyclic compounds other than for terminal methyl groups, it is difficult to interpret these results. The large value (33.0 c.p.s.) reported for V



(see Table I) seems to indicate that geometric factors are involved in these interpretations. It has been suggested²¹ that $J_{P-C-C-H}$ may be proportional to the s-character of the P-C bond, which is consistent with these observations and certain other trends noted in Table I. Although some inconsistencies are evident, vinyl phosphines and compounds with P-Cl bonds tend to display larger $J_{P-C-C-H}$ values, whereas the additional alkyl substitution in t-butyl compounds seems to contribute to lower values.

On the other hand, the additional s-character imposed by the adjacent olefinic function in VI does not increase



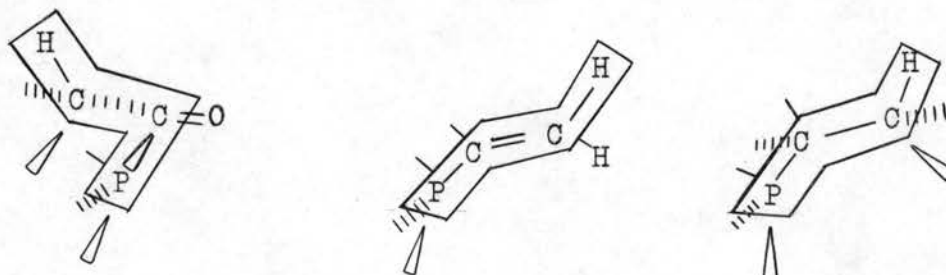
VI

$J_{\text{P-C-C-H}}$ (16 c.p.s.)^{21,46} beyond the usual range for saturated aliphatic phosphine oxides (triethylphosphine oxide shows a value of 16.3 c.p.s.). In the acylphosphonate series I, the carbonyl group seems to actually contribute to a decrease of the corresponding J value.

It is conceivable that, in some systems, an important contribution to the P-C-C-H coupling constant could be the number of molecules existing in conformations in which the P-C-C-H linkage is coplanar. Although there is no evidence for the existence of preferred conformations in I,¹⁵ the presence of p π -d π bonding between the phosphoryl and carbonyl groups in this system has been confirmed by UV studies.¹³ This overlapping could result in a preference for conformers in which the P-C-C-H atoms do not lie in the same plane, resulting in a reduction in the corresponding coupling. Moreover, the extended conjugation in the crotonyl derivative I_o restricts the molecule to the required coplanar arrangement, leading to a large coupling constant (16 c.p.s.) compared to that of γ,γ -dimethylallylphosphonates (7.7 c.p.s.),²¹

although both of these values are surprisingly low. No P-C-C-H coupling was observed in the cinnamoylphosphonate In, but the vinyl protons are difficult to observe due to interference by the aromatic protons, and the product was not obtained in a highly purified state. Thus it is possible that such coupling was obscured.

It seems likely that other factors are involved in the explanation of the observed trends in $J_{\text{P-C-C-H}}$ values in the system studied. The cyclic derivatives Ie-Im displayed spectra that were too complicated to allow definite assignment of J values, and efforts to resolve these difficulties via spin decoupling were unfruitful, owing to limitations of the equipment utilized. Further extension of these studies to other acylphosphonates may reveal new trends, leading to a consistent correlation between P-C-C-H coupling constants and other properties of these unique compounds. An obvious parameter is the bond angle PCC in such systems. In the acyl phosphonates if an angle of about 120° is assumed for the PCC arrangement, it is possible that electronic transmission of magnetic effects is reduced. In the α,β -unsaturated system the P-C-C angle is probably near 120°



but all atoms are coplanar while in the saturated system the angle is near 109° . X-ray analysis seems a requirement for a number of systems before a direct correlation of J_{PCH} can be made with PCH bond angle or any other parameter.

CHAPTER III

EXPERIMENTAL^{a-d}

Preparation of Pivalyl Chloride. This compound and other acid chlorides which were not commercially available were synthesized by the following general procedure. The results are summarized in Table VI. A 100-ml. one-necked flask was fitted with a condenser, a drying tube, and a magnetic stirring bar. A sample (25.5 g., 0.25 mole) of pivalic acid was added to the flask, followed by addition of 36 ml. (59.5 g., 0.50 mole) of thionyl chloride. The mixture was allowed to stand for one day. The excess thionyl chloride was removed by distillation followed by azeotroping with benzene to remove the last traces of the inorganic halide. The remaining material was distilled to

^a All melting points are corrected; all boiling points are uncorrected.

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

^c The nuclear magnetic resonance spectra were determined on a Varian A-60 high resolution spectrometer with a field-sensing stabilizer ("Super Stabilizer") and a model V-6058 proton-proton spin decoupler. The solvent utilized, except where otherwise stated, was carbon tetrachloride containing tetramethylsilane as an internal standard.

^d The microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

yield 3.7 g. (12%) of material boiling at 105°/740 mm.

TABLE VI
PREPARATION AND PROPERTIES OF ACYL CHLORIDES

Chloride	Moles of Acid	Moles of Thionyl Chloride	Yield (per cent)	B.p. °C (mm.)
Pivalyl	0.25	0.50	12	105(740)
Cyclobutane- carbonyl	0.25	1.00	53.4	56(38)
Cyclopentane- carbonyl	0.22	1.00	86.2	73(38)
Cycloheptane- carbonyl	0.10	0.20	53.5	185(25)
Crotonyl	0.33	0.67	42.0	121-5(737)

Preparation of Diethyl Acetylphosphonate (Ia). The following procedure is a modification of that used by Kabachnik.³⁰ This same general procedure was used to prepare all of the esters listed in Table III. A 100-ml. three-necked flask was fitted with a condenser, a drying tube, an immersion thermometer, a pressure-equalizing addition funnel, a nitrogen inlet, and a magnetic stirring bar. The flask was charged with 15.0 g. (0.0903 mole) of triethyl phosphite, and acetyl chloride (7.09 g., 0.0903 mole) was added dropwise with stirring under nitrogen during 1 hour. The rate of addition was adjusted at intervals to maintain the temperature of the reaction mixture below 70°. Effervescence was noted shortly after the addition was started, presumably due

to expulsion of ethyl chloride. The resulting mixture was allowed to stir at room temperature for 1 day and then distilled to yield 12.0 g. (73.6%) of material, b.p. 181-6°/3-4 mm..

Preparation of Diethyl Acetylphosphonate (2,4-Dinitrophenyl)hydrazone. A stock solution of 2,4-dinitrophenylhydrazine was made⁵¹ and used to prepare the 2,4-dinitrophenylhydrazone of each of the dialkyl acylphosphonates listed in Table III by the following procedure.⁵¹ The results are summarized in Table IV. To 25 ml. of the stock solution was added 1 ml. of diethyl acetylphosphonate. The solution was swirled and then allowed to stand at room temperature for 1 day. The resulting slurry was filtered, and the solid material obtained was recrystallized from methanol to yield yellow crystals, m.p. 130-2°.

Attempted Preparation of Dimethyl Phenylacetylphosphonate. The reaction between phenylacetyl chloride (38.7 g., 0.250 mole) and trimethyl phosphite (31.0 g., 0.250 mole) was carried out by the same general procedure as that utilized for the preparation of diethyl acetylphosphonate. After standing for 1 day, the mixture partially solidified. The solid material was removed by filtration and recrystallized 3 times from methylene chloride-petroleum ether to yield white crystals, 18.6 g., m.p. 132-3°. The IR spectrum showed no clearly defined carbonyl absorption but displayed a rather distinct -OH peak at 3390 cm.⁻¹. The NMR spectrum showed a doublet ($J = 12.4$ c.p.s.) at $\delta 6.2$ and a wide absorption near

8.8. Otherwise the spectral evidence was consistent with the proposed structure. A 2,4-dinitrophenylhydrazone formed slowly (1 day) when a methylene chloride solution of the white solid was treated with the stock solution of 2,4-dinitrophenylhydrazine. Recrystallization from methylene chloride-ethanol yielded greenish-yellow crystals melting at $184-5^{\circ}$.

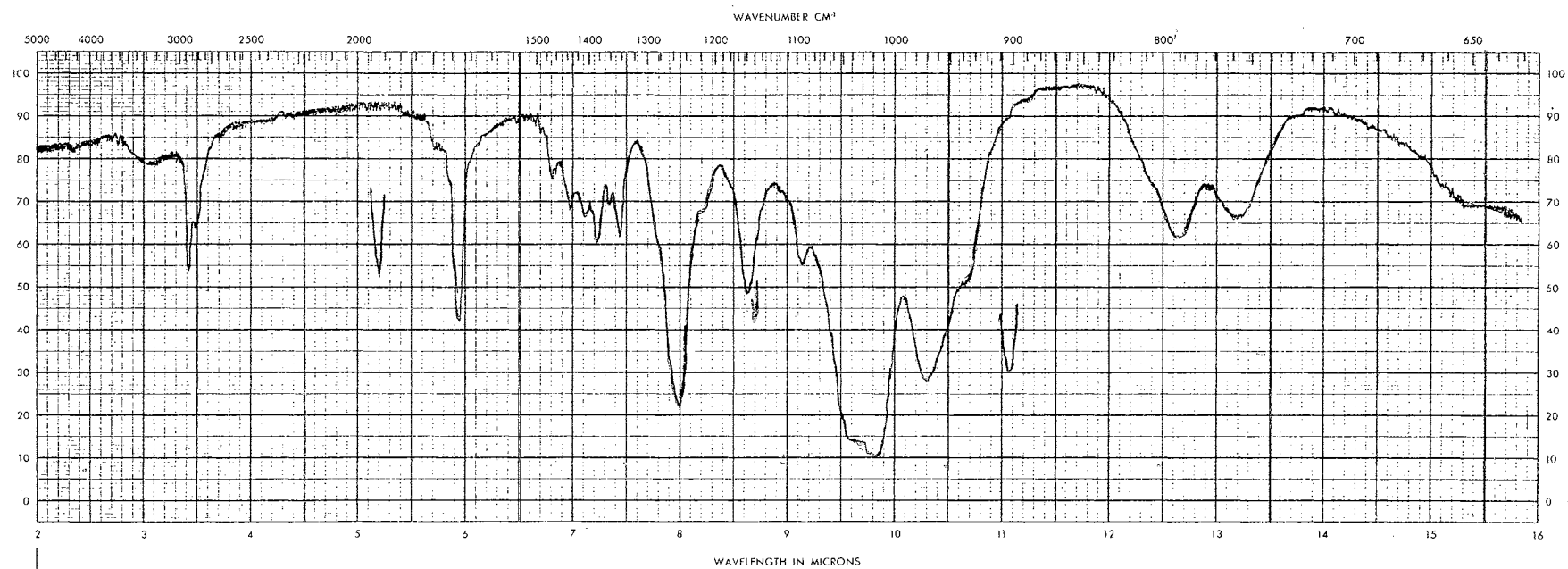
The residual liquid from filtration of the white solid was distilled to give various fractions which all showed carbonyl absorption in the IR spectrum. NMR spectra of these liquids seemed to indicate that they were condensation products.

Attempted Preparation of Diethyl Phenylacetylphosphonate. Following the same procedure as for the preparation of diethyl acetylphosphonate, 6.7 g. (0.043 mole) of phenylacetyl chloride were allowed to react with 7.2 g. (0.043 mole) of triethyl phosphite. Vacuum distillation of the resulting liquid gave 3 fractions. IR and NMR spectra were inconsistent with the structure proposed, and it is thought that condensation products were obtained.

