

THE SYNTHESIS AND PROPERTIES OF
DIALKYL AROYLPHOSPHONATES

By

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CHAPTER I

INTRODUCTION

Since 1914 it has been known that acid chlorides would react with trivalent phosphorus esters in the classical Michaelis-Arbuzov rearrangement. The synthesis of a series of disubstituted acylphosphonates seemed to be a logical extension of the previous preparations of aliphatic acylphosphonates. It was anticipated that the dipole moments of such compounds would provide insight into the ground-state structure of molecules containing the carbonyl-phosphoryl linkage. Nuclear magnetic resonance spectra have not previously been recorded for acylphosphonates, so that such spectra make a useful addition to the physical data previously compiled on phosphorus esters.

CHAPTER II

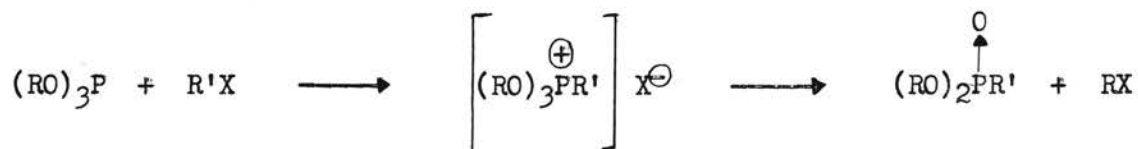
HISTORICAL

Since 1898, when the reaction of trialkyl phosphites with alkyl halides to yield phosphonates was discovered by Michaelis and Kahne (52), the Michaelis-Arbuzov rearrangement has been the most important synthetic means of producing a carbon-phosphorus bond. The general equation for this reaction is:



When R and R' are identical, the reaction assumes the character of a true isomerization, since only a catalytic amount of the alkyl halide is required (47).

The mechanism of the Michaelis-Arbuzov rearrangement has been shown to follow the route below. This sequence involves a slow $\text{S}_{\text{N}}2$ displacement of halogen by the electron pair on phosphorus, resulting in the formation of an intermediate quasiphosphonium salt. This process is



followed by a rapid decomposition of the salt to an alkyl halide and a phosphonate (28). The decomposition is spontaneous in the case of alkyl phosphites, but if R is aryl the intermediates are stable and must often be treated with heat or strong base in order to effect degradation (45, 52). In general, the reactivity of the esters decreases in the order phosphinite > phosphonite > phosphite in the Michaelis-Arbuzov reaction (48). With respect to the halides, the decreasing reactivity is iodide > bromide > chloride and primary > secondary (45).

The Michaelis-Arbuzov rearrangement with trialkyl phosphites has been well documented in the cases of simple alkyl halides (45), carbon tetrahalides (30, 40, 44), trityl bromide (68), dibromides (25), and various other compounds containing the carbon-halogen linkage. The problem has also been extended to bicyclic phosphites (70), tricyclic phosphites (16), phosphonites (26), and phosphinites (60).

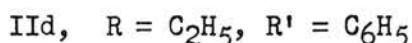
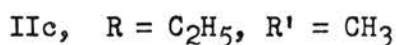
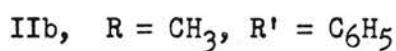
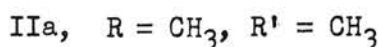
It was shown early that the expected reaction would occur between trialkyl phosphites and acid halides (4). In 1914, Arbuzov and Dunin examined the following reaction in their study of the action of trialkyl phosphites with derivatives of aliphatic esters. However, their other work was concerned with esters halogenated adjacent to the ester carbonyl. A later note in the literature (5) states that because of the death of Dunin that phase of their work was discontinued.



I

The formation of acylphosphonates (1-keto-phosphonates) was not investigated further until 1945, when Kabachnik and Rossiiskaya published a series of papers on the esters of α -keto-phosphonic acids (36, 37).

The reaction in question may be formulated as follows:

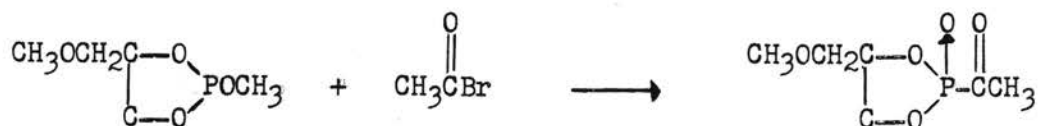


The products were pale yellow, high-boiling liquids in yields of about 65-75 per cent. Characterization was based on formation of *p*-nitrophenylhydrazones, identification of alkaline hydrolysis products, determination of saponification numbers, and reduction with Na/Hg to esters of α -hydroxybenzylphosphonic acid.

In their third paper concerned with the study of esters of α -keto phosphonic acids (38), Kabachnik and co-workers synthesized di-*n*-butyl acetylphosphonate and generally improved their yields by running the reactions below room temperature since the process was exothermic. Assuming that esters of this type should exhibit considerable reactivity of the carbonyl group, Kabachnik undertook the synthesis of some carbonyl derivatives, including phenylhydrazones, bisulfite addition products, and cyanohydrins. These were obtained easily and in yields above 85 per cent.

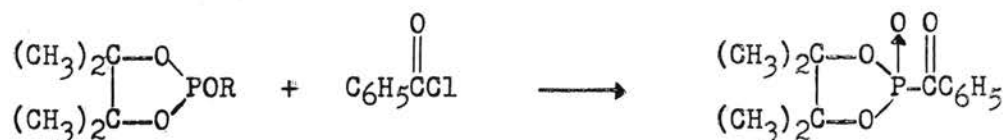
Concurrently with Kabachnik's work, Arbuzov and his co-workers investigated the synthesis and properties of some acylphosphonates. They

synthesized diethyl acetylphosphonate (IIc) in 62 per cent yield and prepared its 2,4-dinitrophenylhydrazone (2). Several cyclic esters of phosphorous acid were successfully obtained in the following manner (10).



III

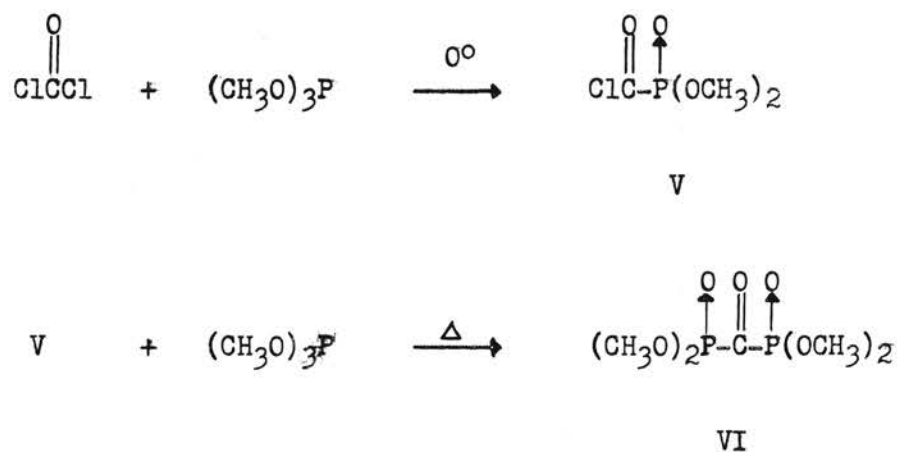
However, attempts to react the analogous ethyl ethoxypropylene phosphite with acetyl bromide yielded an acyclic compound which contained one bromine atom. Similarly ethyl methoxypropylene phosphite and ethyl chloroformate gave non-cyclic products. The following reaction sequence gave identical compounds with R = methyl, ethyl, and propyl (3).



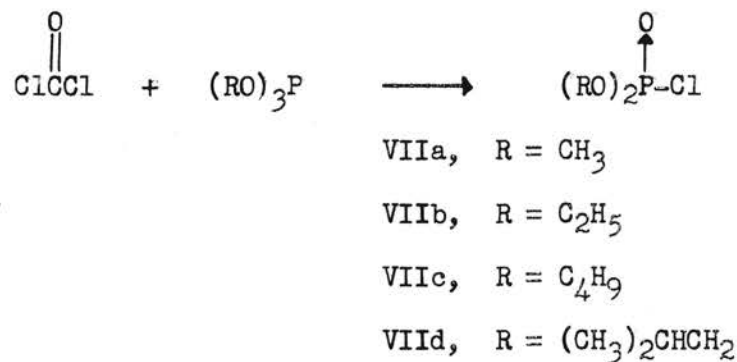
IV

IV was a crystalline product which gave a sharp-melting 2,4-dinitrophenylhydrazone derivative. Almost simultaneously Kamai (41) mentioned the attempted synthesis of diallyl benzoylphosphonate from triallyl phosphite and benzoyl chloride, but the reaction mixture exploded at 185° during attempted distillation, probably as a result of spontaneous polymerization.

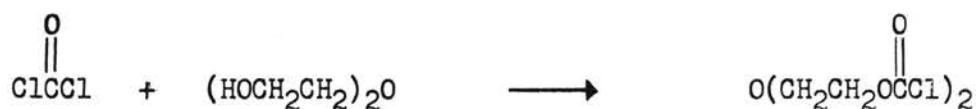
An obvious extension of this work with acid chlorides and trialkyl phosphites is the investigation of the reactivity of phosgene in such condensations. Kabachnik studied this area in 1957 (39) and obtained the following results:



Both the phosphonate (V) and diphosphonate (VI) were obtained in good yield and identified. However, in a similar experiment (58) performed by Pudovik and Platonova, the reaction of phosgene with trialkyl phosphites was described as follows:



The abstracts available on these contradictory publications reveal that the experiments were performed under nearly identical conditions, but no explanation was offered for the discrepancy. Pudovik obtained exactly the same products with oxalyl chloride. The only other work concerning the use of phosgene in phosphite reactions is found in a patent (32), and is shown by the equations below. Thiophosgene was used to make the sulfur analogs of these compounds.



VIII



IX



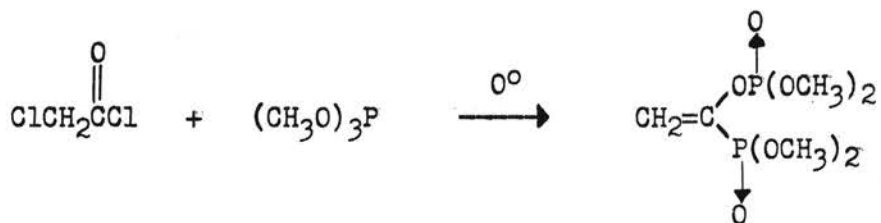
X



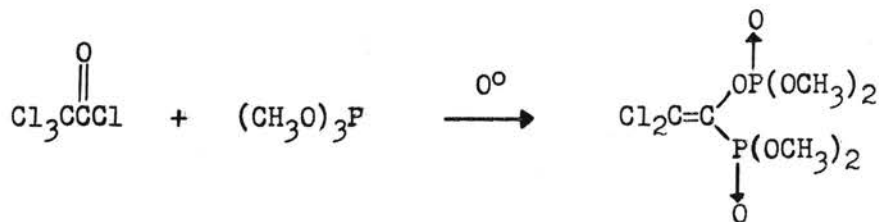
XI

In connection with his work with phosgene, Kabachnik (39) performed a series of experiments in which he studied the reaction of chloroacetyl

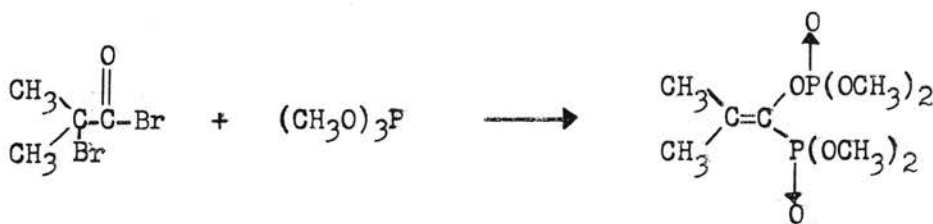
chloride and trichloroacetyl chloride with trimethyl phosphite and triethyl phosphite. Instead of the expected acylphosphonates, vinyl-substituted phosphates were isolated. Pudovik duplicated this work in 1957 (57) and extended it to include the following:



XII



XIII



XIV

These anomalous reactions correspond to those often observed in the condensations of trialkyl phosphites with alkyl halides having the halogen adjacent to a carbonyl group (56).