Preparation of Diethyl (α -Hydroxybenzyl)phosphonate (IV). A Parr hydrogenation apparatus was charged with 12.1 g. (0.0500 mole) of diethyl benzoylphosphonate (prepared by the usual procedure,³⁰ b.p. $168-74^{\circ}/8-10$ mm.), 0.80 g. of platinum oxide (Adams catalyst), and 20 ml. of benzene. The apparatus was evacuated 5 times to aspirator pressure, followed each time by injection of hydrogen gas to a pressure

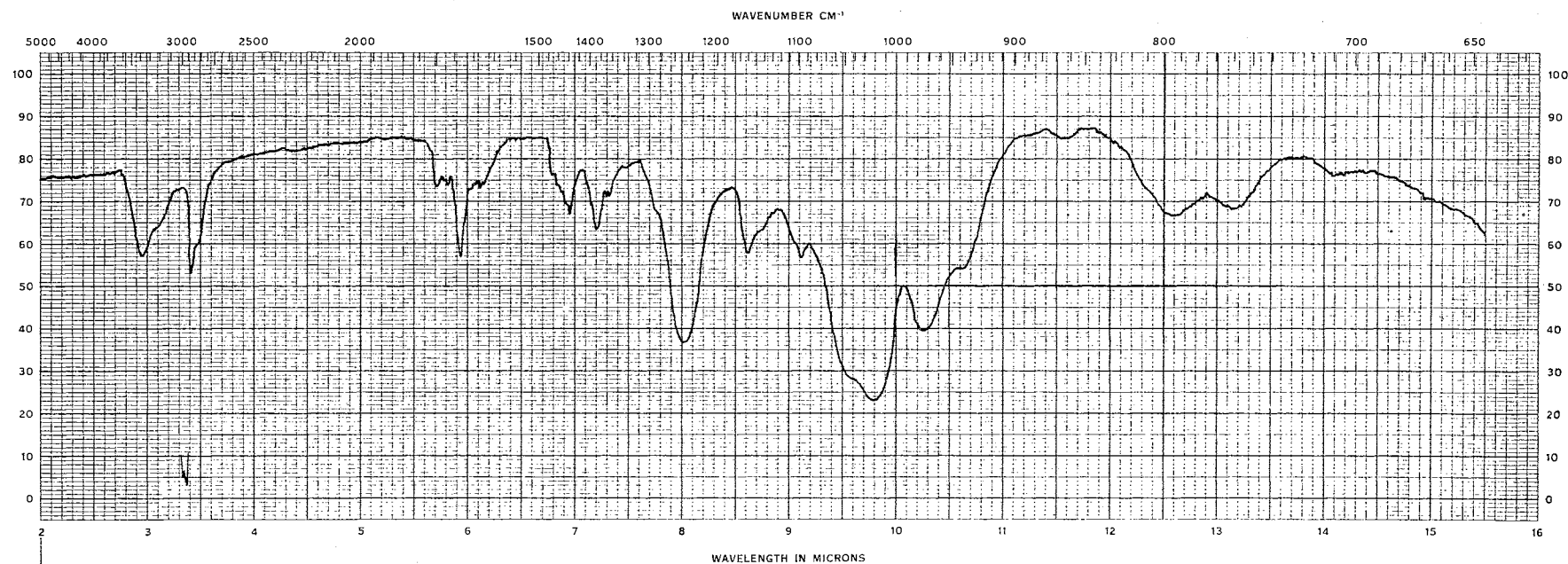
of 30 psig.. The reaction vessel was shaken for 4 hours, during which time the pressure was restored to 30 psig. at approximately 30-minute intervals, allowing pressure drops no greater than 9 psi.. The pressure was then released and the catalyst was removed from the reaction mixture by filtration through Celite filter-aid. The benzene was removed under aspirator pressure, leaving a light-brown liquid which solidified upon standing. The solid material was washed with petroleum ether (b.p. 30-60°) and recrystallized from methylene chloride-petroleum ether. A white, fibrous mass of crystals was obtained, 6.55 g. (49.2%), m.p. 83-4° (reported m.p. 83-4°).²⁵ The IR and NMR (Plate XXV) spectra support the structure proposed.

Plate I



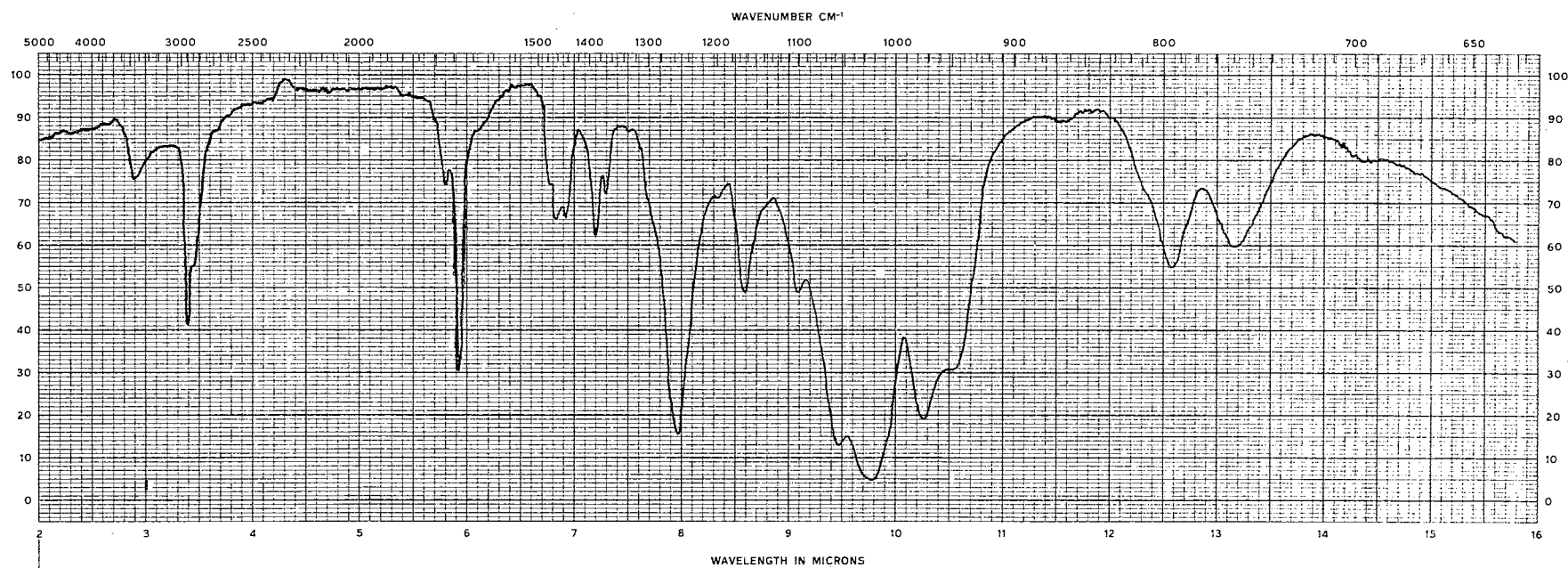
Diethyl Acetylphosphonate (Ia), Film on NaCl Plates

Plate II



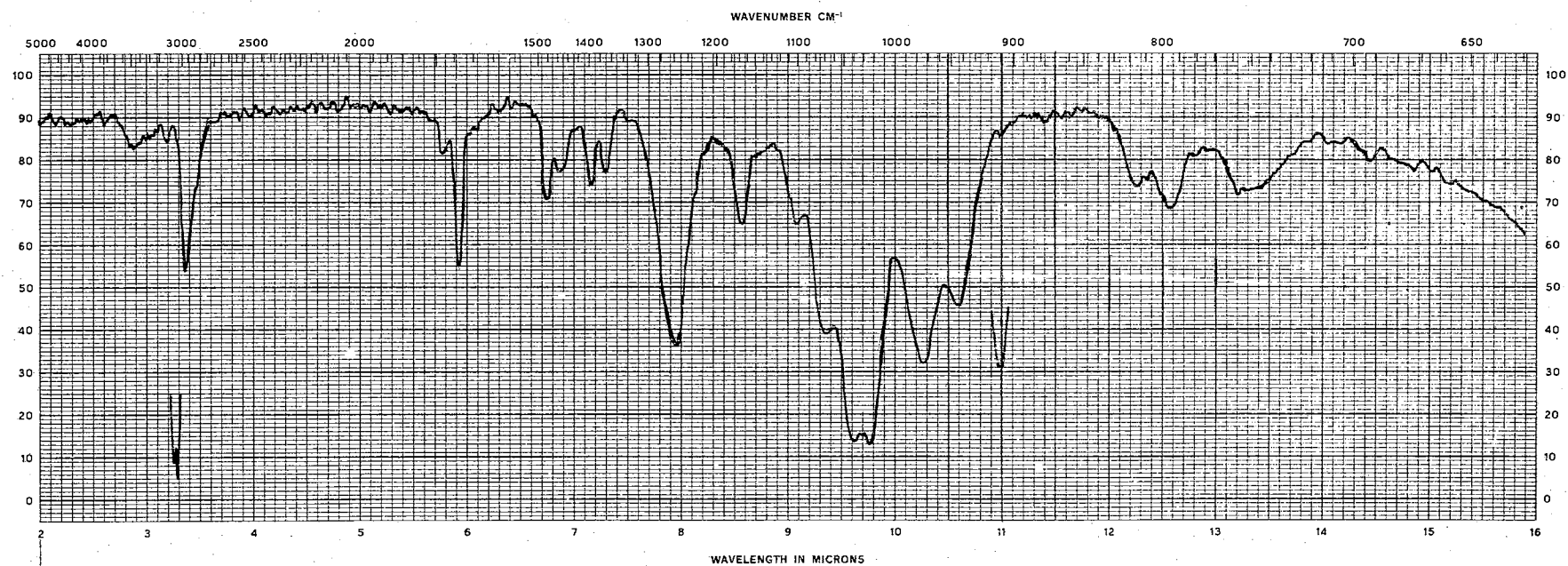
Diethyl Propionylphosphonate (Ib), Film on NaCl Plate

Plate III



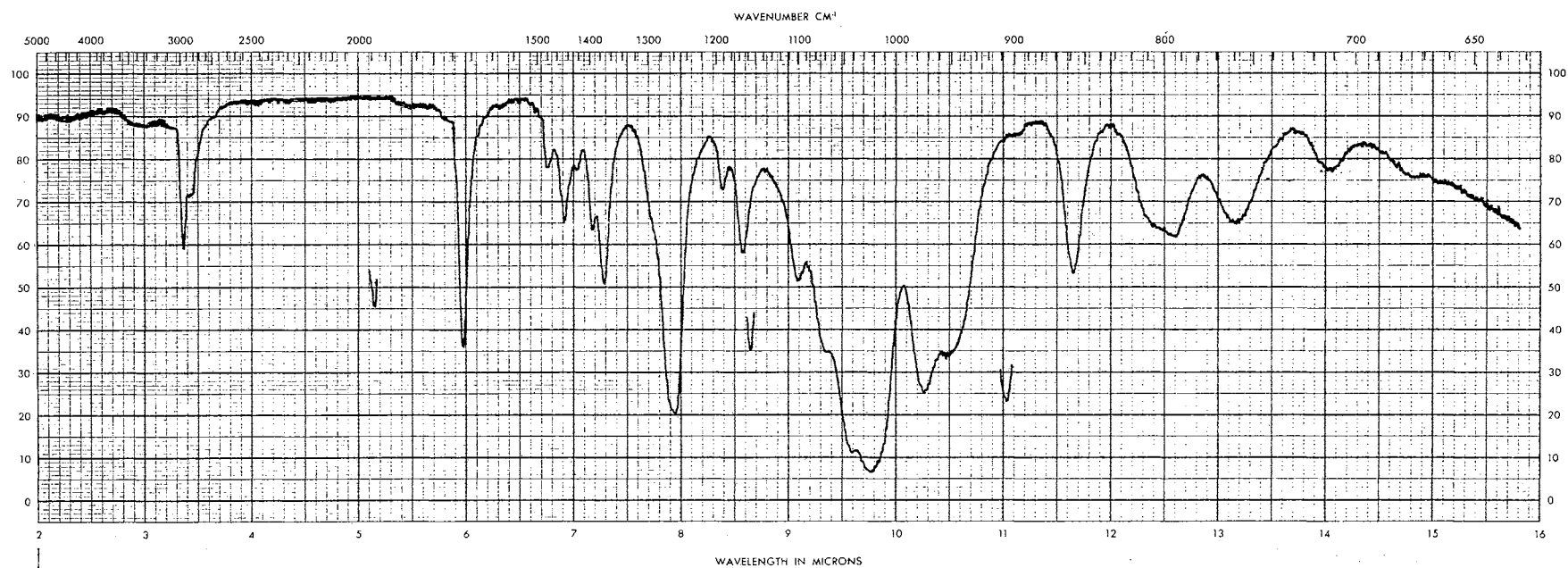
Diethyl Isobutyrylphosphonate (Ic), Film on NaCl Plates

Plate IV



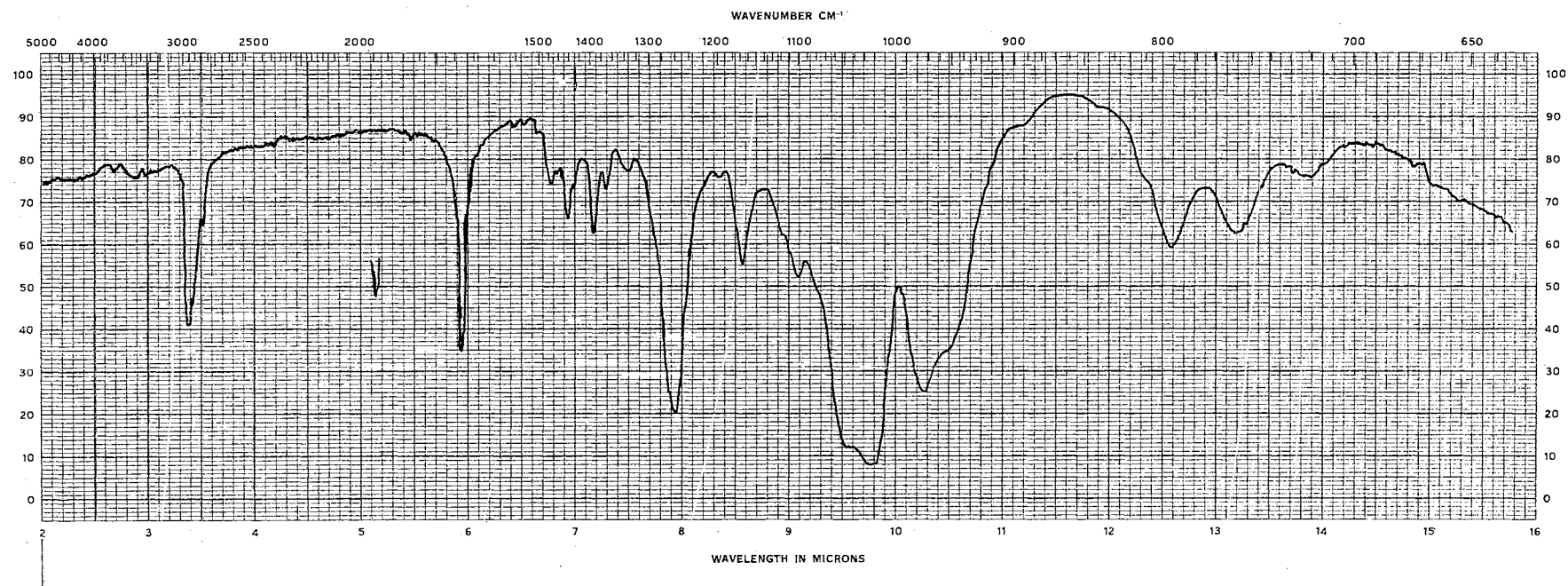
Diethyl Pivalylphosphonate (Id), Film on NaCl Plates