In 1956, Ackerman and co-workers (1) published a study of the preparation and properties of some diethyl acylphosphonates in connection with their interest in derivatives of fatty acids. The acylphosphonates were derived from the reactions of triethyl phosphite with the acid chlorides of the even-numbered fatty acids from C_4 - C_{18} and oleic acid. It was found that these compounds were unstable in the presence of moisture, the rate of hydrolysis decreasing with increasing acyl chain length and size of phosphorus groups. The fact that the acylphosphonates were so much more sensitive to moisture than were the corresponding alkylphosphonates led the authors to postulate formation of a mixed anhydride bond (a) rather than a carbon-phosphorus bond (b). However, molar refractions, infrared

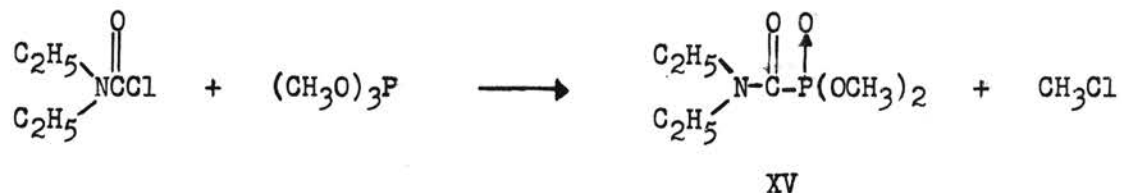


spectra, and polarographic studies indicated the presence of the acylphosphonate bond (b). This physical evidence thus supports the structure predicted by analogy with the corresponding alkylphosphonates and proven by Kabachnik (36, 37) on the basis of chemical reactions.

In 1961, Moss (53) obtained a patent on the preparation of tetraalkyl diphosphonates from the reactions of the acid chlorides of a series of long-chain aliphatic dibasic acids with trimethyl phosphite. Almost quantitative yields of product were realized.

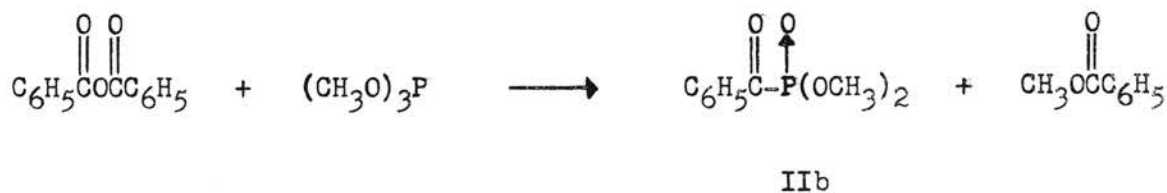
Although the carbamoylphosphonates are not true acylphosphonates, they do contain the carbonyl-phosphoryl linkage and thus should be mentioned. In 1952 Arbusov and Rizpolozhenskii published two papers in

which they described the synthesis of XV (7, 8). Analogous products were isolated in approximately 50 per cent yield from triethyl phosphite, tri-n-propyl phosphite, tri-2-propyl phosphite, tri-n-butyl phosphite, tri-isoamyl phosphite, and tricyclohexyl phosphite. Higher yields (about 70

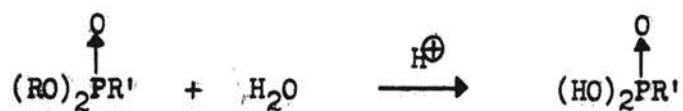


per cent) were obtained by using sodium dialkyl phosphite instead of trialkyl phosphite. Reetz and co-workers (61) fully explored the synthetic value of the above reaction sequence.

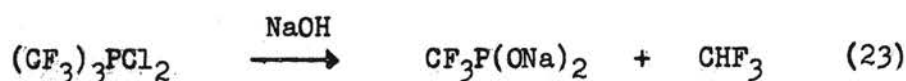
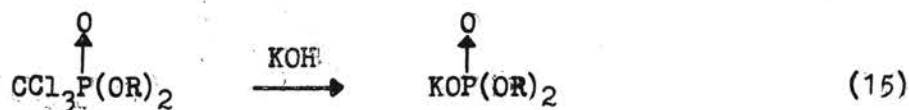
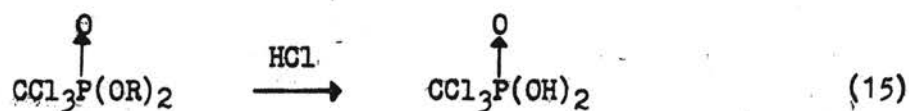
Another variation of the Arbuzov rearrangement which leads to the formation of acylphosphonates is the reaction of trialkyl phosphites with acid anhydrides (42, 46). The desired products have also been obtained using triethyl and tri-n-butyl phosphites with acetic and benzoic anhydrides (20). These compounds appear to have some value as insecticides.



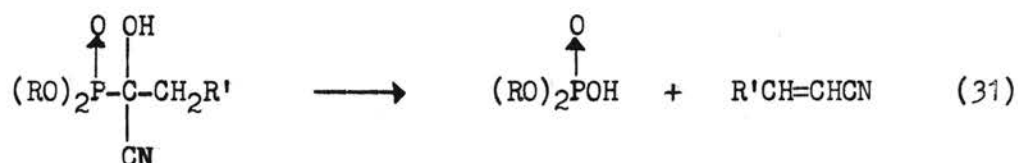
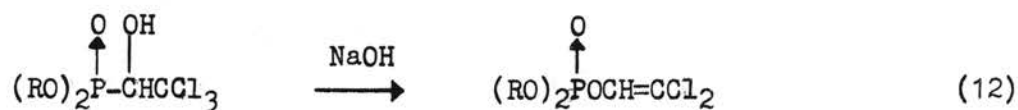
Investigations of the reactions of acylphosphonates have been largely restricted to alcoholysis and hydrolysis. Normally the carbon-phosphorus bond in phosphorus esters is very difficult to cleave as shown by the hydrolysis of normal phosphonates, which react as follows (21):



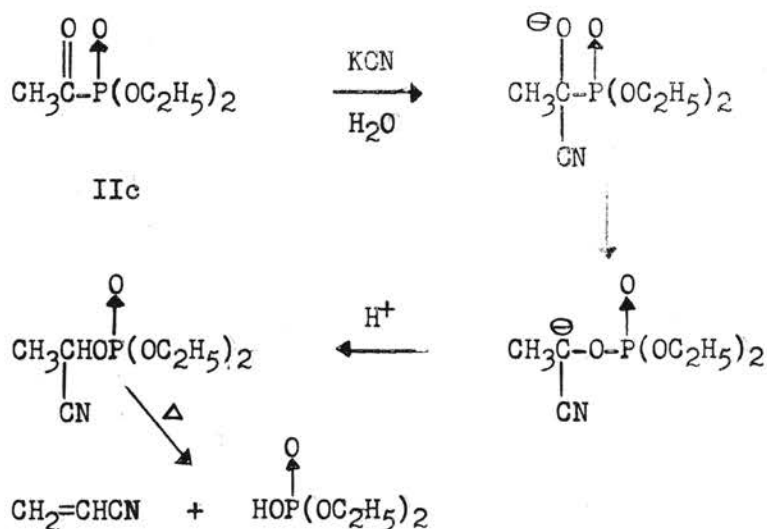
Prolonged heating under reflux with constant-boiling hydrochloric acid may be used for hydrolysis of esters of most phosphonic and phosphinic acids without risk of breaking the carbon-phosphorus bond, which is comparable in strength to the carbon-carbon bond (21). There are, however, certain instances in which a carbon-phosphorus bond may be broken in alkyl phosphorus esters. These situations usually occur under alkaline conditions and are assisted by electron-attracting substituents on the alkyl group. Trichloromethyl and trifluoromethyl groups are thus removed by base as follows:



Dialkyl 2-chloro-1-hydroxyalkylphosphonates and dialkyl 1-cyano-1-hydroxy-alkylphosphonates undergo rearrangements involving rupture of the carbon-phosphorus bonds. The latter of these two reactions was actually a result of an attempt to make a cyanohydrin of an acylphosphonate. Kabachnik

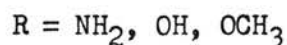
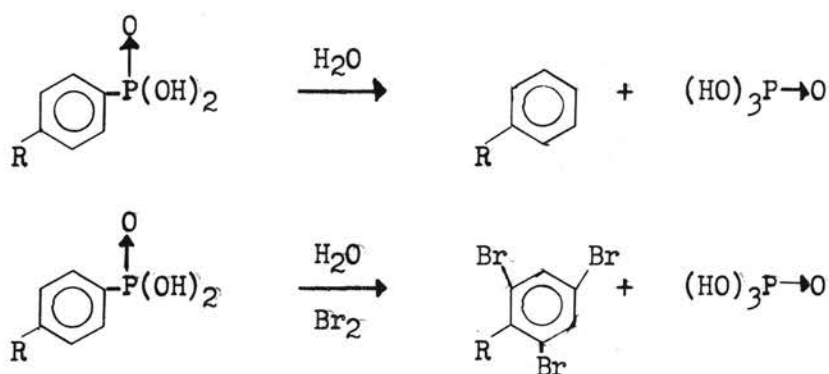


(38) had reported the synthesis of such cyanohydrins in 1947, but Hall and co-workers in 1957 determined that the following reaction sequence was operative (31). It was suggested that the method was of synthetic

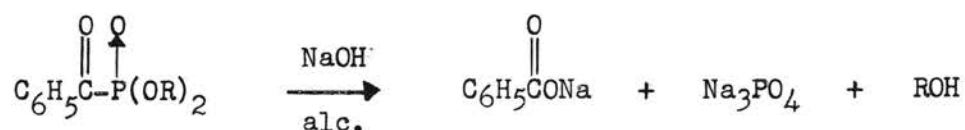


value for the preparation of unsaturated nitriles, provided a β -hydrogen atom was present.

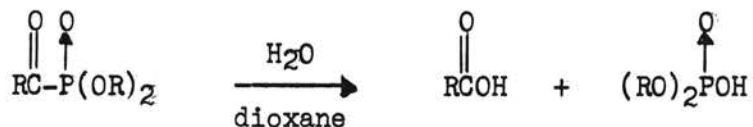
Another situation in which the carbon-phosphorus bond is rendered unstable exists in arylphosphonic acids in which the ortho or para positions are substituted with strong electron-donating groups, such as the amino, methoxy, or hydroxy groups (13). Bell and Kosolapoff investigated such reactions in 1953.



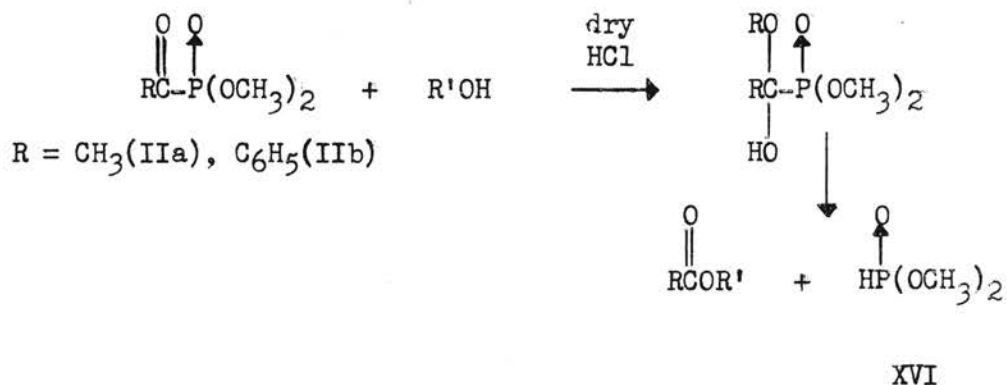
The most common instances in which the carbon-phosphorus bond is cleaved are in the alcoholysis and hydrolysis of acylphosphonates. Evidently the α -carbonyl group so weakens the linkage that it is even more susceptible to cleavage than the ester groups. Normally the following process occurs in such hydrolysis reactions (36):



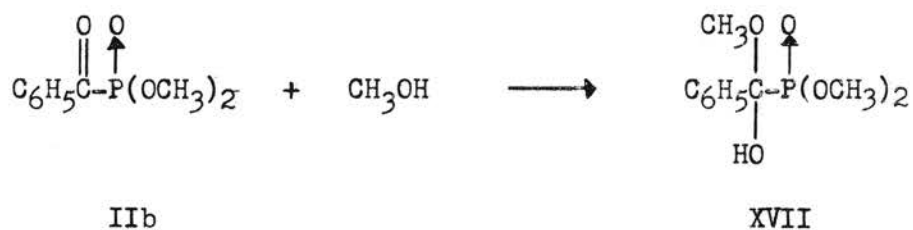
However, partial hydrolysis of the phosphorus ester has also been recorded (1) as follows:



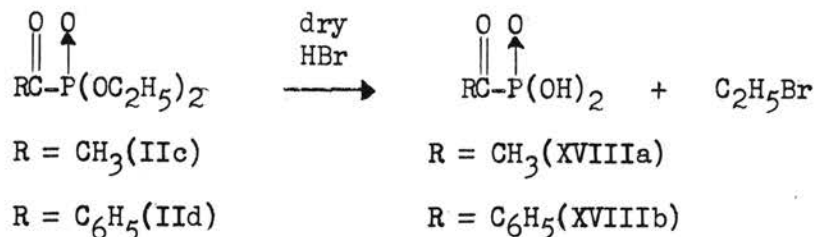
The fact that severance of the carbon-phosphorus bond in the acylphosphonates need not be preceded by hydrolysis of the ester groups and formation of the free phosphonic acid was shown by Kabachnik in his study of the acid-catalyzed degradation of these compounds (37). In experiments using methanol, ethanol, and propanol with dimethyl acetylphosphonate (IIa) and dimethyl benzoylphosphonate (IIb) the following mechanism was thought to be operative:



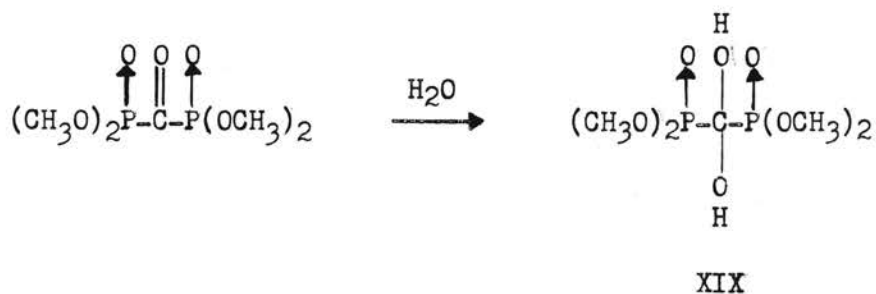
In the absence of dry hydrogen chloride, addition compounds formed.