Plate V



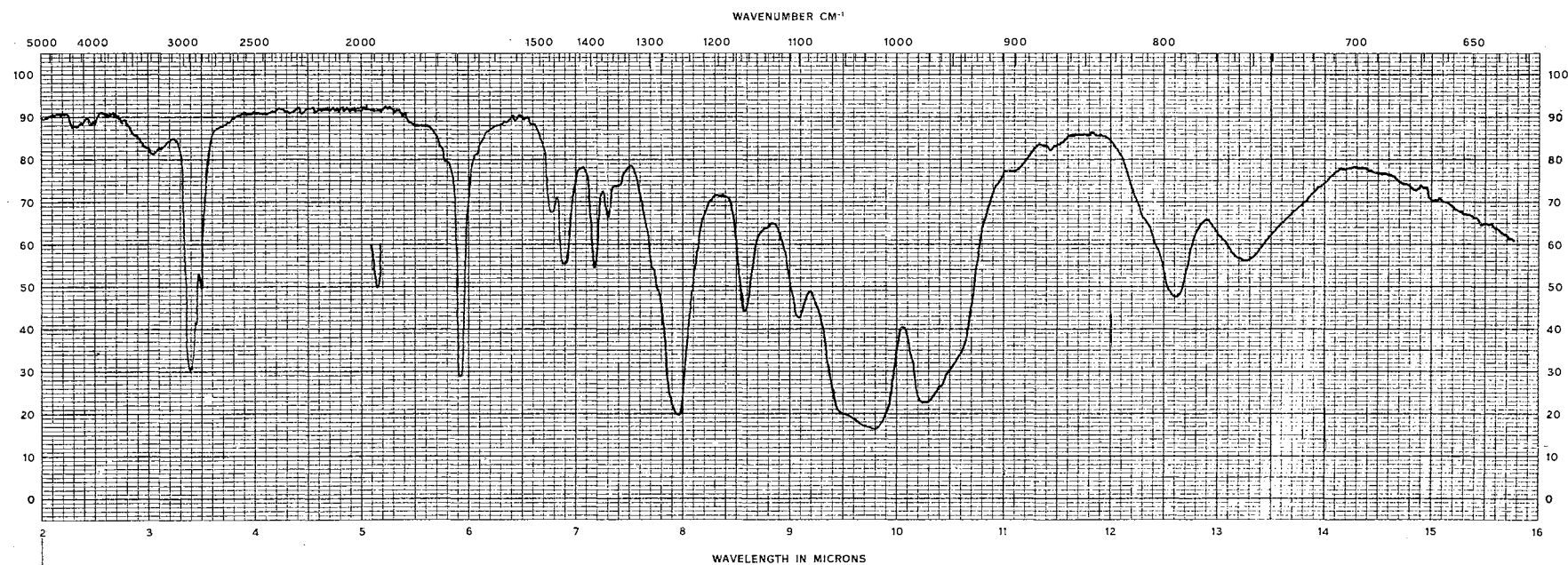
Diethyl Cyclopropanecarbonylphosphonate (Ie), Film on NaCl Plates

Plate VI



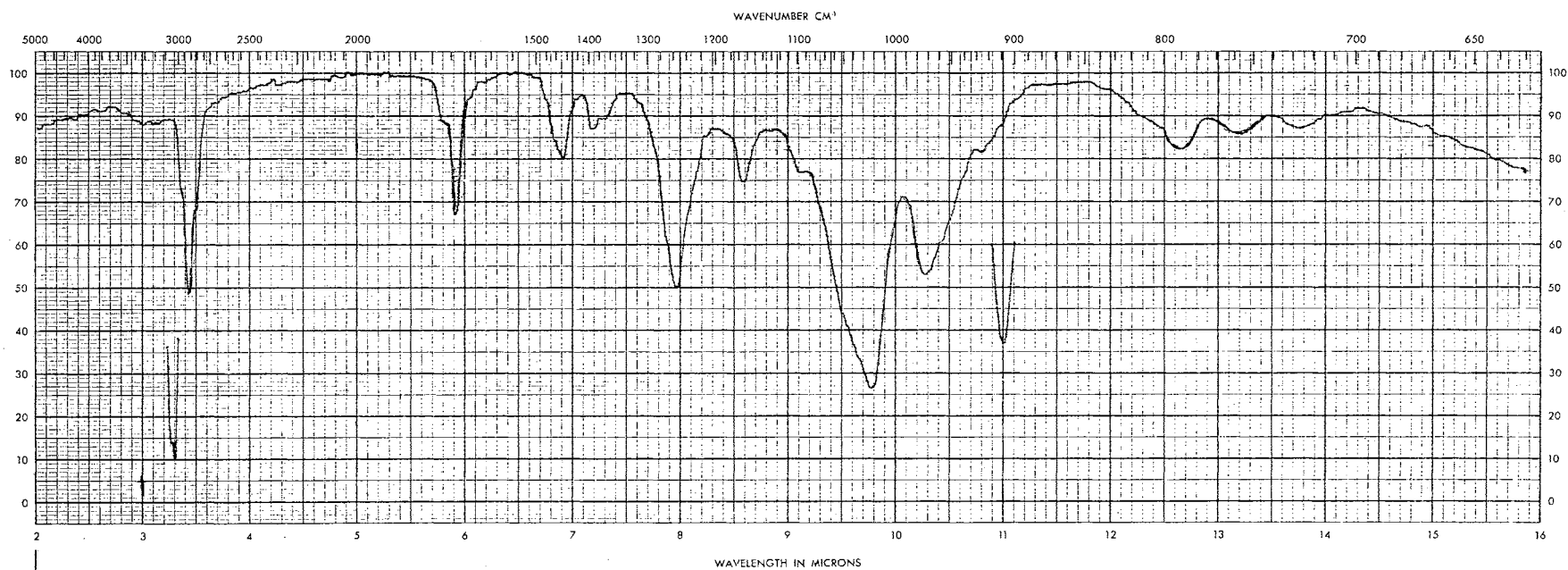
Diethyl Cyclobutanecarbonylphosphonate (If), Film on NaCl Plates

Plate VII



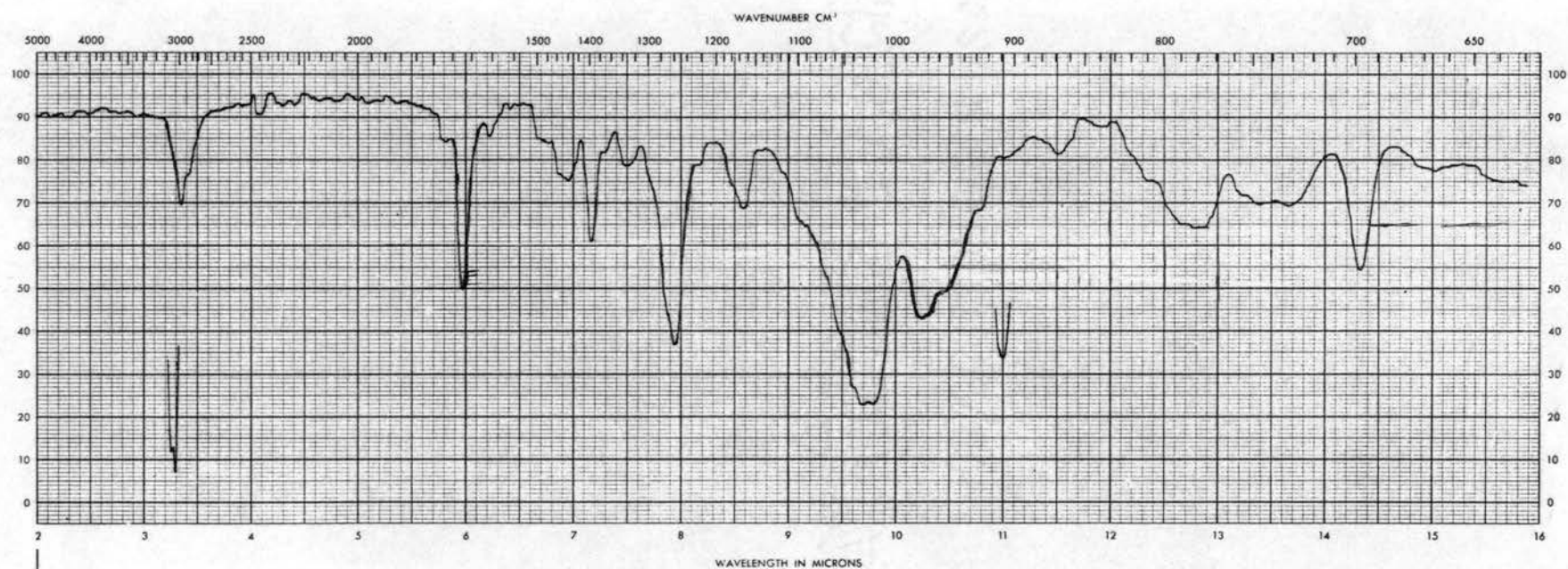
Diethyl Cyclopentanecarbonylphosphonate (Ig), Film on NaCl Plates

Plate VIII



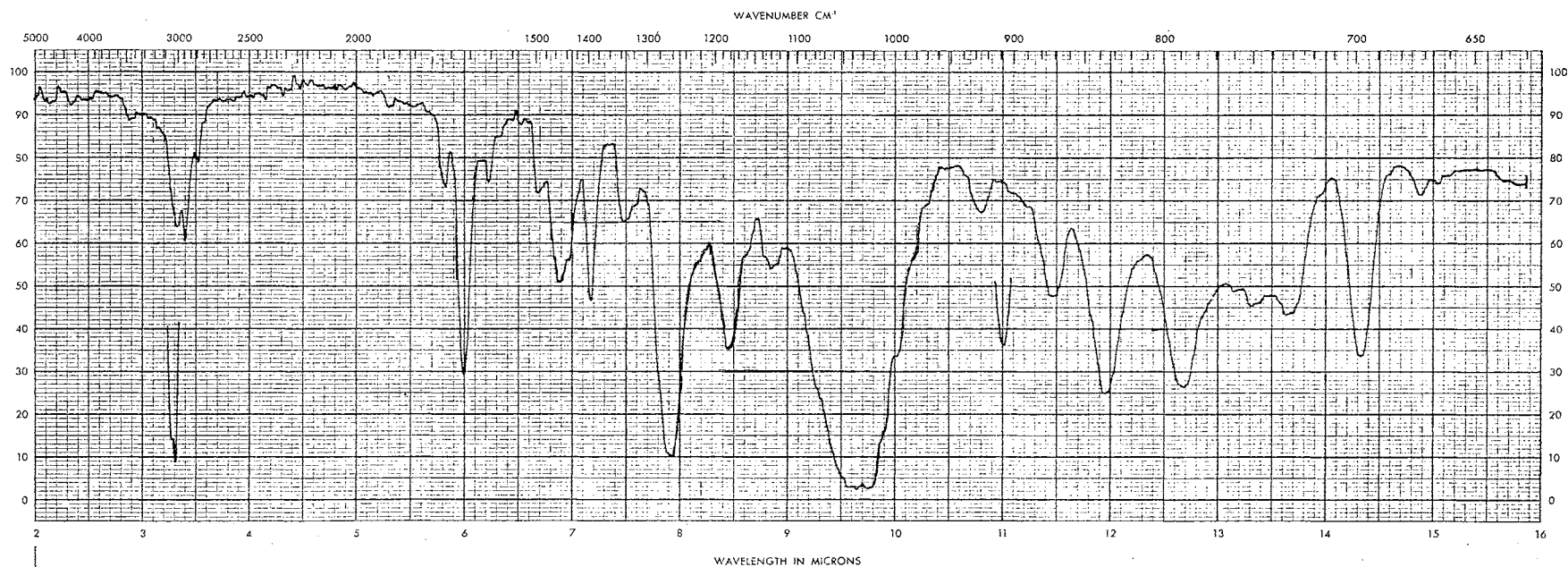
Diethyl Cycloheptanecarbonylphosphonate (Ik), Film on NaCl Plates