A few other reactions of acylphosphonates have been reported. It was shown by Cooke (19) that in the presence of dry hydrogen bromide the following may occur:



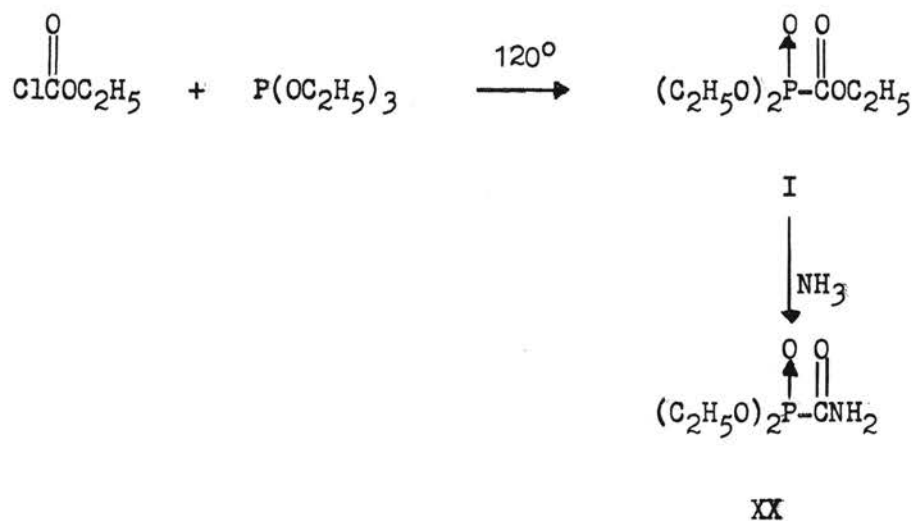
The yields were in the order of 95 per cent, but it took six times as long to achieve the reaction with the benzoylphosphonate (IIId) as with the acetylphosphonate (IIc). Kabachnik (39) reported a quantitative return of product in the following reaction:



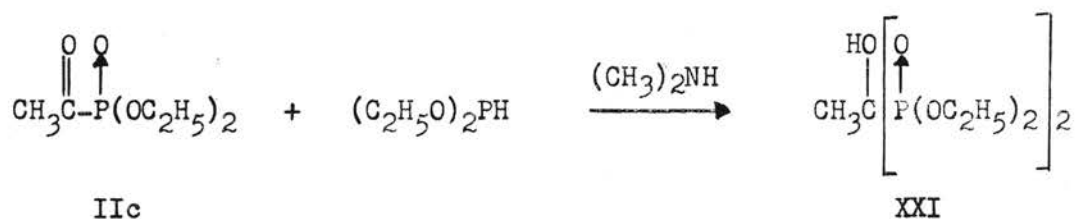
Glycols of this type are inherently unstable and are rarely isolated.

It was mentioned earlier that Reetz and co-workers synthesized carbamoylphosphonates by the treatment of disubstituted carbamoyl chlorides with trialkyl phosphites (61). An alternative route to these compounds was suggested by Nylen (55), in which chloroformates were reacted with trialkyl phosphites, and the resulting products were treated with ammonia,

primary amines, or secondary amines. This is, of course, not a general reaction of acylphosphonates since the carboxylic linkage must be present in order for the amidation to occur.



Another unusual reaction of acylphosphonates was reported by McConnell and Coover (51) in their study of the preparation of 1-hydroxy-alkylidene-diphosphonates. Diethyl isobutyrylphosphonate and IIc were found



to react equally well with diethyl hydrogen phosphite although the carbonyl group might be expected to be sterically hindered by the isopropyl and diethylphosphono groups which bracket it.

All published work concerning the infrared spectra of acylphosphonates is in good agreement with the structures assigned. The phosphoryl band at about 1250 cm.^{-1} and the P-O-C (alkyl) broad band at about 1030 cm.^{-1} have been observed by Ackerman (1) in aliphatic acylphosphonates, by Ketelaar (43) in diethyl benzoylphosphonate (IIId), and by Reetz in carbamoylphosphonates (61). These peak positions agree with those which would be predicted based upon Bellamy's standard reference in the field (14) and with values of corresponding peaks found in other organophosphorus compounds.

Although information concerning phosphorus-31 nuclear magnetic resonance is plentiful, relatively few investigations have been performed on the proton magnetic resonance of the esters of phosphorus acids. In 1959 Axtmann published a paper on the study of phosphates (11) in which it was observed that the phosphorus-31 atom is capable of splitting the proton responses of compounds containing the P-O-CH linkage. Dudek verified this work in a study on cyclic phosphates (22). Prohaska and Siddall (66, 67) observed such splitting plus an additional splitting in various esters of arylphosphoric, arylphosphonic, arylphosphinic and phenylphosphonous acids. This second effect they attributed to the existence of preferred rotational isomers caused by the diamagnetic anisotropy of the benzene ring present. Nuclear magnetic resonance data dealing specifically with acylphosphonates has not been reported previous to our work.

Dipole measurement studies on phosphorus esters are extremely rare. In 1957 it was shown by Raman spectra that bis(dialkylphosphinothioyl) compounds were symmetrical, having the two adjacent thiophosphoryl groups opposed (18). A logical extension of this work would be to verify or

disprove such a structure by dipole moment measurements. Various carbamoylphosphonates have been shown to have an average moment value of 2.96 Debye, a value close to the value of 3.33 Debye calculated for free rotation of the carbamoyl group (9). This approximates also the average value of 2.90 Debye found for a series of alkylphosphonates (6). Recently in this laboratory Hildebrand (34) employed dipole moment measurements to elucidate the stereochemistry of the reaction of a tricyclic phosphite with a series of alkyl halides.

CHAPTER III

DISCUSSION OF RESULTS AND CONCLUSIONS

The Michaelis-Arbuzov reaction has been widely investigated with phosphites, phosphonites, and phosphinites and a great number of alkyl halides. However, the studies of acyl halides in such reactions have been primarily restricted to a few reactions of the acid halides of long-chain mono- and dibasic aliphatic acids, benzoyl chloride, phosgene, chloroformates, and carbamoyl halides. In view of the limited work done in the area, attempted synthesis of disubstituted aroylphosphonates was undertaken via reactions of aroyl chlorides and phosphites.

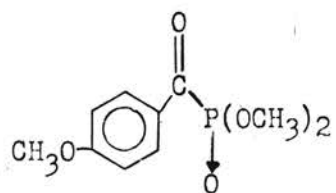
In nearly all cases the condensations were exothermic but could be controlled by the rate of addition of phosphite. The general preparative procedure consisted of the dropwise addition of phosphite to aroyl chloride in a three-neck, round-bottom flask fitted with reflux condenser, addition funnel, nitrogen inlet, calcium chloride drying tube, liquid immersion thermometer, and magnetic stirring bar. As the phosphite was added the reaction mixtures became yellow in color and began to evolve methyl chloride in the case of trimethyl phosphite or ethyl chloride in the case of triethyl phosphite. With the phosphites of higher molecular weight the alkyl halide generated remained in the reaction mixture and



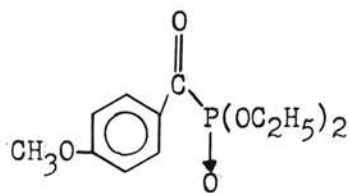
had to be distilled. Reactions utilizing trialkyl phosphites proceeded at room temperature, but triphenyl phosphite exerted no noticeable effect until the mixture had been heated for two hours at 115°. This would be expected in view of the extreme stability of the quasiphosponium intermediates from the reactions of aryl-substituted phosphorus esters with alkyl halides (45). Once the intermediate did begin to decompose, however, the reaction mixture turned yellow and began to reflux at the boiling point of chlorobenzene.

In most cases the disubstituted aroylphosphonates were distilled to facilitate purification, but the diallyl ester was not purified in this manner because an explosion was reported in the attempted distillation of diallyl benzoylphosphonate (41). Repeated attempts to distill the di-2-propyl aroylphosphonate resulted in the sublimation of benzoic acid, although all reactions had been performed in a nitrogen atmosphere. This compound was therefore prepared from equimolar amounts of tri-2-propyl phosphite and *p*-anisoyl chloride and was analyzed for phosphorus in a crude form after removal of the isopropyl chloride. The analysis agreed well with the calculated phosphorus content, and the infrared spectrum (Plate V) and proton magnetic resonance spectrum (Plate XV) showed very little evidence of impurity. Thus it may be inferred that the reaction proceeded almost quantitatively. The 2,4-dinitrophenylhydrazones (correct analyses and infrared spectra) of the diallyl and di-2-propyl esters were used as further proof of the structures of the phosphonates.

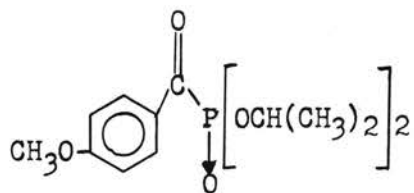
Compounds successfully prepared from *p*-anisoyl chloride included dimethyl *p*-anisoylphosphonate (XXII), diethyl *p*-anisoylphosphonate (XXIII), di-2-propyl *p*-anisoylphosphonate (XXIV), di-*n*-butyl *p*-anisoylphosphonate (XXV), diallyl *p*-anisoylphosphonate (XXVI), and diphenyl *p*-anisoylphos-



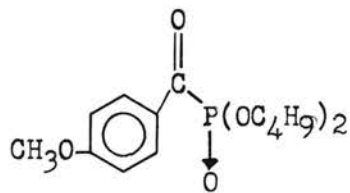
XXII



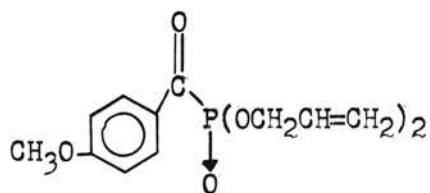
XXIII



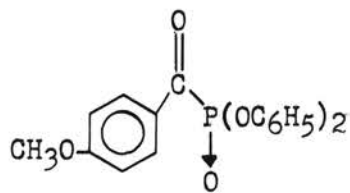
XXIV



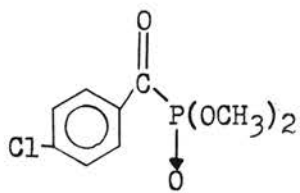
XXV



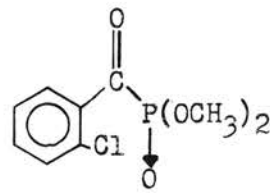
XXVI



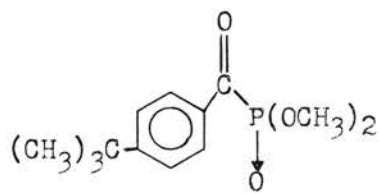
XXVII



XXVIII



XXIX

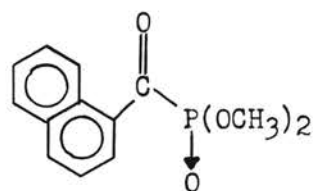


XXX

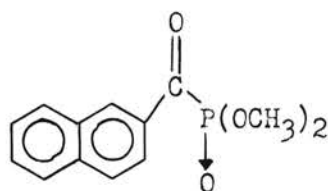
phosphate (XXVII). In addition, dimethyl (p-chlorobenzoyl)phosphate (XXVIII), dimethyl (o-chlorobenzoyl)phosphate (XXIX), and dimethyl (p-tert-butylbenzoyl)phosphate (XXX) were synthesized to extend the scope of the study. Thus the phosphate ester groups have been varied in the p-anisoylphosphates and ester groups have been held constant in compounds with varying substitution, both of substituent and position, on the benzoyl fragment.

In general, the phosphates easily formed highly-colored 2,4-dinitrophenylhydrazones which were characterized by elemental analysis and infrared spectra (Table I). The procedure used for preparing these derivatives consisted of the addition of 0.5 g. of the parent disubstituted arylphosphate to 25 ml. of a stock solution of 2,4-dinitrophenylhydrazine in sulfuric acid-methanol. Recrystallization from methanol or methanol-ethyl acetate produced samples which were analyzed for nitrogen and phosphorus. The formation of the 2,4-dinitrophenylhydrazones of diallyl p-anisoylphosphate (XXVI) and di-2-propyl p-anisoylphosphate (XXIV) provided a means of identification of XXVI and XXIV since they were not purified by distillation. Diphenyl p-anisoylphosphate (XXVII) did not react with 2,4-dinitrophenylhydrazine, probably because of the hindrance presented by the two ester phenyl groups present.