Plate IX



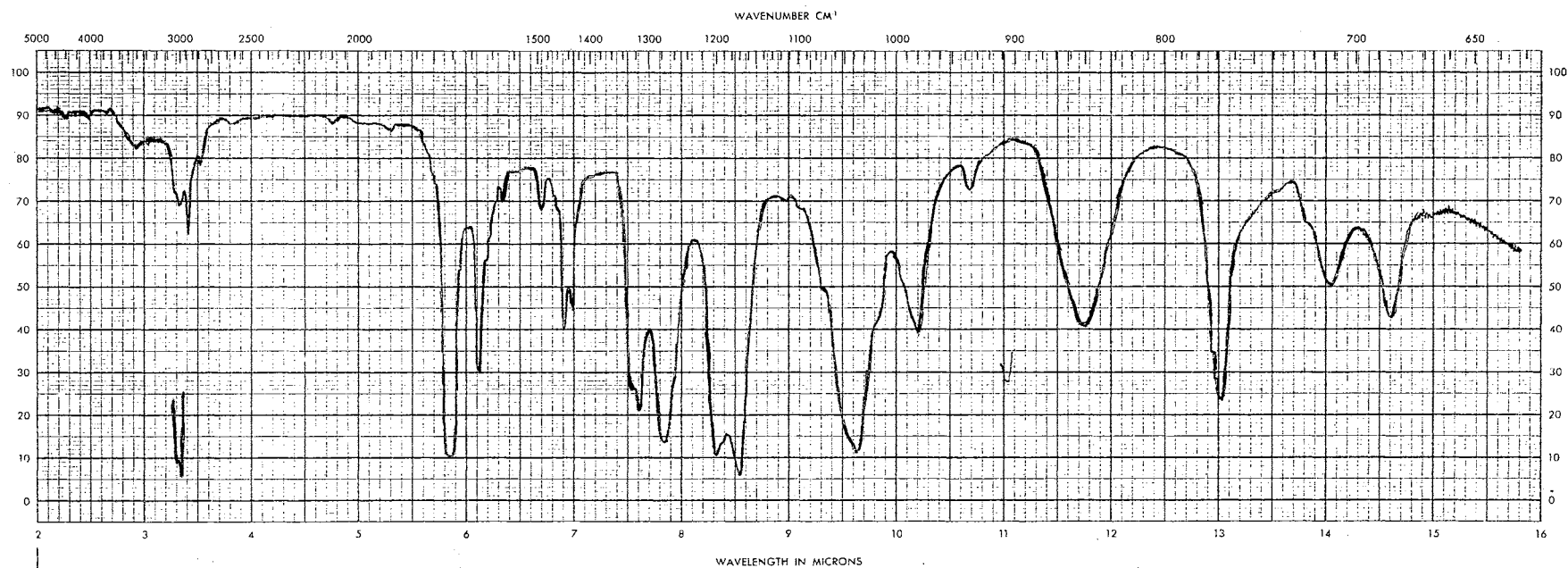
Diethyl trans-2-Phenylcyclopanecarbonylphosphonate (II), Film on NaCl Plates

Plate X



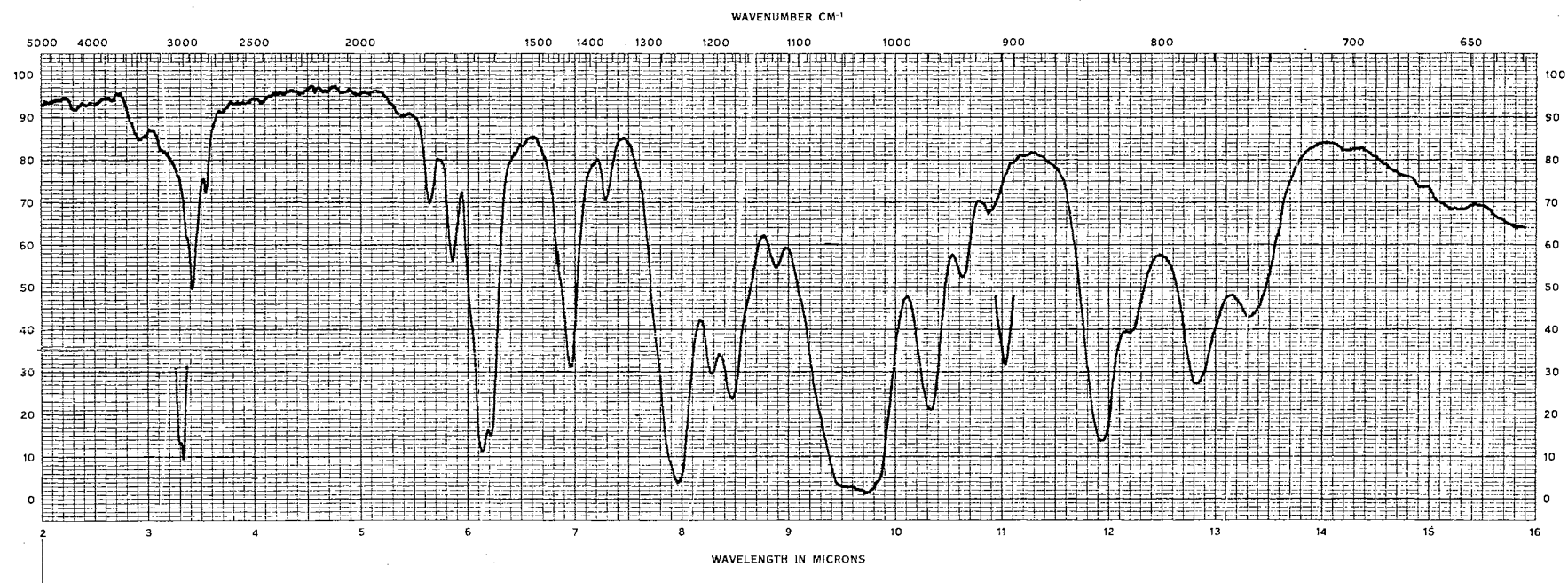
Dimethyl trans-2-Phenylcyclopropanecarbonylphosphonate (Im), Film on NaCl Plates

Plate XI



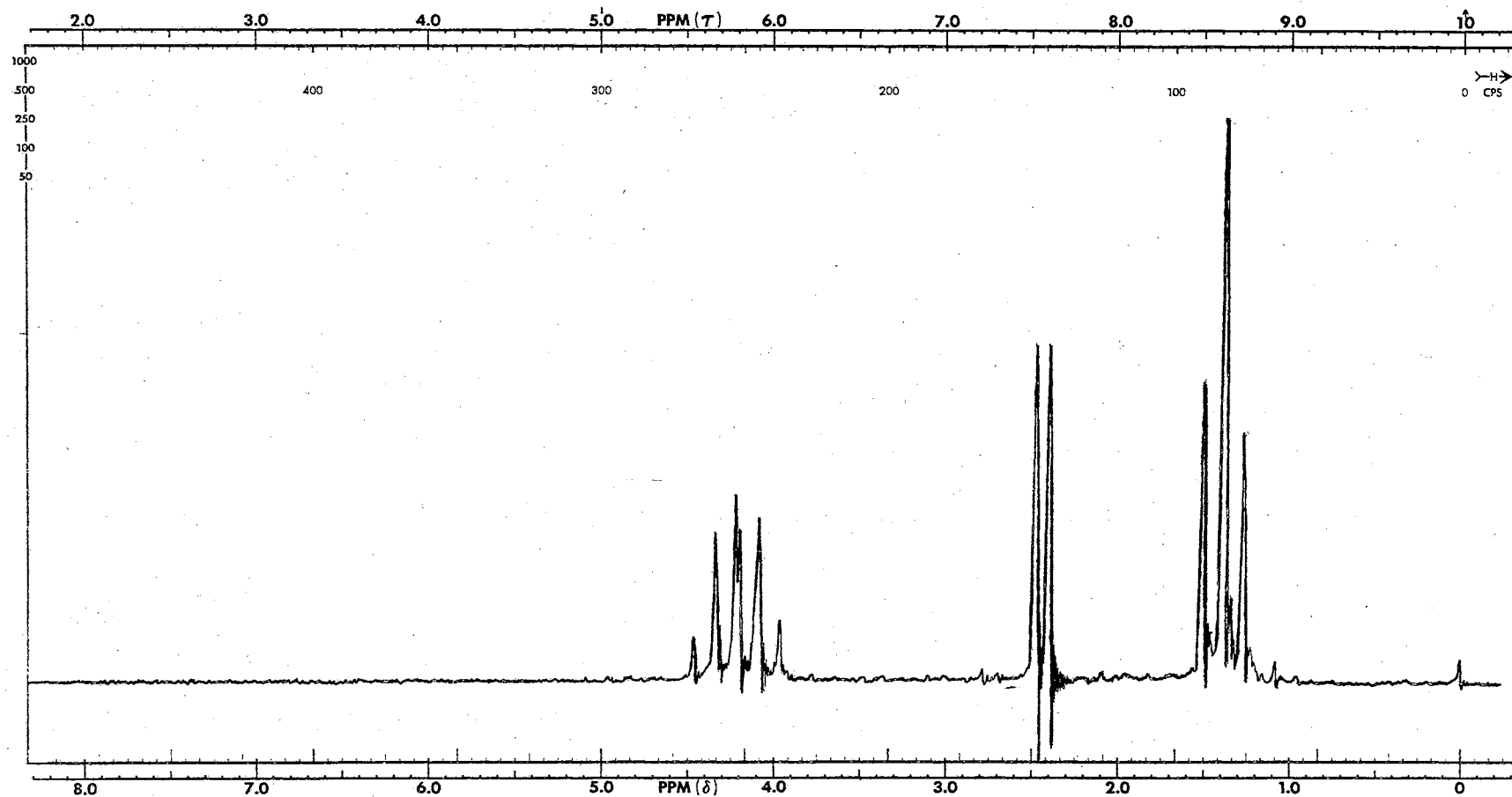
Dimethyl Cinnamoylphosphonate (In), Film on NaCl Plates

Plate XII



Dimethyl Crotonylphosphonate (Io), Film on NaCl Plates

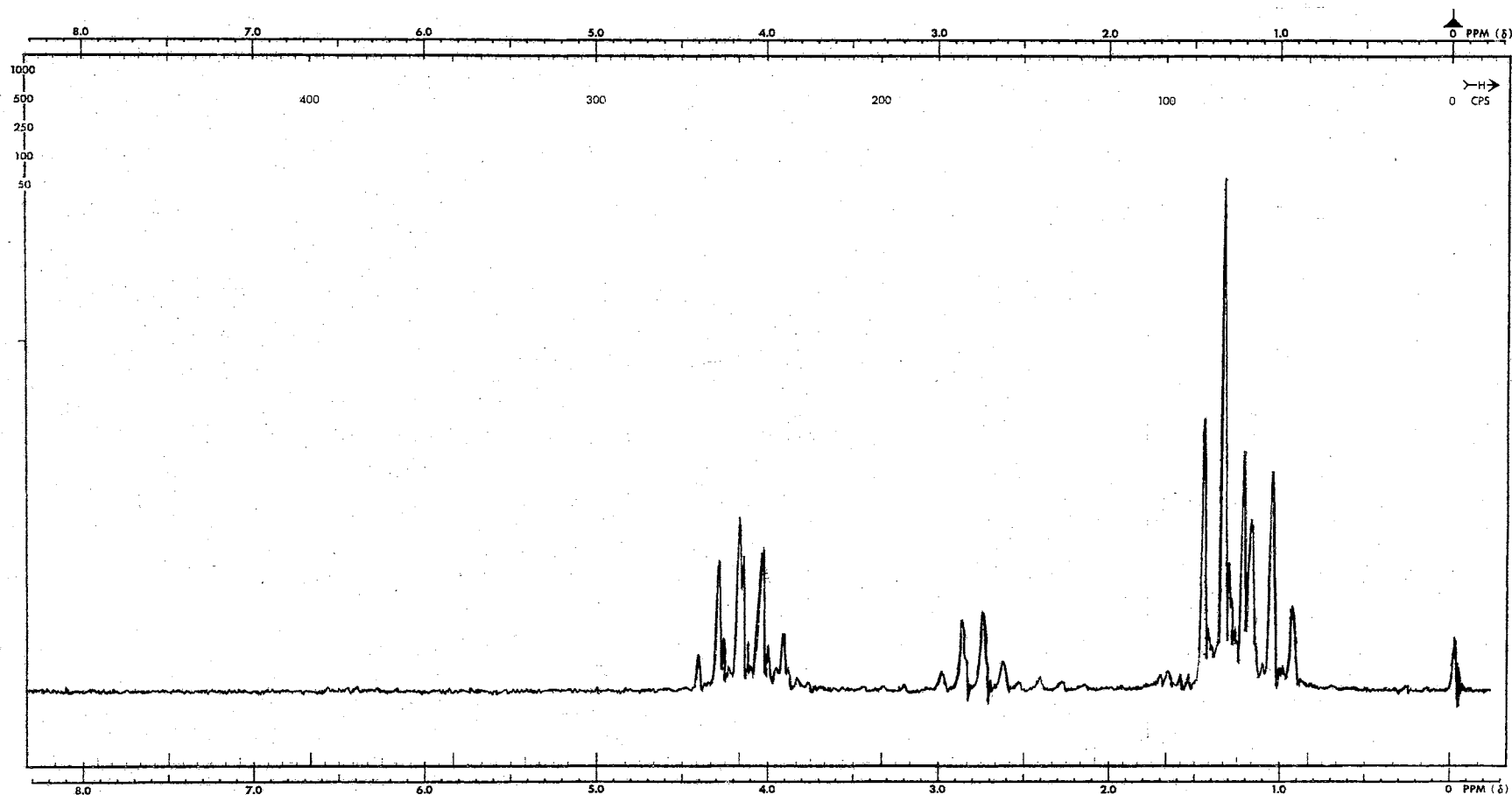
Plate XIII



Diethyl Acetylphosphonate (Ia)

Solvent CCl₄ R.F. Field 0.05 mG S.W. . . 500 cps S.A. . . 2.0
 F.B. 400 cps S.T. 250 sec S.O. . . 000 cps I.A. . . off