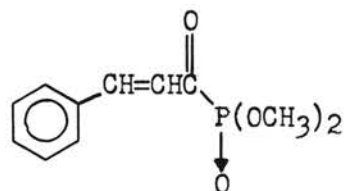
The ease of formation of the 2,4-dinitrophenylhydrazones in most cases suggests regeneration of the carbonyl compounds from phenylhydrazones as a possible method of purification. Attempts to synthesize dimethyl 1-naphthoylphosphate (XXXI), dimethyl 2-naphthoylphosphate (XXXII), dimethyl cinnamoylphosphate (XXXIII), and dimethyl (p-methylcinnamoyl)phosphate (XXXIV) indicated that some method other than vacuum distillation would be valuable in the purification of higher molecular



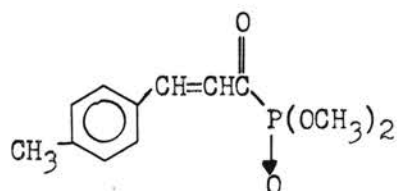
XXXI



XXXII



XXXIII



XXXIV

weight dialkyl aroylphosphonates. The preparative method previously described was used in the attempted syntheses of these compounds, except that in the cases of XXXII, XXXIII, and XXXIV ether was used as a solvent for the solid aroyl chlorides. The reactions appeared to proceed satisfactorily with the appearance of a yellow color and the evolution of methyl chloride, but unsatisfactory elemental analyses imply that regular distillation techniques are unsatisfactory for the purification step. Infrared spectra agreed well with the expected structures containing the carbonyl, phosphoryl, and P-O-C (alkyl) functional groups.

Physical studies of acylphosphonates have been limited to infrared and ultraviolet data, polarographic studies, molar refraction measurements (1), and a small amount of dipole moment work on carbamoylphosphonates (9). The only publication concerning the physical properties of aroylphosphonates describes the infrared spectrum (43) of diethyl benzoylphosphonate (IIId). The extent of conjugation of the carbonyl group

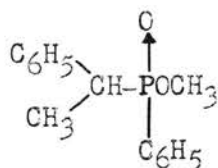
with the phosphoryl group apparently is significant, since the carbonyl absorbance appears at 1650 cm.^{-1} in dimethyl benzoylphosphonate (IIb) (Plate I) and at 1689 cm.^{-1} in acetophenone. This conjugative effect was one of Ackerman's (1) arguments in support of the carbonyl-phosphoryl bond rather than a mixed anhydride bond in acylphosphonates. The phosphoryl absorbance of about 1260 cm.^{-1} and the P-O-C (alkyl) absorbance of about 1025 cm.^{-1} observed in the dialkyl aroylphosphonate infrared spectra approximates the values quoted by Bellamy (14) for these functional groups.

Ultraviolet absorption spectra should prove interesting in the aroylphosphonate series. A preliminary spectrum taken of dimethyl benzoylphosphonate (IIb) in carbon tetrachloride showed strong absorbance in the region from 270 to 320 μ . Acetophenone absorbs from 240 to 280 μ in a water solution and benzil at 370 μ . A comprehensive study of this problem is planned in this laboratory.

It is in the proton magnetic resonance spectra of these compounds that several interesting facts appear. On the whole, the spectra are very simple, but in every case involving a dimethyl ester, a doublet is seen in the region of 4.0 delta. This indicates that in some way the single peak which would be expected to occur for the hydrogens of the two equivalent methoxy groups has been split. The most reasonable explanation for this was first given by Axtmann in 1959 in a study of the proton magnetic resonance spectra of a series of trialkyl phosphates (11). It was shown at that time that $P^{31}\text{-H}^1$ splitting occurs in the P-O-C (alkyl) group, and the coupling constant of 11 c.p.s. for trimethyl phosphate corresponds to that observed in our dimethyl aroylphosphonates. Likewise, Axtmann's values of $J = 8.4$ c.p.s. for triethyl phosphate and

$J = 6.6$ c.p.s. for tri-2-propyl phosphate approximate the values of 7 c.p.s. and 8 c.p.s. measured for diethyl *p*-anisoylphosphonate (XXIII) (Plate XIV) and di-2-propyl *p*-anisoylphosphonate (XXIV) (Plate XV), respectively. These values have been verified by Finegold in a comparison study with P^{31} spectra (24), by Dudek with acyclic and cyclic phosphates (22), and by Prohaska and Siddall (66) in work on the proton magnetic resonance spectra of many phenyl-substituted phosphorus esters. Examination of the trimethyl phosphite spectrum indicates that such splitting also occurs in trivalent phosphorus esters.

Prohaska and Siddall observed that, in addition to the P^{31} - H^1 splitting, a second doubling of peaks could occur in the spectra of various esters of arylphosphorus acids (66, 67). This they attributed to the magnetic anisotropy of the benzene ring, placing the seemingly equivalent ester protons in the compounds in different electronic environments. In the compound methyl 1-phenylethyl-phenylphosphinate (XXXV), for instance, the methoxy hydrogens appear as a quartet. One splitting is due to the influence of the phosphorus atom, and one splitting is due to the

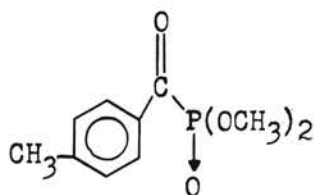


XXXV

fact that alternately either one or two protons are in the vicinity of the aromatic ring. The same resonance doubling was observed in some benzylphosphonates, leading to the expectation that in disubstituted benzoylphosphonates this might also be the case. No evidence was found of

splitting other than that attributable to phosphorus in our dimethyl esters. In addition, resonance splitting of γ -methyl protons, observed by Prohaska and Siddall (66, 67) in their diethyl esters, did not occur. However, the doublet attributable to γ -methyl protons in the spectrum of di-2-propyl *p*-anisoylphosphonate (XXIV) (Plate XV) did appear to be split again. Perhaps this is due to resonance splitting. If this is true, then the benzene ring in the aroylphosphonate series is so located as to exert an influence in cases where the ester groups are larger than ethyl. A study of the nuclear magnetic resonance spectra of aroylphosphonates containing fused rings would be valuable. The spectra of highly purified dimethyl 1-naphthoylphosphonate (XXXI) and dimethyl 2-naphthoylphosphonate (XXXII) might exhibit resonance splitting. A series of cyclohexanoylphosphonates prepared by Nagabhushanam (54) did not show such splitting, but there is some doubt as to whether the cyclohexane ring, even if attached directly to phosphorus, possesses a field sufficient to cause it.

Another interesting problem presented itself when the proton magnetic resonance spectra of the para-disubstituted aroylphosphonates were examined. Richards and Schaefer (63) have shown in a study of the spectra of a series of para-disubstituted benzene derivatives that chemical shifts vary widely with changes in substituents. However, the coupling constants remain within the range of 8.1 - 9.2 c.p.s. in these A_2B_2 systems. Their value of $J = 8.9$ c.p.s. for *p*-2-propylbenzaldehyde is comparable to our value of 9 c.p.s. for the *p*-anisoylphosphonates (Plates XIII-XVI, XX) and for dimethyl (*p*-chlorobenzoyl)phosphonate (XXVIII) (Plate XVIII) and dimethyl (*p*-tert-butylbenzoyl)phosphonate (XXX) (Plate XVII). Hellwege (33) observed $J = 8$ c.p.s. for the aromatic protons in dimethyl *p*-toloylphosphonate (XXXVI).

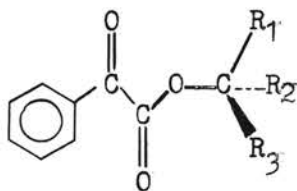


XXXVI

The distances between the two sets of aromatic peaks in the dialkyl aroylphosphonates is also worthy of note. This has been called the field separation and has been found to be fairly constant in the p-anisoylphosphonate series, varying from 75 to 78 c.p.s. An exceptionally low value is found in the case of diphenyl p-anisoylphosphonate (XXVII) (Plate XX), which has a field separation of 60 c.p.s. Considerably lower values occur in the compounds with chlorine (44 c.p.s.) (Plate XVIII), methyl (51 c.p.s.) (33), and tert-butyl (40 c.p.s.) (Plate XVII) groups in the para position. There are no other published values for phosphonates upon which to base a comparison, but Varian Associates (17) offers values of 27 c.p.s. for p-chloroacetophenone, 15 c.p.s. for p-chlorobenzaldehyde, 49 c.p.s. for p-methoxybenzaldehyde, and 66 c.p.s. for p-methoxybenzoic acid. The field separation values shown by Varian for p-methoxyaniline (3 c.p.s.), p-methoxytoluene (15 c.p.s.), and p-ethoxyaniline (4 c.p.s.) imply that para-disubstituted compounds with both substituents electron-donating have low field separations. Carbonyl compounds with a para-chloro substituent fall into a middle range of 15 c.p.s. to 44 c.p.s. The disubstituted aroylphosphonates and other carbonyl compounds substituted with electron-donating groups, published by Varian (17), appear to have very high field separation values, ranging from 49 c.p.s. to 78 c.p.s. A study of the spectra of para-disubstituted

compounds with two strong electron-withdrawing groups would be helpful in substantiating such a relationship. A *p*-nitro arylphosphonate is a logical choice. It is interesting to note that (*p*-trifluoromethyl)-aniline has a field separation of 14 c.p.s. (17), a low value if the above generalization is valid, but steric factors may also play a part in this case.

The first question which comes to mind when one looks at the disubstituted arylphosphonates is that of the possibility of a preferred structure in the ground state. It is only logical to assume that the two areas of highest electron density in any molecule would assume positions as far apart as possible. There are two similar cases in which this is known to be true. Certain α -diketones, those which are involved in Cram's rule of asymmetric synthesis for example, have the following opposed carbonyl structure (29):



XXXVII

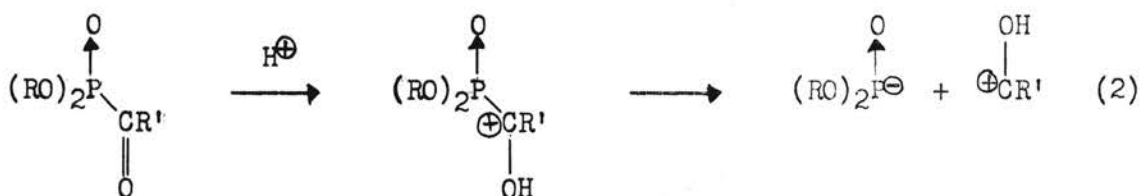
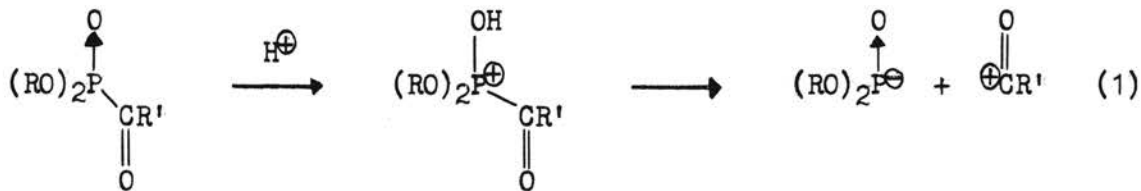
Certainly the analogy between XXXVII and the arylphosphonates is obvious. In addition, compounds which are in the bis(dialkylphosphinothioyl) series have been shown by Raman spectra to exist with the phosphorothioyl groups opposed. The dipole moments measured at $25^\circ \pm 0.1$ in carbon tetrachloride for dimethyl benzoylphosphonate (IIb) (2.93 ± 0.05 D.), dimethyl *p*-anisoylphosphonate (XXII) (3.20 ± 0.05 D.), and dimethyl (*p*-chlorobenzoyl)phosphonate (XXVIII) (2.64 ± 0.05 D.) indicate that in

these compounds there is no such preferred opposed carbonyl-phosphoryl structure. These values come very close to those of 2.96 D. (average) measured by Arbuzov (9) for a series of carbamoylphosphonates and 2.96 D. (average) for a series of dialkyl alkylphosphonates (6).