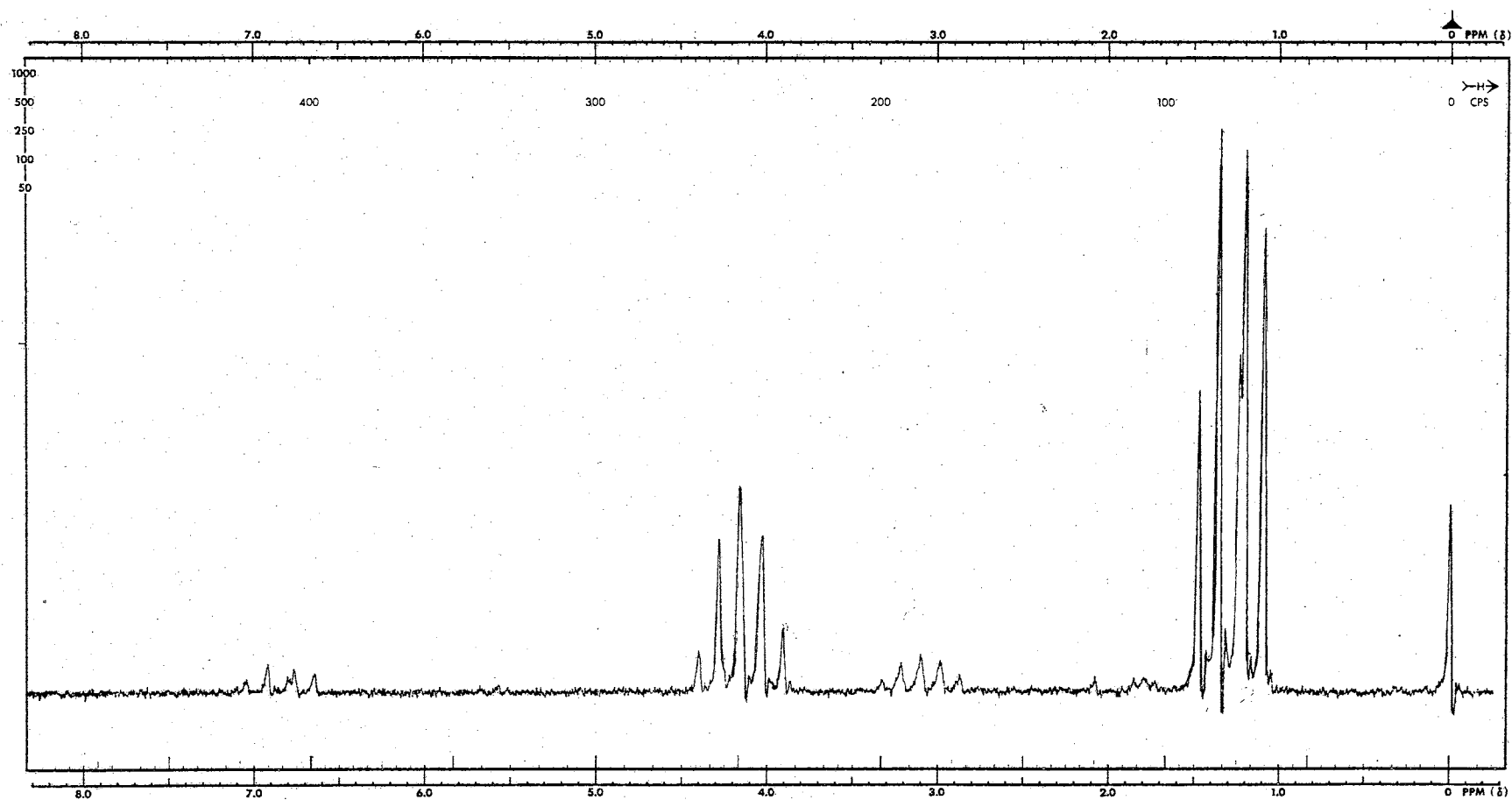
Plate XIV



Diethyl Propionylphosphonate (Ib)

Solvent	CCl ₄	R.F. Field	0.05 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

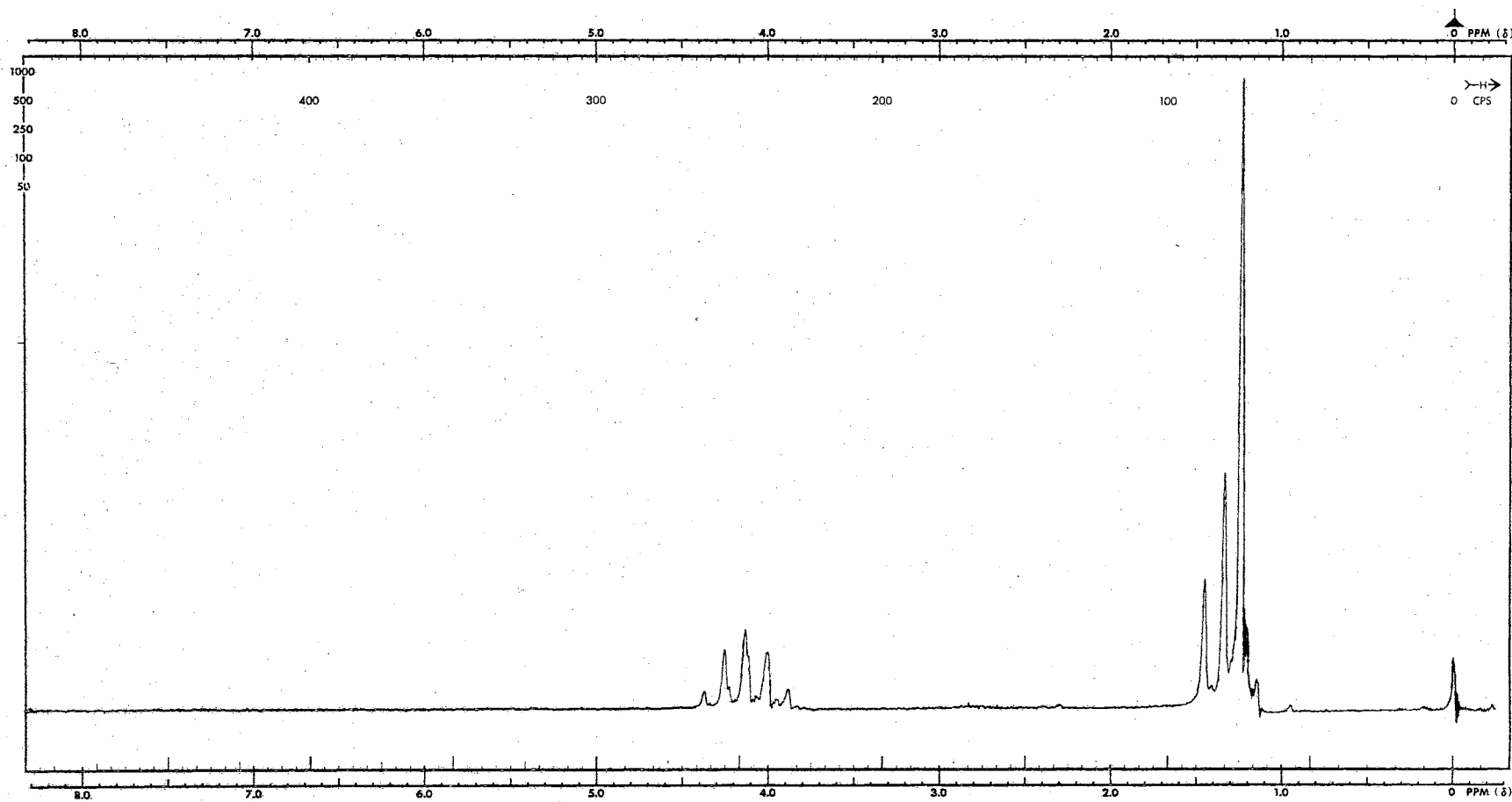
Plate XV



Diethyl Isobutyrylphosphonate (Ic)

Solvent	CCl ₄	R.F. Field	0.05 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

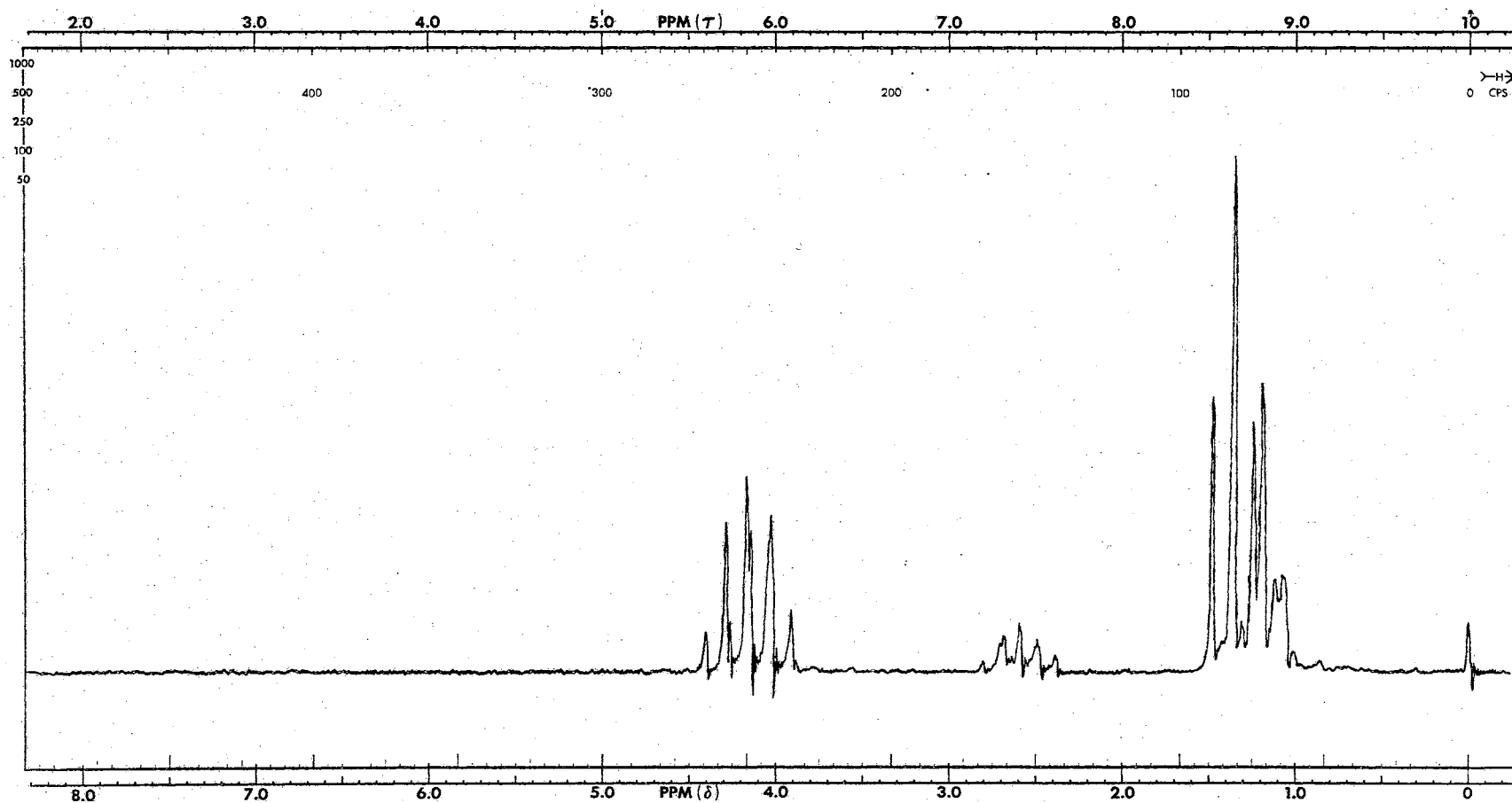
Plate XVI



Diethyl Pivalylphosphonate (Id)

Solvent	CCl ₄	R.F. Field	0.05 mG	S.W.	500 cps	S.A.	0.8
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