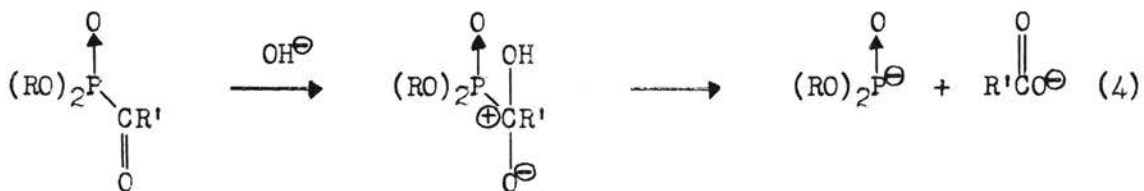
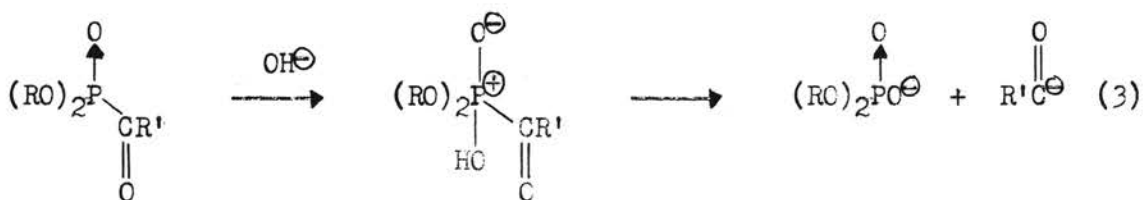
The dipole moments of benzaldehyde, *p*-anisaldehyde, and *p*-chlorobenzaldehyde have been reported as 2.75, 3.70, and 2.03 D., respectively (71). It is not surprising that the benzaldehyde and *p*-chlorobenzaldehyde values are lower than those of the corresponding aroylphosphonates, the added increment being due to the phosphonate portions of the molecule. However, the fact that the moment of dimethyl *p*-anisoylphosphonate (XXII) is lower than that of *p*-anisaldehyde leads to the speculation that in the phosphonate the methoxy group is sufficiently electron-donating to significantly increase the electronegativity on the carbonyl oxygen. This could prolong the lifetime of the opposed carbonyl-phosphoryl configuration and lower the dipole moment. The moment of dimethyl (*p*-nitrobenzoyl)phosphonate would be helpful in disproving or substantiating this theory.

The comparison of acid- and base-catalyzed hydrolysis of dimethyl *p*-anisoylphosphonate (XXII) shows the basic catalysis to proceed infinitely faster than the acid counterpart. One would infer this from literature references on such hydrolysis reactions (21, 36, 37), but no actual comparison has been published. In the acid hydrolysis of any compound containing a carbonyl-phosphoryl bond there are two possibilities for mechanistic speculation, one involving initial attack of the proton at the phosphoryl oxygen (Equation 1) and the other involving initial attack of the proton at the carbonyl oxygen (Equation 2). The fact that a carboxylic acid is obtained as a product strongly indicates that Equ-

tion 1 is operative. In order for cleavage to occur as shown in Equation 2, a carbene would be generated, for which no experimental evidence

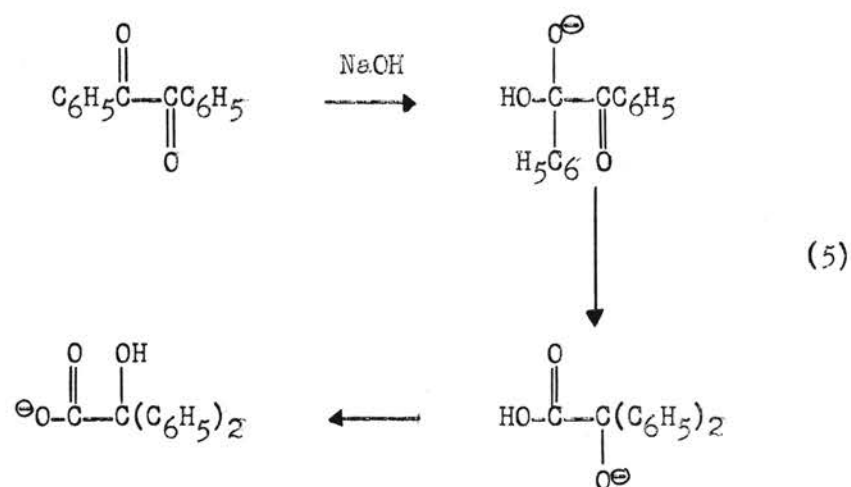


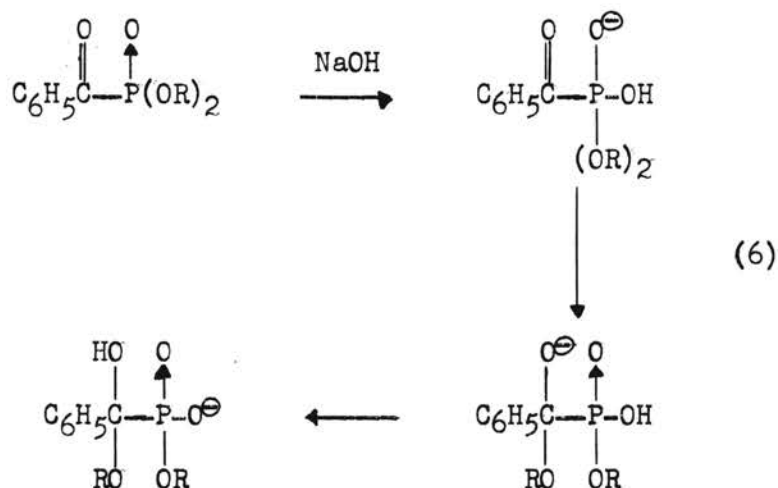
was found. In basic catalysis there are also two possibilities of mechanism. Equation 3 is logical if the phosphoryl atom is attacked by the hydroxyl group. Equation 4 illustrates a mechanism involving attack of the hydroxyl at the carbon. This would seem to be the more likely mechanism, and it would produce the isolated benzoic acid. Rigorous proof



of mechanism would require identification of the phosphorus compound formed in an inert atmosphere since any dialkyl hydrogen phosphonate formed might oxidize to the phosphoric acid diester in the presence of oxygen. Kabachnik (36) used identification of the alkaline hydrolysis products of diethyl benzoylphosphonate (IIId) as his proof of structure, but he took his reaction to the final hydrolysis products of benzoic acid and sodium phosphate.

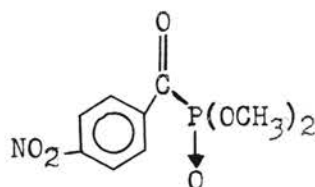
It is well known (29) that certain aromatic α -diketones, benzil being the most common example, will undergo the benzilic acid rearrangement in strong base (Equation 5). The conditions are those of very concentrated base and continuous heating. It is conceivable that a similar reaction might occur upon heating of a dialkyl aroylphosphonate in strong base (Equation 6). However, the extreme sensitivity of the carbonyl-phosphoryl bond to base makes the rearrangement seem highly unlikely.





The attempted reductions of dimethyl benzoylphosphonate (IIb) apparently failed because of the extreme sensitivity of the carbonyl-phosphoryl linkage to cleavage, particularly in base. Low temperature catalytic hydrogenation is an obvious experiment which should be attempted. Immediate identification of the desired dimethyl benzylphosphonate should be possible by comparison of the proton magnetic resonance and infrared spectra with those obtained by Hildebrand (34).

Attempts to prepare dimethyl *p*-nitrobenzoylphosphonate (XXXVIII) failed repeatedly and present quite an interesting problem. Apparently the nitro substituent interferes with the normal Michaelis-Arbuzov reaction of

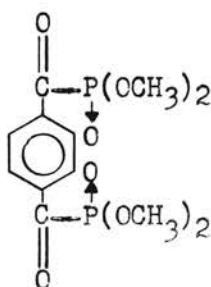


XXXVIII

p-nitrobenzoyl chloride with trimethyl phosphite. A colorful reaction occurs in ether as the addition of the phosphite provokes a darkening

of the yellow color of the acid chloride solution to deep red and a subsequent fading to pale yellow. Simultaneously there is formation of a red precipitate which disappears and is followed by the appearance of a yellow precipitate, which emerges as the final product. No 2,4-dinitrophenylhydrazone could be made from the crude reaction mixture or from the recrystallized solid product, and the infrared spectrum of the solid does not correspond to that of the other phosphonates studied. Elemental analysis showed no phosphorus present.

The attempted synthesis of tetramethyl terephthaloyldiphosphonate (XXXIX) was undertaken in the hope of initiating a study of chelation of phosphoryl compounds. The reaction apparently proceeded as expected although with more difficulty than was anticipated. Heating the reaction



XXXIX

mixture was required to facilitate reaction. Impurity of the terephthaloyl chloride used probably prevented successful completion of the experiment, but further work in this area is planned.

In summary, a series of dialkyl aroylphosphonates and their 2,4-dinitrophenylhydrazones have been synthesized and characterized. Proton magnetic resonance spectra of the aroylphosphonates have been examined and analyzed with respect to field separation values and $P^{31}-H^1$ splitting

in the phosphorus ester groups. The dipole moments of dimethyl benzoylphosphonate (IIb), dimethyl *p*-anisoylphosphonate (XXII), and dimethyl (*p*-chlorobenzoyl)phosphonate (XXVIII) indicate that an opposed carbonylphosphoryl structure does not exist for any substantial length of time.

CHAPTER IV

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

Preparation of p-Anisoyl Chloride. A one-neck, 250 ml., round-bottom flask fitted with a reflux condenser, calcium chloride drying tube, and magnetic stirring bar was charged with 76.0 g. (0.50 mole) of p-anisic acid (m. p. 184°) and 238.0 g. (2.0 mole) of thionyl chloride (b. p. 79°/741 mm.). The mixture was stirred for two days at room temperature during which time evolution of hydrogen chloride and sulfur dioxide was observed. After excess thionyl chloride was distilled, the homogeneous reaction mixture was fractionated to yield a colorless product boiling at 255-60°/741 mm., 79.0 g. (92.6 per cent, lit. b. p. 106-7°/4 mm.) (72). The freshly distilled product was kept in a desiccator over anhydrous calcium chloride to prevent hydrolysis which was found to occur within five minutes exposure to the atmosphere.

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

²The infrared spectra were determined on a Beckman IR-5 with sodium chloride cells.

³The microanalyses were performed by Mid West Laboratories, Indianapolis, Indiana.

⁴The proton magnetic resonance spectra were determined by Mr. D. Mike Hellwege, Oklahoma State University, with a Varian Model A-60 high-resolution spectrometer fitted with a field-sensing stabilizer ("Super Stabilizer"). The solvent is indicated on the spectra. Tetramethylsilane was used as an internal standard.

⁵Dipole moment measurements were determined by Dr. John G. Verkade, Iowa State University, Department of Chemistry.

Preparation of Cinnamoyl Chloride. A one-neck, 100 ml., round-bottom flask fitted with a reflux condenser, calcium chloride drying tube, and magnetic stirring bar was charged with 53.5 g. (0.45 mole) of thionyl chloride and 22.2 g. (0.15 mole) of cinnamic acid (m. p. 133°). The mixture was stirred for eighteen hours at room temperature. After excess thionyl chloride was azeotroped with benzene at reduced pressure, the dark residual liquid was vacuum distilled to yield 22.4 g. (89.6 per cent) of a light yellow product, b. p. 75-7°/ 0.2 mm. (lit. b. p. 150-5°/ 20 mm.) (64). Steam was passed through the condenser jacket to prevent solidification. The liquid crystallized upon standing, m. p. 35°. The product was stored in a desiccator over anhydrous calcium chloride to prevent hydrolysis.

Preparation of p-Methylcinnamoyl Chloride. A one-neck, 100 ml., round-bottom flask fitted with reflux condenser, calcium chloride drying tube, and magnetic stirring bar was charged with 8.11 g. (0.05 mole) of p-methylcinnamic acid (m. p. 199-201°) and 17.85 g. (0.15 mole) of thionyl chloride. The mixture was stirred at room temperature until a homogeneous solution resulted. The previously described workup procedure was followed to yield 6.3 g. (70.0 per cent) of a white crystalline product, m. p. 71-2°. Although this compound is surely not new, the acid being commercially available, no literature reference was found concerning its physical properties. An elemental analysis was performed.

Anal. Calcd. for C₁₀H₉ClO:

C, 66.49; H, 5.02; Cl, 19.63

Found: C, 66.78; H, 5.12; Cl, 19.58.

Infrared analysis of this compound in Nujol (Plate I) shows bands characteristic of acid chloride carbonyl (1742 cm.^{-1}) (65), para-disubstituted benzene (807 cm.^{-1}) (65), trans-disubstituted olefin (974 cm.^{-1}) (14), and aryl-conjugated olefin (1603 cm.^{-1}) (14). Peaks attributable to the Nujol are located at 2924 , 1447 , and 1379 cm.^{-1} .

Preparation of 1-Naphthoyl Chloride. A one-neck, 100 ml., round-bottom flask fitted with a reflux condenser, calcium chloride drying tube, and magnetic stirring bar was charged with 17.22 g. (0.10 mole) of 1-naphthoic acid (m. p. $161-3^{\circ}$) and 47.6 g. (0.40 mole) of thionyl chloride. The mixture was stirred for ten hours and the same workup procedure was followed to yield 14.9 g. (78.0 per cent) of a yellow liquid, b. p. $125-8^{\circ}/3\text{ mm.}$ (lit. b. p. $167^{\circ}/10\text{ mm.}$) (49). The product was stored in a desiccator over anhydrous calcium chloride.

Preparation of 2-Naphthoyl Chloride. A one-neck, 100 ml., round-bottom flask fitted with reflux condenser, calcium chloride drying tube, and magnetic stirring bar was charged with 8.61 g. (0.05 mole) of 2-naphthoic acid (m. p. 184°) and 23.8 g. (0.20 mole) of thionyl chloride. The mixture was stirred at room temperature for five hours and after the workup yielded a white solid, 9.5 g. (100 per cent), m. p. $45-6^{\circ}$ (lit. m. p. 52°) (62).

Preparation of Dimethyl Benzoylphosphonate (IIb). This procedure, and that used in preparing the subsequent acylphosphonates, is a modification of that used by Kabachnik (36). A three-neck, 200 ml., round-bottom flask fitted with reflux condenser, calcium chloride drying tube, addition funnel, nitrogen inlet, liquid immersion thermometer, and magnetic stirring bar was charged with 5.65 g. (0.03 mole) of benzoyl chloride (b.

p. 198°/ 760 mm.). Trimethyl phosphite, 4.96 g., 0.04 mole (b. p. 107°/ 741 mm.), was added dropwise, with stirring under a nitrogen stream, to produce an exothermic reaction with the evolution of methyl chloride. The temperature of the yellow mixture was maintained between 25-30° by adjustment of the rate of addition. When the evolution of methyl chloride had ceased, the mixture was stirred at room temperature for four hours. Vacuum distillation of the product yielded 2.5 g. (30.0 per cent) of material boiling at 146-50°/ 4 mm. (lit. b. p. 141°/ 2.5 mm.) (36).

The infrared spectrum of IIb (Plate II) exhibits bands characteristic of conjugated carbonyl (1650 cm^{-1}), phosphoryl (1258 cm^{-1}) (1), the P-O-C (alkyl) linkage (1034 cm^{-1}) (1), and monosubstituted benzene (688 cm^{-1}) (14). Other prominent peaks are present at 1598, 1450, 1231, 1181, 1000, 837, and 781 cm^{-1} .

The nuclear magnetic resonance spectrum (Plate XII) shows a doublet centered at 3.82 delta (methoxy hydrogens) with $J = 11$ c.p.s., a multiplet centered at 7.47 delta (aromatic hydrogens), and a multiplet centered at 8.17 delta (aromatic hydrogens).

Preparation of Dimethyl Benzoylphosphonate (2,4-Dinitrophenyl)-hydrazone. A stock solution of 2,4-dinitrophenylhydrazine was made by dissolving 6 g. of the reagent (m. p. 198-9°) in 30 ml. concentrated sulfuric acid and adding this to 40 ml. of water and 140 ml. of 95% ethanol. Preparation of the derivative was by the method of Shriner and Fuson (65). To 25 ml. of the above solution was added 0.5 g. of dimethyl benzoylphosphonate (IIb). Immediately a heavy yellow precipitate formed which, after recrystallization from methanol, had a m. p. of 192-3°. The infrared spectrum of this compound is described in Table I.

Anal. Calcd. for $C_{15}H_{15}N_4O_7P$:

N, 14.21; P, 7.86.

Found: N, 14.05; P, 7.58.

Preparation of Dimethyl p-Anisoylphosphonate (XXII). The procedure for the preparation of this phosphonate was essentially the same as previously described. The reagents used were 5.12 g. (0.03 mole) of p-anisoyl chloride (b. p. 255-60°/ 741 mm.), and trimethyl phosphite, 4.96 g. (0.04 mole). Vacuum distillation of the product yielded 4.5 g. (61.6 per cent) yellow liquid, b. p. 165-74°// 2.5 mm. An analytical sample boiled at 170°/ 2.5 mm.

Anal. Calcd. for $C_{10}H_{13}O_5P$:

C, 49.19; H, 5.37; P, 12.68.

Found: C, 48.92; H, 5.56; P, 12.55.

The infrared spectrum for XXII (Plate III) exhibits bands characteristic of conjugated carbonyl (1648 cm.^{-1}), the phosphoryl linkage (1269 cm.^{-1}), the P-O-C (alkyl) linkage (1033 cm.^{-1}), and para-disubstituted benzene (805 cm.^{-1}). Prominent peaks are also present at 1725, 1600, 1530, 1475, 1430, 1320, 1176, 1122, 848, 763, and 736 cm.^{-1} .

The nuclear magnetic resonance spectrum (Plate XIII) shows a doublet centered at 3.80 delta (phosphorus ester methoxy hydrogens) with $J = 11\text{ c.p.s.}$, a singlet at 3.80 delta (aromatic ether methoxy hydrogens), and doublets centered at 6.90 delta (aromatic hydrogens meta to carbonyl group) and 8.13 delta (aromatic hydrogens ortho to carbonyl group) with

$J_{AB} = 9$ c.p.s., $J_{AA} = 1$ c.p.s., $J_{BB} = 0$, and a field separation of 75 c.p.s.

Preparation of Dimethyl p-Anisoylphosphonate (2,4-Dinitrophenyl)-hydrazone. To 25 ml. of the 2,4-dinitrophenylhydrazine stock solution was added 0.5 g. of dimethyl p-anisoylphosphonate (XXII). An orange precipitate formed, m. p. 203-4° after recrystallization from methanol-ethyl acetate. The characteristic peaks of the infrared spectrum of this compound are shown in Table I.

Anal. Calcd. for $C_{16}H_{17}N_4O_8P$:

N, 13.20; P, 7.30.

Found: N, 12.75; P, 6.92.

Preparation of Diethyl p-Anisoylphosphonate (XXIII). The procedure for the preparation of this phosphonate is as previously described. The reagents used were 5.12 g. (0.03 mole) of p-anisoyl chloride (b. p. 255-60°/ 741 mm.) and triethyl phosphite (b. p. 150-3°/ 741 mm.), 6.64 g. (0.04 mole). Vacuum distillation of the product yielded 6.5 g. (79.6 per cent) of yellow liquid, b. p. 150-62°/0.4 mm. A sample with b. p. 158-9°/0.4 mm. was analyzed.

Anal. Calcd. for $C_{12}H_{17}O_5P$:

C, 52.94; H, 6.29; P, 11.38.

Found: C, 52.89; H, 6.27; P, 11.56.

The infrared spectrum for XXIII (Plate IV) exhibits bands characteristic of conjugated carbonyl (1650 cm.^{-1}), phosphoryl (1264 cm.^{-1}),

the P-O-C (alkyl) linkage (1025 cm.^{-1}), and para-disubstituted benzene (801 cm.^{-1}). Other prominent peaks appear at 1595, 1505, 1430, 1318, 1176, 976, 918, 843, 755, and 733 cm.^{-1} .

The nuclear magnetic resonance spectrum (Plate XIV) of XXIII shows a triplet centered at 1.34 delta (methyl hydrogens) with $J = 7\text{ c.p.s.}$, a singlet at 3.87 delta (methoxy hydrogens), a quartet centered at 4.16 delta (methylene hydrogens) with $J = 7\text{ c.p.s.}$, and doublets centered at 6.98 delta (aromatic hydrogens meta to carbonyl) and 8.27 delta (aromatic hydrogens ortho to carbonyl) with $J_{AB} = 9\text{ c.p.s.}$, $J_{AA} = 1\text{ c.p.s.}$, $J_{BB} = 0$, and a field separation of 73 c.p.s.

Preparation of Diethyl p-Anisoylphosphonate (2,4-Dinitrophenyl)-hydrazone. To 25 ml. of the 2,4-dinitrophenylhydrazine stock solution was added 0.5 g. of diethyl p-anisoylphosphonate (XXIII). A red precipitate formed, m. p. $177-8^{\circ}$ from methanol. The infrared spectrum of this compound is described in Table I.

Anal. Calcd. for $C_{18}H_{21}N_4O_8P$:

C, 47.79; H, 4.68; N, 12.39; P, 6.85.

Found: C, 47.59; H, 4.74; N, 12.13; P, 6.75.

Preparation of Di-2-propyl p-Anisoylphosphonate (XXIV). The previously described apparatus was charged with 2.45 g. (0.0144 mole) of p-anisoyl chloride. Tri-2-propyl phosphite, 3.00 g. (b. p. $63-4^{\circ}/11\text{ mm.}$), was added dropwise. The 2-propyl chloride liberated was removed by flash evaporator and a sample of the crude residual yellow liquid was sent for analysis. Previous attempts to distill the product had led to the sublimation of a white solid which proved to be p-anisic acid (m. p. 184°).

Anal. Calcd. for $C_{14}H_{21}O_5P$:

P, 10.32.

Found: P, 10.38.

The infrared spectrum (Plate V) of the crude compound shows maxima characteristic of conjugated carbonyl (1644 cm.^{-1}), phosphoryl (1257 cm.^{-1}), the P-O-C (alkyl) linkage (998 cm.^{-1}), and para-disubstituted benzene (800 cm.^{-1}). Other peaks appear at 1594, 1515, 1388, 1176, 1108, 939, 884, and 843 cm.^{-1} .

The nuclear magnetic resonance spectrum (Plate XV) shows a doublet centered at 1.27 delta (methyl hydrogens) with $J = 6\text{ c.p.s.}$, a singlet at 3.83 delta (methoxy hydrogens), a heptet centered at 4.65 delta (tertiary hydrogen) with $J = 8\text{ c.p.s.}$, and doublets centered at 6.90 delta (aromatic hydrogens meta to carbonyl) and 8.20 delta (aromatic hydrogens ortho to carbonyl) with $J_{AB} = 8\text{ c.p.s.}$, $J_{AA} = 1\text{ c.p.s.}$, $J_{BB} = 0$, and a field separation of 78 c.p.s.

Preparation of Di-2-propyl p-Anisoylphosphonate (2,4-Dinitrophenyl)-hydrazone. To 25 ml. of the stock solution of 2,4-dinitrophenylhydrazine was added 0.5 g. of crude di-2-propyl p-anisoylphosphonate (XXIV). A red precipitate formed which was recrystallized from methanol to give a product with m. p. $144-6^\circ$. The infrared spectrum of this compound is described in Table I.

Anal. Calcd. for $C_{20}H_{25}N_4O_8P$:

N, 11.66; P, 6.45.

Found: N, 11.61; P, 6.20.

Preparation of Di-n-butyl p-Anisoylphosphonate (XXV). The reactants used were 5.12 g. (0.03 mole) of p-anisoyl chloride and 7.50 g. (0.03 mole) of tri-n-butyl phosphite (b. p. 118-20°/ 7 mm.). Vacuum distillation of the reaction mixture yielded 4.3 g. (43.9 per cent) of a yellow liquid, b. p. 170-8°/ 2 mm. An analytical sample distilled at 175°/ 2 mm.

Anal. Calcd. for C₁₆H₂₅O₅P:

C, 58.53; H, 7.68; P, 9.43.

Found: C, 58.40; H, 7.61; P, 9.16.

The infrared spectrum for XXV (Plate VI) exhibits bands characteristic of conjugated carbonyl (1709 cm.⁻¹), phosphoryl (1263 cm.⁻¹), the P-O-C (alkyl) linkage (1030 cm.⁻¹), and para-disubstituted benzene (802 cm.⁻¹). Other maxima appeared at 1639, 1594, 1510, 1486, 1316, 1175, and 843 cm.⁻¹.

The nuclear magnetic resonance spectrum (Plate XVI) shows a triplet centered at 0.9 delta (methyl hydrogens) with J = 7 c.p.s., a multiplet ranging from 1.12 to 1.90 delta (methylene hydrogens), a singlet at 3.82 delta (methoxy hydrogens), a quartet centered at 4.13 delta (hydrogens on carbon adjacent to phosphorus ester oxygen) with J = 9 c.p.s., and doublets centered at 6.93 delta (aromatic hydrogens meta to carbonyl) and 8.22 delta (aromatic hydrogens ortho to carbonyl) with J_{AB} = 9 c.p.s., J_{AA} = 1 c.p.s., J_{BB} = 0, and a field separation of 77 c.p.s.

Preparation of Di-n-butyl p-Anisoylphosphonate (2,4-Dinitrophenyl)-hydrazone. To 25 ml. of the stock solution of 2,4-dinitrophenylhydrazine

was added 0.5 g. of di-n-butyl p-anisoylphosphonate (XXV). An orange precipitate formed which was recrystallized from methanol, yielding a product with m. p. 127-9°. The infrared spectrum of this compound is described in Table I.

Anal. Calcd. for $C_{22}H_{29}N_4O_8P$:

N, 11.02; P, 6.09.

Found: N, 11.26; P, 5.85.

Attempted Preparation of Diallyl p-Anisoylphosphonate (XXVI). The previously described apparatus was charged with 5.12 g. (0.03 mole) of p-anisoyl chloride, to which was added dropwise 8.08 g. (0.04 mole) of triallyl phosphite (b.p. 84°/ 12 mm.). During the addition of the phosphite heat was generated which resulted in refluxing of the mixture at 45° (b.p. of allyl chloride), indicating that the expected reaction did occur. No attempt was made to vacuum distill the product since Kamai (41) had reported that diallyl benzoylphosphonate had exploded during attempted distillation.