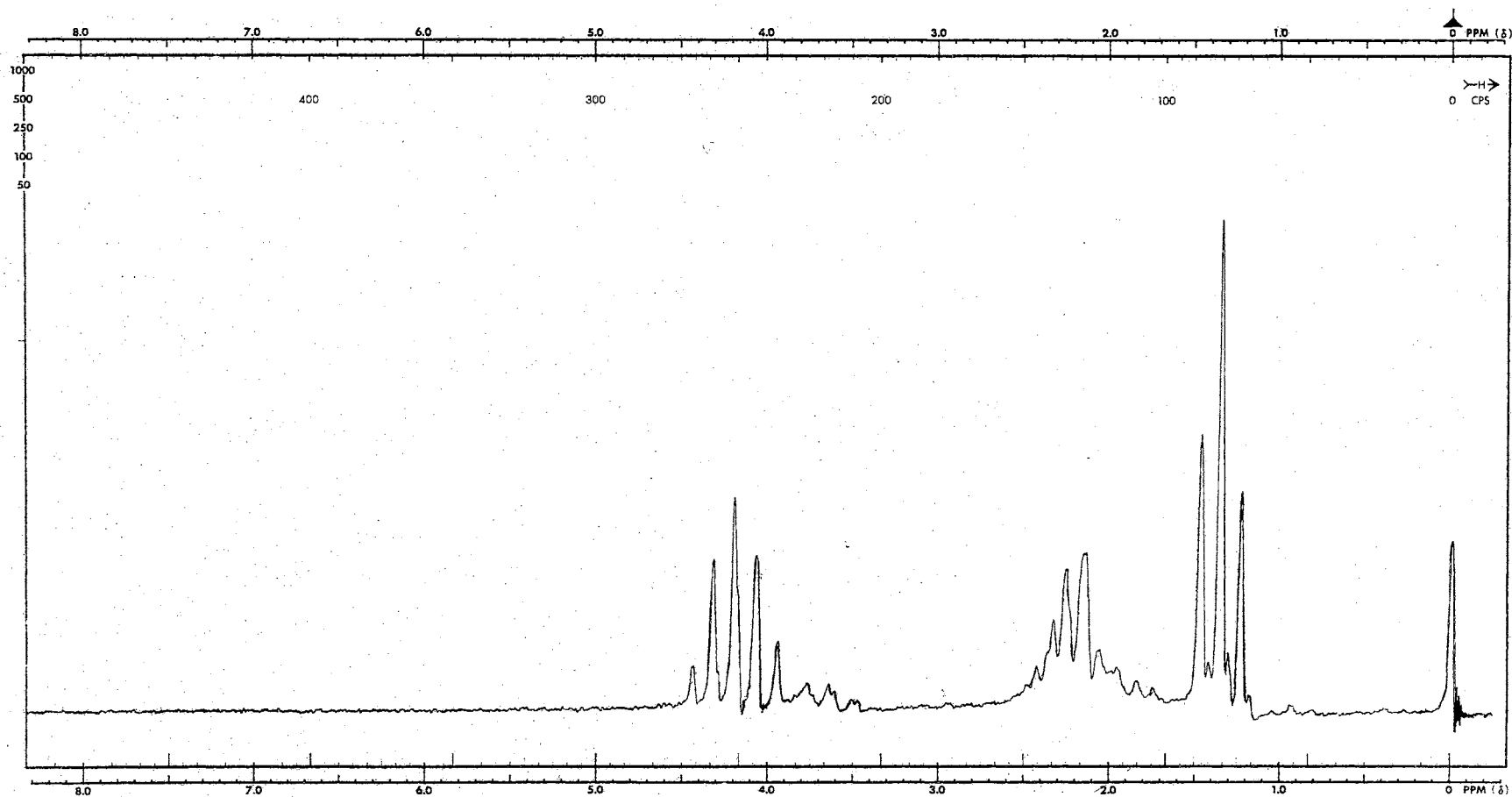
Plate XVII



Diethyl Cyclopropanecarbonylphosphonate (Ie)

Solvent	CCl ₄	R.F. Field	0.05 mG	S.W.	500 cps	S.A.	2.0
F.B.	4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

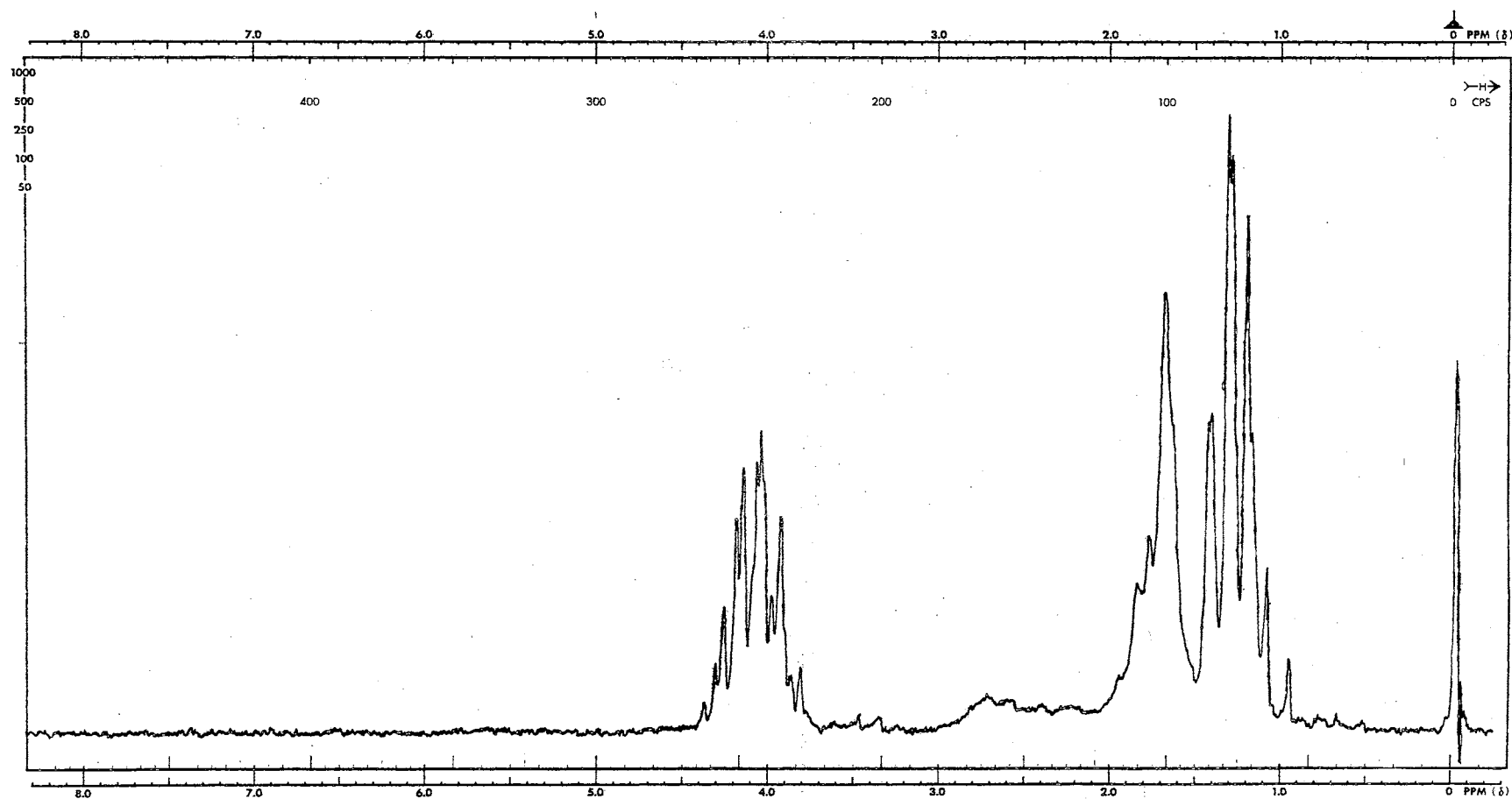
Plate XVIII



Diethyl Cyclobutanecarbonylphosphonate (If)

Solvent CCl₄ R.F. Field 0.05 mG S.W. . . . 500 cps S.A. . . . 2.0
 F.B. 4.0 cps S.T. 250 sec S.O. . . . 000 cps I.A. . . . off

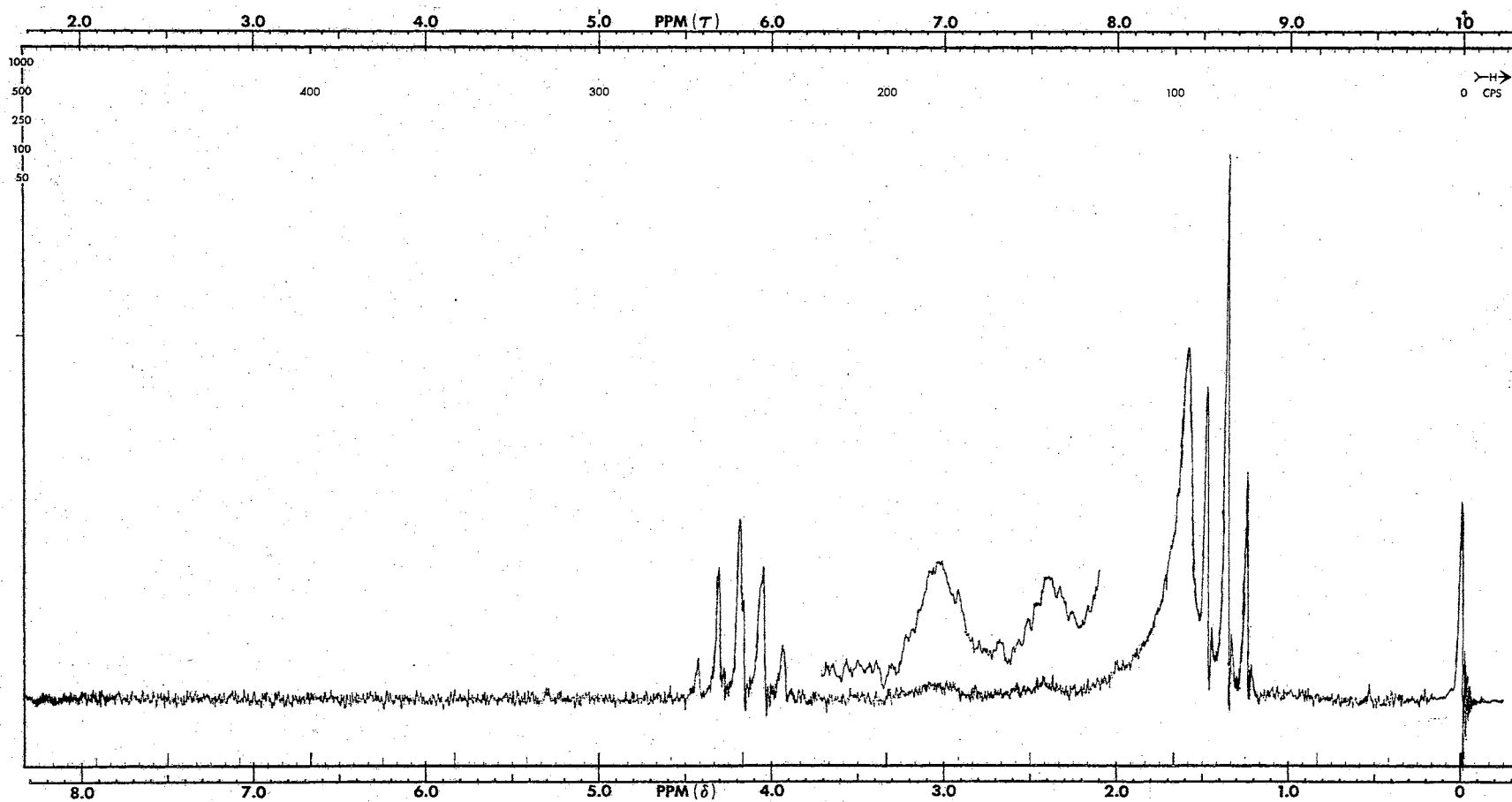
Plate XIX



Diethyl Cyclopentanecarbonylphosphonate (Ig)

Solvent	CCl ₄	R.F. Field	0.05 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

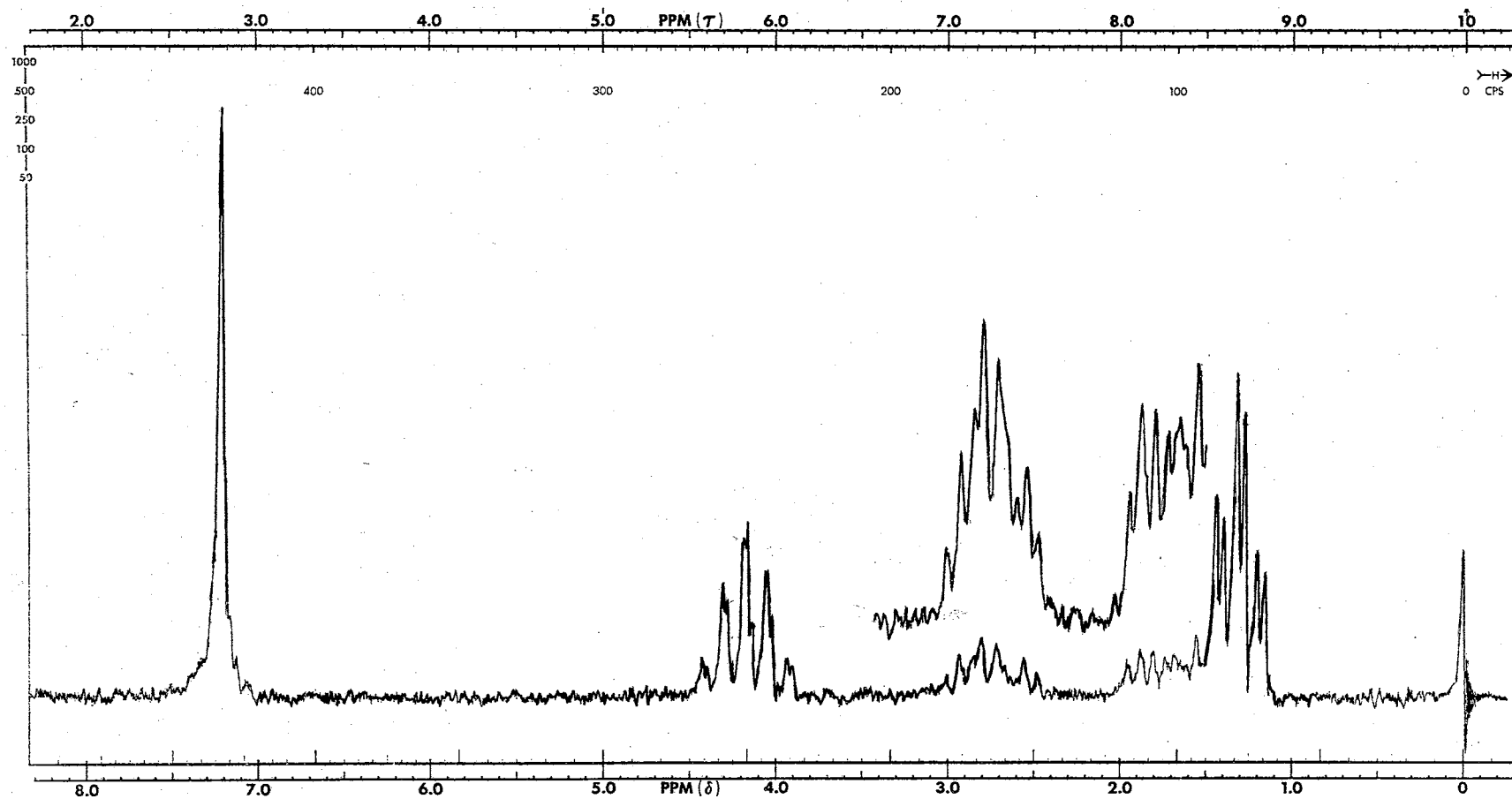
Plate XX



Diethyl Cycloheptanecarbonylphosphonate (Ik)