Preparation of Diallyl p-Anisoylphosphonate (2,4-Dinitrophenyl)-hydrazone. To 25 ml. of 2,4-dinitrophenylhydrazine stock solution was added 0.5 g. of the crude diallyl p-anisoylphosphonate (XXVI). A dark red precipitate formed with m. p. 123-5° after recrystallization from methanol. The infrared spectrum of this compound is described in Table I.

Anal. Calcd. for $C_{20}H_{20}N_4O_8P$:

N, 11.76; P, 6.50.

Found: N, 11.65; P, 6.57.

Preparation of Dimethyl (p-tert-Butylbenzoyl)phosphonate (XXX).⁶

The apparatus previously described was charged with 9.85 g. (0.05 mole) of p-tert-butylbenzoyl chloride (b. p. 84-6°/ 0.8 mm.). Trimethyl phosphite, 7.45 g. (0.06 mole), was added dropwise. Vacuum distillation of the reaction mixture yielded 6.0 g. (44.4 per cent) of a yellow liquid, b. p. 171-3°/ 1.2 mm.

Anal. Calcd. for $C_{13}H_{19}O_4P$:

C, 57.77; H, 7.09; P, 11.46.

Found: C, 57.24; H, 7.00; P, 10.72.

The infrared spectrum (Plate VII) of the product exhibits maxima characteristic of conjugated carbonyl (1639 cm.^{-1}), phosphoryl (1266 cm.^{-1}), the P-O-C (alkyl) linkage (1031 cm.^{-1}), and para-disubstituted benzene (775 cm.^{-1}). Other prominent peaks appear at 1597, 1462, 1190, 847, and 724 cm.^{-1} .

The nuclear magnetic resonance spectrum (Plate XVII) of XXX shows a singlet at 1.33 delta (methyl hydrogens), a doublet centered at 3.84 delta (methoxy hydrogens) with $J = 11\text{ c.p.s.}$, and doublets centered at 7.48 delta (aromatic hydrogens meta to carbonyl) and 8.15 delta (aromatic hydrogens ortho to carbonyl) with $J_{AB} = 9\text{ c.p.s.}$, $J_{AA} = 1\text{ c.p.s.}$, $J_{BB} = 0$, and a field separation of 40 c.p.s.

⁶The author gratefully acknowledges that compound XXX was prepared by Mr. Jesse Moore.

Preparation of Dimethyl (p-tert-Butylbenzoyl)phosphonate (2,4-Dinitrophenyl)hydrazone. To 25 ml. of the stock solution of 2,4-dinitrophenylhydrazine was added 0.5 g. of dimethyl (p-tert-butylbenzoyl)phosphonate (XXX). An orange precipitate formed which, after recrystallization from methanol, had a m. p. of 155-6°. The infrared spectrum of this compound is described in Table I.

Anal. Calcd. for $C_{19}H_{23}N_4O_7P$:

N, 12.44; P, 6.88.

Found: N, 12.65; P, 6.65.

Preparation of Dimethyl (p-Chlorobenzoyl)phosphonate (XXVIII). The reagents used were 5.25 g. (0.03 mole) of p-chlorobenzoyl chloride (b. p. 200°/ 760 mm.) and trimethyl phosphite, 4.96 g. (0.04 mole). Vacuum distillation of the product yielded 4.3 g. (57.3 per cent) of yellow liquid with b. p. 130-8°/ 1.5 mm. An analytical sample distilled at 136°/ 1.5 mm.

Anal. Calcd. for $C_9H_{10}ClO_4P$:

C, 43.48; H, 4.06; P, 12.46.

Found: C, 43.56; H, 4.35; P, 12.26.

The infrared spectrum (Plate VIII) of XXVIII shows bands characteristic of conjugated carbonyl (1647 cm.^{-1}), phosphoryl (1263 cm.^{-1}), the P-O-C (alkyl) linkage (1032 cm.^{-1}), and para-disubstituted benzene (775 cm.^{-1}). Other absorption is evident at 1578, 1404, 1228, 1179, 1090, 949, 855, and 720 cm.^{-1} .

The nuclear magnetic resonance spectrum (Plate XVIII) shows a doublet centered at 3.90 delta (methoxy hydrogens) with $J = 11$ c.p.s., doublets centered at 7.53 delta (aromatic hydrogens meta to carbonyl) and 8.25 delta (aromatic hydrogens ortho to carbonyl) with $J_{AB} = 9$ c.p.s., $J_{AA} = 1$ c.p.s., $J_{BB} = 0$, and a field separation of 44 c.p.s.

Preparation of Dimethyl (p-Chlorobenzoyl)phosphonate (2,4-Dinitrophenyl)hydrazone. To 25 ml. of the 2,4-dinitrophenylhydrazine stock solution was added 0.5 g. of dimethyl (p-chlorobenzoyl)phosphonate (XXVIII). An orange precipitate immediately formed which, after recrystallization from methanol, had m. p. of 164-7°. The infrared spectrum of this compound is described in Table I.

Anal. Calcd. for $C_{15}H_{14}ClN_4O_7P$:

N, 13.07; P, 7.22.

Found: N, 13.04; P, 7.03.

Preparation of Dimethyl (o-Chlorobenzoyl)phosphonate (XXIX). The starting reagents were 5.25 g. (0.03 mole) of o-chlorobenzoyl chloride (b. p. 230°/ 773 mm.) and trimethyl phosphite, 4.96 g. (0.04 mole). Vacuum distillation of the product yielded 4.0 g. (50.7 per cent) of a yellow liquid with b. p. 102-9°/ 0.1 mm.

Anal. Calcd. for $C_9H_9ClO_4P$:

C, 43.48; H, 4.06; P, 12.46.

Found: C, 43.25; H, 4.34; P, 12.44.

The infrared spectrum (Plate IX) of this acylphosphonate shows bands characteristic of conjugated carbonyl (1672 cm.^{-1}), phosphoryl (1261 cm.^{-1}), the P-O-C (alkyl) linkage (1036 cm.^{-1}), and ortho-disubstituted benzene ($778, 737\text{ cm.}^{-1}$) (14). Other prominent peaks appear at $1721, 1579, 1461, 1426, 1215, 1179, 942,$ and 836 cm.^{-1} .

The nuclear magnetic resonance spectrum (Plate XIX) shows a doublet centered at 3.87 delta (methoxy hydrogens) with $J = 11\text{ c.p.s.}$, a multiplet centered at 7.50 delta (aromatic hydrogens), and a multiplet centered near 8.30 delta (aromatic hydrogens).

Preparation of Dimethyl (o-Chlorobenzoyl)phosphonate (2,4-Dinitrophenyl)hydrazone. To 20 ml. of the stock solution of 2,4-dinitrophenylhydrazine was added 0.5 g. of dimethyl (o-chlorobenzoyl)phosphonate (XXIX). A dark yellow precipitate immediately formed, m. p. $112-3^{\circ}$ after recrystallization from methanol. The infrared spectrum of this compound is described in Table I.

Anal. Calcd. for $\text{C}_{15}\text{H}_{14}\text{ClN}_2\text{O}_7\text{P}$:

N, 13.07; P, 7.22.

Found: N, 12.92; P, 7.08.

Preparation of Dimethyl 2-Naphthoylphosphonate (XXXII). The previously described apparatus was charged with 5.72 g. (0.03 mole) of 2-naphthoyl chloride (m. p. $45-6^{\circ}$). To this was added dropwise 4.96 g. (0.04 mole) of trimethyl phosphite. Vacuum distillation of the product yielded 3.8 g. (48.1 per cent) of a yellow liquid, b. p. $164-7^{\circ}/1\text{ mm.}$

Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{O}_4\text{P}$:

P, 11.72.

Found: P, 11.89.

The infrared spectrum of XXXII (Plate X) shows bands characteristic of conjugated carbonyl (1653 cm.^{-1}), phosphoryl (1282 cm.^{-1}), and the P-O-C (alkyl) linkage (1042 cm.^{-1}). Other maxima appear at 1633, 1124, 840, and 751 cm.^{-1} .

Attempted Preparation of Diphenyl p-Anisoylphosphonate (XXVII).

The apparatus described previously was charged with 5.12 g. (0.03 mole) of p-anisoyl chloride. Triphenyl phosphite (b. p. $200-1^{\circ}/5\text{ mm.}$), 12.40 g. (0.04 mole), was added dropwise and the reaction mixture was heated to reflux at 130° (b. p. of chlorobenzene, approximately) for six hours. The solution darkened and then faded to a pale yellow color. Vacuum distillation of the product yielded 11.0 g. (99.5 per cent) of a colorless liquid, b. p. $147-53^{\circ}/1\text{ mm.}$ An analytical sample boiled at $150^{\circ}/1\text{ mm.}$

Anal. Calcd. for $\text{C}_{20}\text{H}_{17}\text{O}_5\text{P}$:

C, 65.22; H, 4.65; P, 8.41.

Found: C, 66.77; H, 4.97; P, 4.44.

The infrared spectrum of the product (Plate XI) exhibits maxima characteristic of conjugated carbonyl (1724 cm.^{-1}) and phosphoryl (1278 cm.^{-1}). Other prominent peaks appear at 1607, 1587, 1485, 1194, 1162, 1077, 1026, 970, 841, 762, 746, and 689 cm.^{-1} . The peaks at 1077 and 1026 cm.^{-1} correspond exactly to bands found in the infrared spectra of triphenyl phosphite, triphenyl phosphate, and diphenyl hydrogen phosphonate.

Although the elemental analysis of the compound isolated in this reaction is not within acceptable limits, the nuclear magnetic resonance spectrum (Plate XX) of the compound would indicate that much of XXVII is present. There is a singlet at 3.78 delta (methoxy hydrogens), doublets centered at 6.87 delta (aromatic hydrogens meta to the carbonyl) and 8.03 delta (aromatic hydrogens ortho to the carbonyl) with $J_{AB} = 9$ c.p.s., $J_{AA} = J_{BB} = 0$, and a field separation of 60 c.p.s. A strong multiplet is in the region of 7.00 to 7.40 delta (aromatic hydrogens).

This compound would not form a 2,4-dinitrophenylhydrazone either before or after the distillation.

Attempted Preparation of Tetramethyl Terephthaloyldiphosphonate (XXXIX).

The previously described apparatus was charged with 6.09 g. (0.03 mole) of terephthaloyl chloride (m. p. 82-4°). To this was added dropwise 7.44 g. (0.06 mole) of trimethyl phosphite. The mixture darkened and became a viscous liquid which sat for eight hours at room temperature without any apparent change. It was then heated and evolution of methyl chloride occurred as the mixture turned to a pale lemon yellow color. Attempted distillation of the mixture yielded only a low-boiling colorless fraction whose infrared spectrum corresponded to that of dimethyl hydrogen phosphonate. There was a dark polymeric residue in the distillation flask. The crude reaction mixture did form an orange (2,4-dinitrophenyl)hydrazone which was not purified.

Attempted Preparation of Dimethyl (p-Nitrobenzoyl)phosphonate (XXXVIII).

The previously described apparatus was charged with 5.56 g. (0.03 mole) of p-nitrobenzoyl chloride (m. p. 72°) in 50 ml. anhydrous ether (b. p. 34-5°/ 760 mm.). Trimethyl phosphite, 4.96 g. (0.04 mole) was added

dropwise. No noticeable change occurred in the reaction mixture until all of the trimethyl phosphite had been added. Then the pale yellow solution abruptly changed to a deep orange color with a red precipitate present. Attempts to isolate a sample of the precipitate were unsuccessful as the isolated sample changed to a yellow homogeneous solution, which also occurred when the entire reaction mixture was refluxed under nitrogen for two hours. Evaporation of the ether solvent yielded a pale yellow solid which when recrystallized from methylene chloride-Skelley F had a m. p. of 183-5°. Analysis of this material showed no phosphorus present and carbon-hydrogen analysis of C, 52.77, and H, 3.07. Attempts to form a 2,4-dinitrophenylhydrazone from either the crude reaction mixture or the purified solid material failed.

Attempted Preparation of Dimethyl Cinnamoylphosphonate (XXXIII).

The previously described apparatus was changed with 5.00 g. (0.03 mole) of cinnamoyl chloride (m. p. 35°) and 50 ml. anhydrous ether. Trimethyl phosphite, 4.96 g. (0.04 mole), was added dropwise. When the evolution of methyl chloride had ceased the ether was removed with a flash evaporator and the yellow reaction mixture was fractionated to yield 3.0 g. (41.7 per cent), b. p. 105-7°/0.5 mm.

Anal. Calcd. for $C_{11}H_{13}O_4P$:

C, 55.00; H, 5.46; P, 12.90.

Found: C, 48.54; H, 5.76; P, 12.34.

The infrared spectrum of XXXIII shows maxima characteristic of conjugated carbonyl (1718 cm.^{-1}), phosphoryl (1273 cm.^{-1}), the P-O-C (alkyl)

linkage (1063 cm.^{-1}), and an olefinic bond (1639 cm.^{-1}). Other prominent peaks appear at 1612 , 1507 , 1574 , 1449 , 1190 , 980 , 888 , and 754 cm.^{-1} .