Solvent	CCl ₄	R.F. Field	0.05 mG	S.W.	500 cps	S.A.	6.3
F.B.4.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

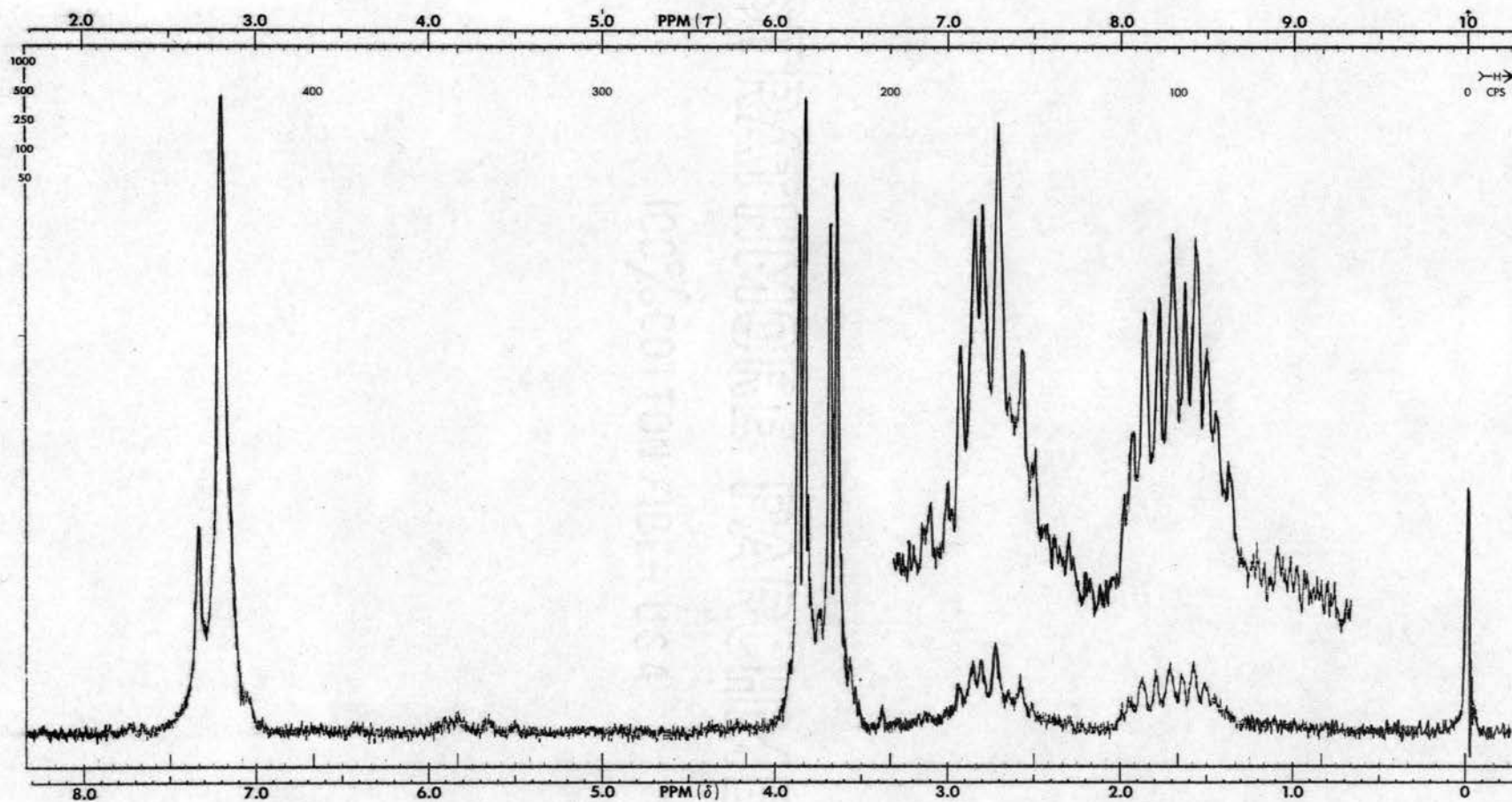
Plate XXI



Diethyl trans-2-Phenylcyclopropanecarbonylphosphonate (I1)

Solvent	CCl ₄	R.F. Field	0.05 mG	S.W.	500 cps	S.A.	8.0
F.B.2.0 cps	S.T.	250 sec	S.O.	000 cps	I.A.	off

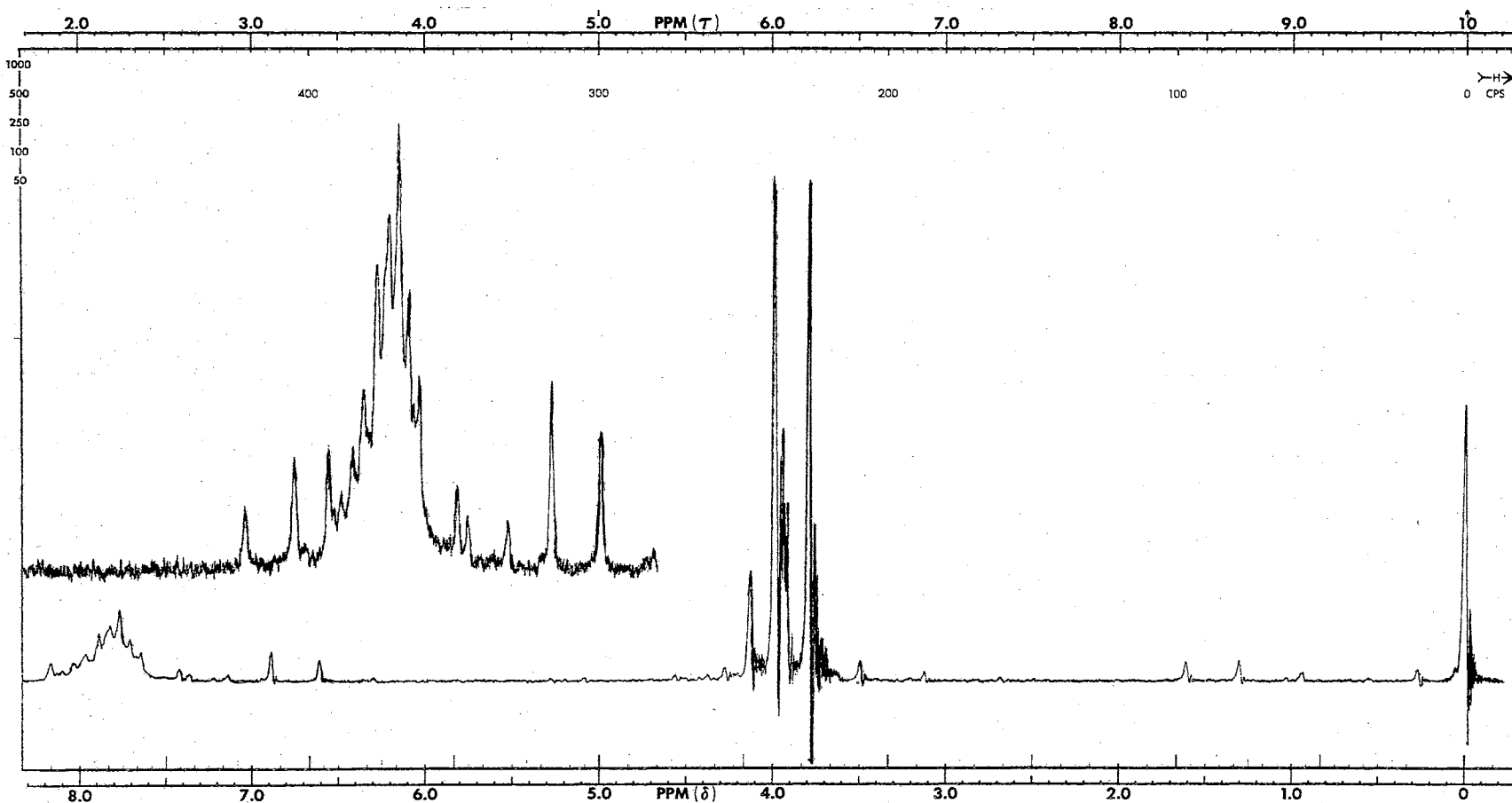
Plate XXII



Dimethyl trans-2-Phenylcyclopropanecarbonylphosphonate (Im)

Solvent CCl ₄	R.F. Field 0.05 mG	S.W. . . . 500 cps	S.A. . . . 6.3
F.B. 4.0 cps	S.T. 500 sec	S.O. . . . 000 cps	I.A. . . . off

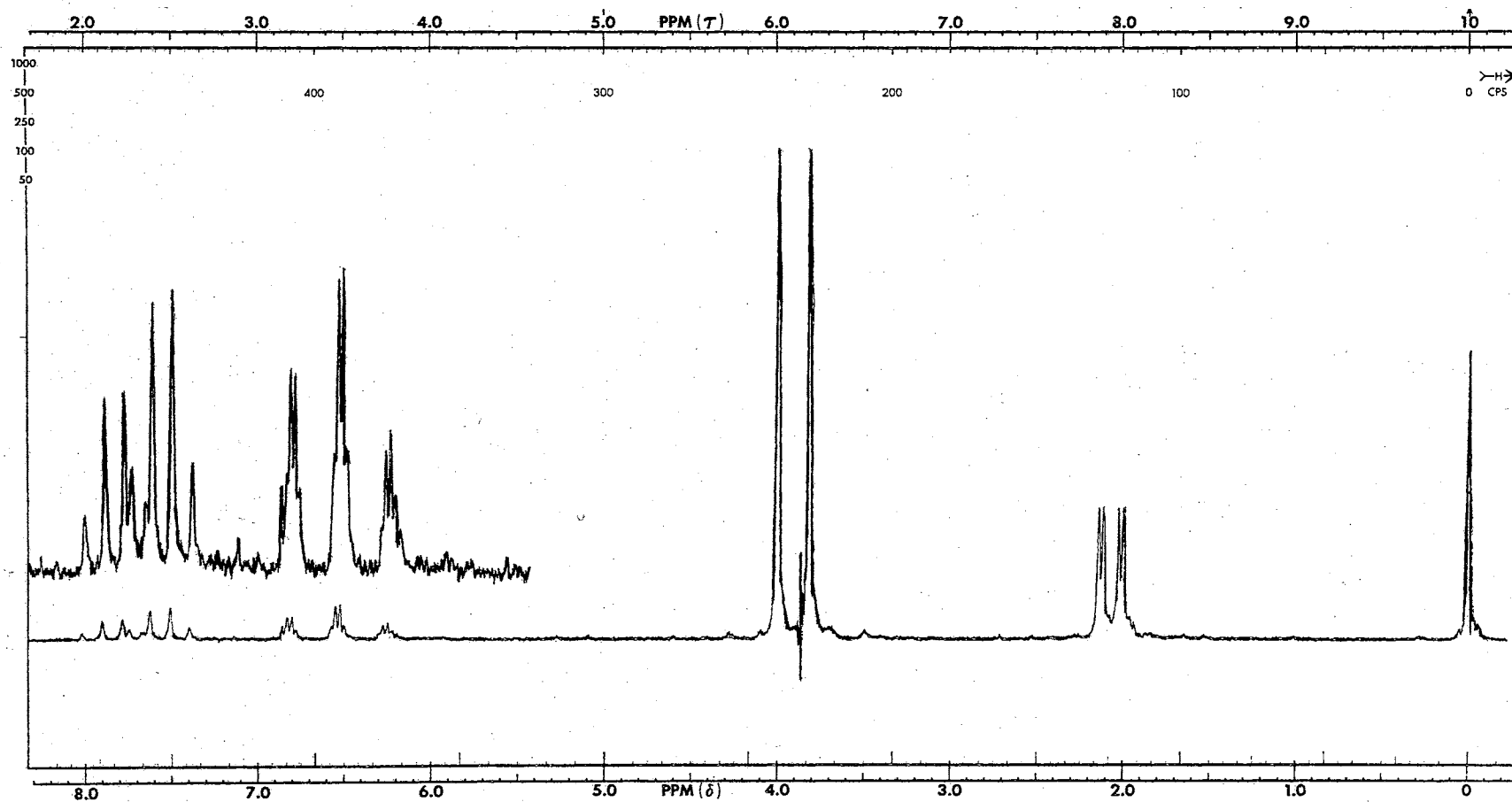
Plate XXIII



Dimethyl Cinnamoylphosphonate (In)

Solvent	CCl ₄	R.F. Field	0.05 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

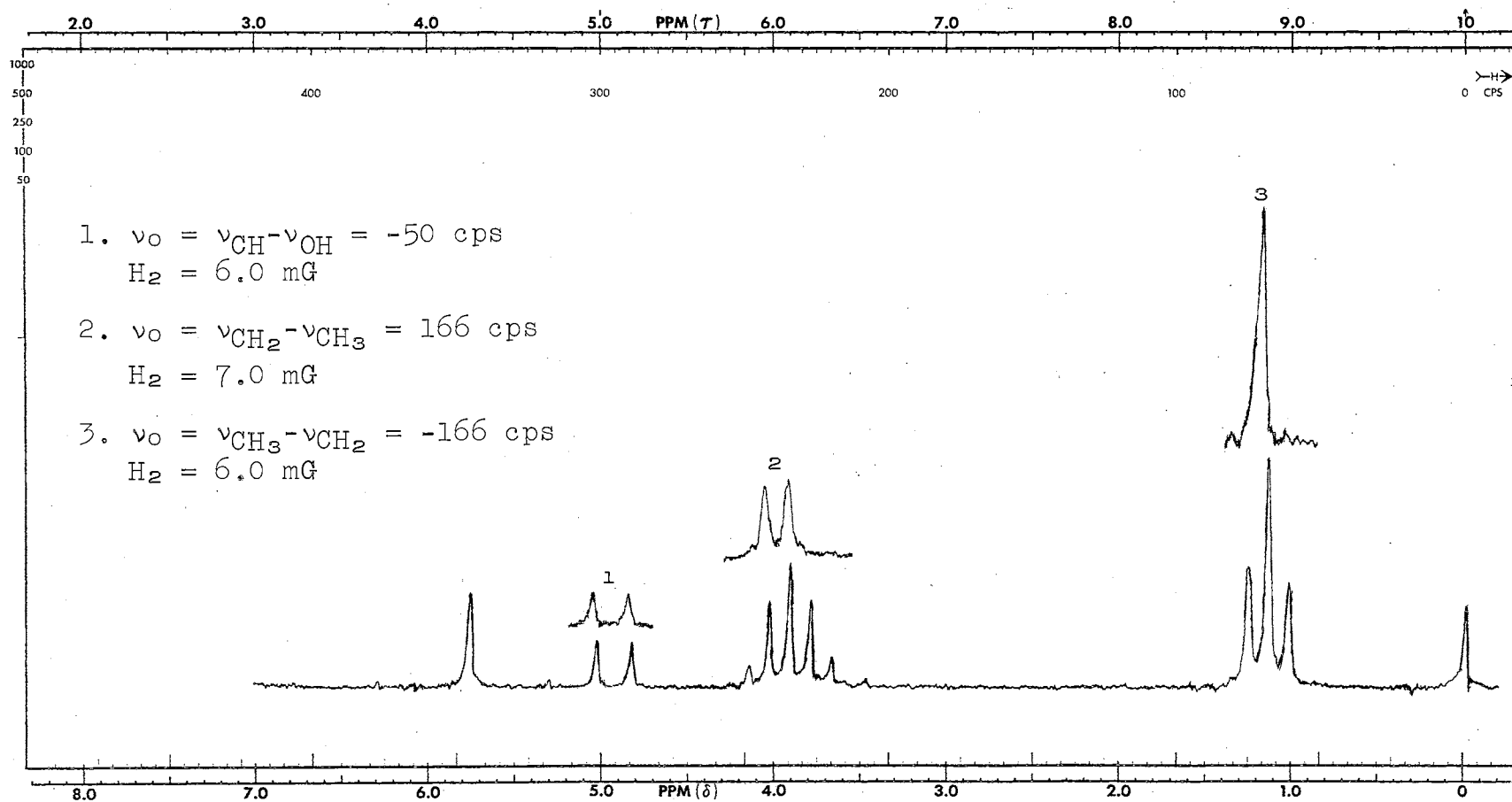
Plate XXIV



Dimethyl Crotonylphosphonate (Io)

Solvent	CCl ₄	R.F. Field	0.075 mG	S.W.	500 cps	S.A.	1.6
F.B.4.0 cps	S.T.	500 sec	S.O.	000 cps	I.A.	off

Plate XXV



Diethyl (α -Hydroxybenzyl)phosphonate (IV)

Solvent $CHCl_3$	R.F. Field 0.05 mG	S.W. 500 cps	S.A. . . . 3.2
F.B. 2.0 cps	S.T. 250 sec	S.O. 000 cps	I.A. . . . off

BIBLIOGRAPHY

1. Ackerman, B., Jordan, T. A., Eddy, C. R., and Swern, D., J. Am. Chem. Soc., 78, 4444 (1956).
2. Anderson, W. A., Freeman, R., and Reilly, C. A., J. Chem. Phys., 39, 1518 (1963).
3. Angstadt, H. P., J. Am. Chem. Soc., 86, 5040 (1964).
4. Arbuzov, A. E. and Azanovskaya, M. M., Dokl. Akad. Nauk SSSR, 58, 1961 (1947); Chem. Abstr., 42, 1886 (1948).
5. Arbuzov, A. E., and Azanovskaya, M. M., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 473 (1949); Chem. Abstr., 44, 1905 (1950).
6. Arbuzov, A. E. and Dunin, A. A., Ber., 60, 291 (1927).
7. Arbuzov, A. E. and Dunin, A. A., J. Russ. Phys. Chem. Soc., 46, 295 (1914); Chem. Abstr., 8, 2551 (1914).
8. Arbuzov, A. E., Zoroastrova, V. M., and Rizpolozhenskii, N. I., Bull. Akad. Sci. URSS, Classe Sci. Chim., 208 (1948); Chem. Abstr., 42, 4932 (1948).
9. Arbuzov, B. A. and Bogonostseva, N. P., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 484 (1953); Chem. Abstr., 48, 9905 (1954).
10. Axtmann, R. C., Shuler, W. E., and Eberly, J. H., J. Chem. Phys., 31, 850 (1959).
11. Bene, G. J., Duval, E., Finaz, A., Hochstrasser, G., and Koide, S., Phys. Letters, 1, 34 (1963).
12. Berlin, K. D., Austin, T. H., and Nagabhushanam, M., J. Org. Chem., 30, 1267 (1965).
13. Berlin, K. D. and Burpo, D. H., J. Org. Chem., in press.
14. Berlin, K. D., Hellwege, D. M., and Nagabhushanam, M., J. Org. Chem., 30, 1265 (1965).

15. Berlin, K. D. and Taylor, H. A., J. Am. Chem. Soc., 86, 3862 (1964).
16. Blackburn, G. M., Cohen, J. S., and Todd, A. R., Tetrahedron Letters, 2873 (1964).
17. Charrier, C., Simonnin, M. P., Chodkiewicz, W., and Cadiot, P., Compt. Rend., 258, 1537 (1964).
18. Cohen, J. S., Tetrahedron Letters, 3491 (1965).
19. Denney, D. B. and Gough, S. T. D., J. Am. Chem. Soc., 87, 138 (1965).
20. Denney, D. B. and Relles, H. M., Tetrahedron Letters, 573 (1964).
21. Dudek, G., J. Chem. Phys., 33, 624 (1960).
22. Epstein, M. and Buckler, S. A., J. Am. Chem. Soc., 83, 3279 (1961).
23. Finegold, H., J. Am. Chem. Soc., 82, 2641 (1960).
24. Fitch, S. J., J. Am. Chem. Soc., 86, 61 (1964).
25. Gawron, O., Grelecki, C., Reilly, W., and Sands, J., J. Am. Chem. Soc., 75, 3591 (1953).
26. Gordon, M., Ph.D. Thesis, University of Pittsburgh, 1965.
27. Hammond, P. R., J. Chem. Soc., 1370 (1962).
28. Hendrickson, J. B., Maddox, M. L., Sims, J. J., and Kaesz, H. D., Tetrahedron, 20, 449 (1964).
29. Kabachnik, M. I. and Rossiiskaya, P. A., Bull. Acad. Sci. URSS, Classe Sci. Chim., 163 (1947); Chem. Abstr., 42, 4132 (1948).
30. Kabachnik, M. I. and Rossiiskaya, P. A., Bull. Acad. Sci. URSS, Classe Sci. Chim., 364 (1945); Chem. Abstr., 40, 4688 (1946).
31. Kabachnik, M. I. and Rossiiskaya, P. A., Bull. Acad. Sci. URSS, Classe Sci. Chim., 597 (1945); Chem. Abstr., 41, 88 (1947).
32. Kabachnik, M. I. and Rossiiskaya, P. A., Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 48 (1957); Chem. Abstr., 51, 10366 (1957).

33. Kamai, G. and Kukhtin, V. A., Zh. Obshch. Khim., 27, 949 (1957); Chem. Abstr., 52, 3665 (1958).
34. Karplus, M. and Grant, D. M., Proc. Nat. Acad. Sci. US, 45, 1269 (1959).
35. Köhler, H. J., Z. Physik. Chem., 226, 283 (1946).
36. Mannatt, S. L., Juvinall, G. L., and Elleman, D. D., J. Am. Chem. Soc., 85, 2664 (1963).
37. Martin, G. and Mavel, G., Compt. Rend., 253, 644 (1961).
38. Martin, G. and Mavel, G., Compt. Rend., 253, 2523 (1961).
39. Martin, G. and Mavel, G., Compt. Rend., 255, 2095 (1962).
40. McConnell, R. L. and Coover, H. W., Jr., J. Am. Chem. Soc., 78, 4450 (1956).
41. Moss, R. D., U. S. Patent 3,012,054 (1961); Chem. Abstr., 57, 4698 (1962).
42. Muller, N. and Pritchard, D. E., J. Chem. Phys., 31, 786, 1471 (1959).
43. Narasimhan, P. T. and Rogers, M. T., J. Chem. Phys., 34, 1049 (1961).
44. Pudovik, A. N. and Platonova, R. N., Zh. Obshch. Khim., 29, 507 (1959); Chem. Abstr., 54, 254 (1960).
45. Quin, L. D., Peters, J. A., Griffin, C. E., and Gordon, M., Tetrahedron Letters, 3689 (1964).
46. Ramirez, F., Madan, O. P., and Smith, C. P., J. Am. Chem. Soc., 86, 5339 (1964).
47. Ramirez, F., Madan, O. P., and Smith, C. P., Tetrahedron Letters, 201 (1965).
48. Ramirez, F., Ramanathan, N., and Desai, N. B., J. Am. Chem. Soc., 85, 3465 (1963).
49. Reetz, T., Chadwick, D. H., Hardy, E. E., and Kaufman, S. J. Am. Chem. Soc., 77, 3813 (1955).
50. Saunders, B. C. and Simpson, P., J. Chem. Soc., 3351 (1963).
51. Schmutzler, R. and Reddy, G. S., Inorg. Chem., 4, 191 (1965).

52. Seyferth, D., Eistert, M. A., and Heeren, J. K., J. Organometal. Chem., 2, 101 (1964).
53. Seyferth, D., Welch, D. E., and Heeren, J. K., J. Am. Chem. Soc., 86, 1100 (1964).
54. Shriner, R. L., Fuson, R. C., and Curtin, D. Y., "The Systematic Identification of Organic Compounds," J. Wiley and Sons, New York, N. Y., 1956.
55. Shuler, W. E. and Axtmann, R. C., U. S. At. Energy Comm., 13 pp. (1960).
56. Siddall, T. H., III, and Prohaska, C. A., J. Am. Chem. Soc., 84, 2502 (1962).
57. Siddall, T. H., III, and Prohaska, C. A., J. Am. Chem. Soc., 84, 3467 (1962).
58. Stothers, J. B. and Robinson, J. R., Can. J. Chem., 42, 967 (1964).
59. Sturtz, G., Bull. Soc. Chim. France, 2333 (1964).
60. Taylor, H. A., Master's Thesis, Oklahoma State University, 1964.
61. Verkade, J. G., Huttemann, T. J., Fung, M. K., and King, R. W., Inorg. Chem., 4, 83 (1965).
62. Weitkamp, H. and Korte, F., Z. Anal. Chem., 204, 245 (1964).
63. Yamasaki, T., Sci. Rept. Res. Inst., Tohoku Univ., Ser. A, 11, 73 (1959).

VITA

Dale Michael Hellwege

Candidate for the Degree of

Doctor of Philosophy

Thesis: I. THE STEREOSPECIFICITY OF THE MICHAELIS-ARBUZOV
REARRANGEMENT IN 4-t-BUTYLCYCLOHEXYLDIPHENYL-
PHOSPHINITE

II. NMR ANALYSIS OF SUBSTITUTED PHOSPHONATES

Major Field: Organic Chemistry

Biographical:

Personal Data: The author was born in Enid, Oklahoma, on August 2, 1940, the son of Dale Myron and Elsie Hellwege. On May 30, 1964, he married Nancy Jane Roberts. He now has one son, Darren Michael, born January 12, 1966.

Education: The author graduated from Okmulgee High School, Okmulgee, Oklahoma, in 1958. In September, 1958, he entered Oklahoma State University, Stillwater, Oklahoma, where he received a Bachelor of Science Degree in Chemistry in August, 1962. In September, 1962, he was admitted to the Graduate School of Oklahoma State University, Stillwater, Oklahoma.

Professional Experience: The author was a graduate teaching assistant in the fall of 1962, the spring of 1965, and the fall of 1965. He also served as a graduate research assistant from September, 1962 to January, 1966.

Membership in Professional Societies: The author is a member of the American Chemical Society, Phi Lambda Upsilon, and Sigma Xi.