Attempted Preparation of Dimethyl (p-Methylcinnamoyl)phosphonate (XXXIV). The previously described apparatus was charged with 5.42 g. (0.03 mole) of p-methylcinnamoyl chloride (m. p. $71-2^{\circ}$) and 50 ml. of anhydrous ether. Trimethyl phosphite, 4.96 g. (0.04 mole), was added. When reaction had ceased the ether was evaporated and the yellow reaction mixture distilled, yielding 3.0 g. (39.5 per cent), b. p. $155-60^{\circ}/0.7\text{ mm.}$

Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{O}_4\text{P}$:

C, 56.69 ; H, 5.95 .

Found: C, 53.84 ; H, 6.27 .

The infrared spectrum of XXXIV exhibits bands characteristic of conjugated carbonyl (1720 cm.^{-1}), phosphoryl (1275 cm.^{-1}), the P-O-C (alkyl) linkage (1065 cm.^{-1}), an olefinic linkage (1639 cm.^{-1}), and para-disubstituted benzene (813 cm.^{-1}). Other maxima appear at 1612 , 1587 , 1575 , 1450 , 1190 , 980 , and 840 cm.^{-1} .

Attempted Preparation of Dimethyl 1-Naphthoylphosphonate (XXXI). The previously described apparatus was charged with 5.72 g. (0.03 mole) of 1-naphthoyl chloride (b. p. $125-8^{\circ}/3\text{ mm.}$). Trimethyl phosphite, 4.96 g. , 0.04 mole, was added. Vacuum distillation of the reaction mixture yielded 3.2 g. (40.5 per cent) of product, b. p. $148-53^{\circ}/1.5\text{ mm.}$

Anal. Calcd. for $\text{C}_{13}\text{H}_{13}\text{O}_4\text{P}$:

C, 59.10; H, 4.96; P, 11.72.

Found: C, 56.81; H, 5.47; P, 11.05.

The infrared spectrum of XXXI shows bands characteristic of conjugated carbonyl (1724 cm.^{-1}), phosphoryl (1250 cm.^{-1}), and the P-O-C (alkyl) linkage (1053 cm.^{-1}). Other maxima appear at 1639, 1515, 1451, 1191, 1150, 980, 840, 813, 775, and 746 cm.^{-1} .

Acid Hydrolysis of Dimethyl p-Anisoylphosphonate (XXII). A one-neck, 50 ml., round-bottom flask fitted with reflux condenser and magnetic stirring bar was charged with 2.44 g. (0.01 mole) of XXII and 10 ml. of .1 N. hydrochloric acid. The reaction mixture was stirred for four hours at room temperature without any noticeable change in composition. After twenty-four hours stirring 1.50 g. (98.7 per cent) of p-anisic acid, m. p. 184° from ether, was filtered from the reaction mixture.

Alkaline Hydrolysis of Dimethyl p-Anisoylphosphonate (XXII). A one-neck, 50 ml., round-bottom flask fitted with reflux condenser and magnetic stirring bar was charged with 2.44 g. (0.01 mole) of XXII and 10 ml. of .1 N. sodium hydroxide. Within fifteen minutes a heavy white precipitate was apparent in the reaction mixture. After twenty-four hours the solid material was filtered off and the free p-anisic acid was regenerated from its sodium salt by treatment with .1 N. hydrochloric acid. The acid, 1.43 g. (94.1 per cent), had a m. p. of 184° after recrystallization from ether.

Attempted Clemmensen Reduction of Dimethyl Benzoylphosphonate (IIb).

The method used is a modification of that found in "Organic Reactions",

I, 155 (50). A mixture consisting of 25 g. of powdered zinc, 5.0 g. of mercuric chloride, 3 ml. of concentrated hydrochloric acid, and 3 ml. of water was placed in a 250 ml., one-neck, round-bottom flask and was stirred with a magnetic stirrer for five minutes. The supernatant liquid was discarded and the solid material was covered with 47 ml. concentrated hydrochloric acid and 50 ml. of water. A solution of 21.4 g. (0.1 mole) of IIb in 50 ml. of toluene was added to the flask, and the mixture was stirred at room temperature for twenty-four hours. Within five hours the yellow color of the phosphonate had completely disappeared; after ten hours a white precipitate was evident in the mixture. Filtration of the mixture yielded 12.0 g. (98.2 per cent) of benzoic acid, m. p. 122°.

Attempted Wolff-Kishner Reduction of Dimethyl Benzoylphosphonate

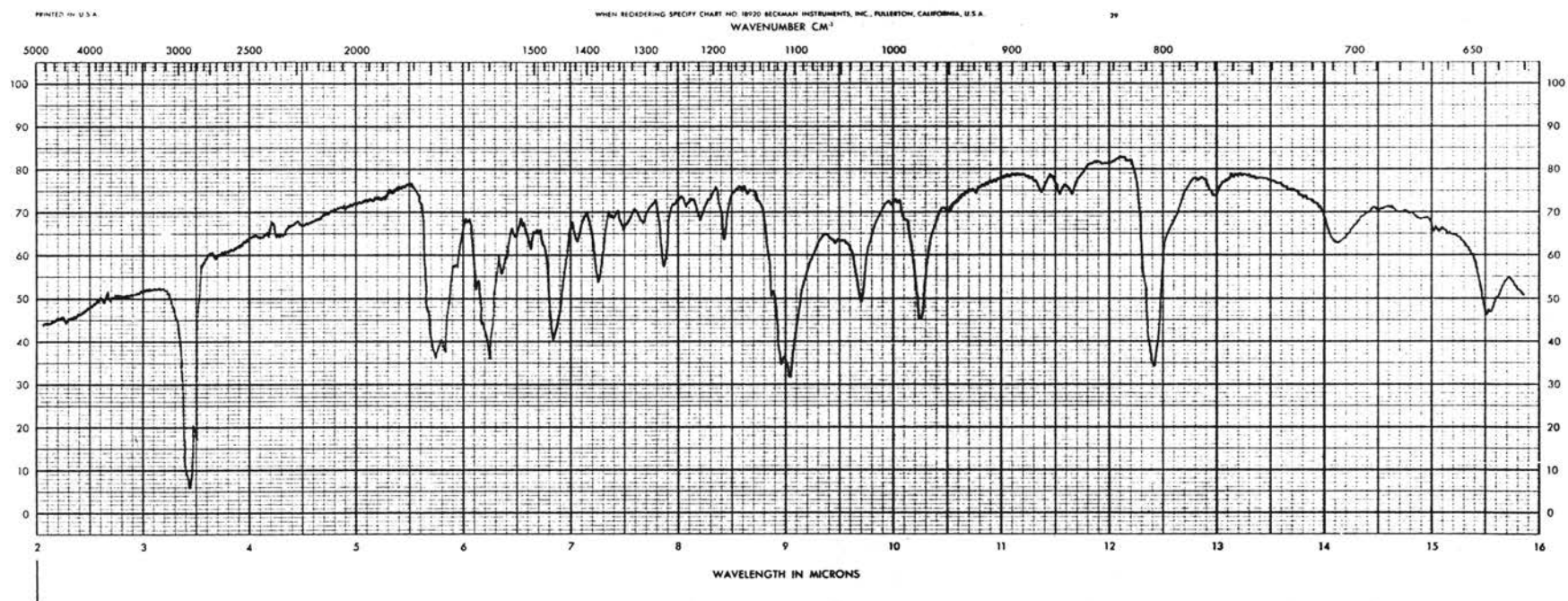
(IIb). The method used is a modification of that found in Fuson's "Reactions of Organic Compounds" (27, 69). A mixture of 5.50 g. (0.0256 mole) of IIb, 8 g. of potassium hydroxide, 150 ml. of trimethylene glycol, and 15 ml. of 85 per cent hydrazine hydrate was placed in a 250 ml., one-neck, round-bottom flask. After three hours at reflux the water present was distilled, and the mixture refluxed at 200° for four hours. The reaction mixture was then neutralized with 10 per cent hydrochloric acid and extracted with benzene. The organic layer was dried over anhydrous calcium chloride, and the benzene was distilled. The residual white precipitate was recrystallized from ether and found to be benzoic acid, m. p. 122°.

A second attempt at reduction was planned in which the hydrazone was to be prepared and dried before reduction. However, only benzoic acid was obtained upon addition of the phosphonate to 85 per cent hydrazine hydrate.

TABLE I
 INFRARED SPECTRA OF 2,4-DINITROPHENYLHYDRAZONES

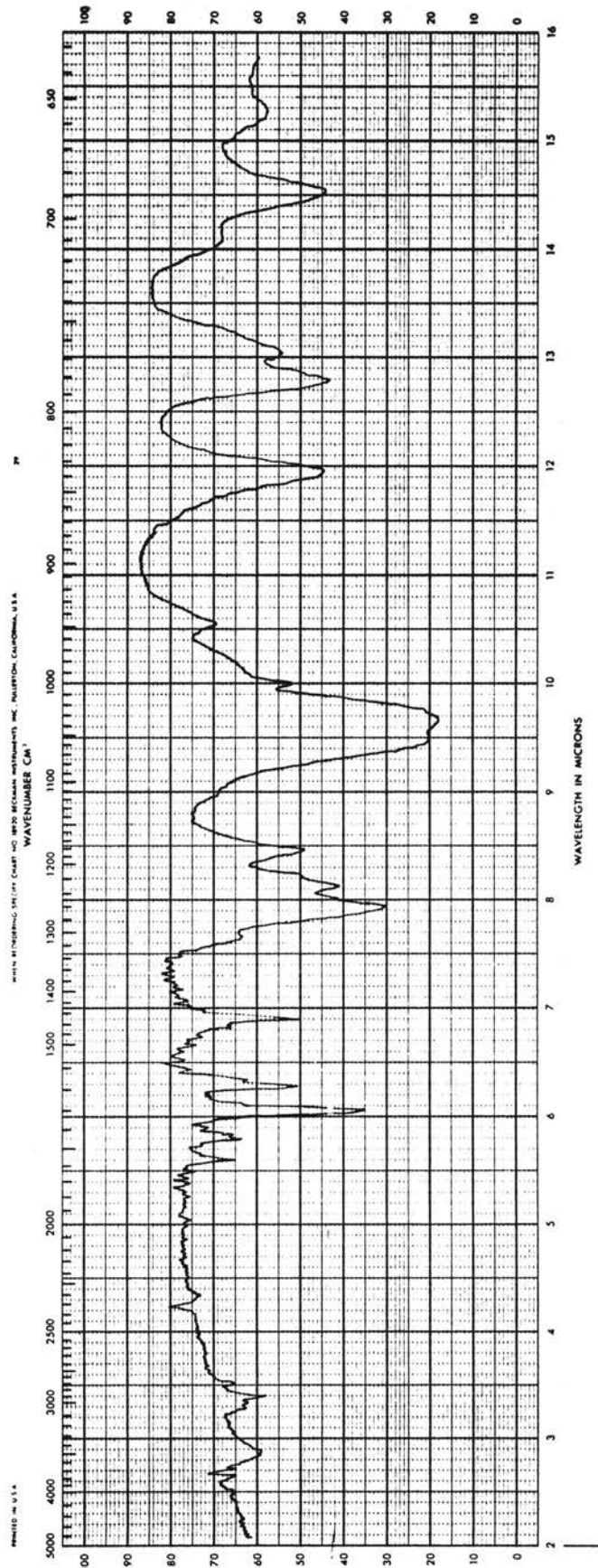
| Parent Compound | Characteristic Maxima (cm. ⁻¹) | | | |
|--|--|-------|-----------------------------|-------------------------------|
| | P→O | P-O-C | Aromatic NO ₂ | <u>para</u> -disub. phenyl |
| Dimethyl Benzoyl- phosphonate | 1283 | 1030 | 1509, 1349 | --- |
| Dimethyl <u>p</u> -Anisoyl- phosphonate | 1285 | 1033 | 1503, 1338 | 799 |
| Diethyl <u>p</u> -Anisoyl- phosphonate | 1260 | 1032 | 1495, 1332 | 797 |
| Di-2-propyl <u>p</u> -Anisoyl- phosphonate | 1263 | 1009 | 1508, 1338 | 796 |
| Di- <u>n</u> -butyl <u>p</u> -Anisoyl- phosphonate | 1277 | 1031 | 1499, 1336 | 799 |
| Diallyl <u>p</u> -Anisoyl- phosphonate | 1261 | 1020 | 1495, 1333 | 808 |
| Dimethyl (<u>p</u> - <u>tert</u> -Butyl- benzoyl)phosphonate | 1280 | 1041 | 1509, 1335 | 796 |
| Dimethyl (<u>p</u> -Chloro- benzoyl)phosphonate | 1279 | 1041 | 1510, 1340 | 794 |
| Dimethyl (<u>o</u> -Chloro- benzoyl)phosphonate | 1253 | 1010 | 1503, 1336 | --- |

Plate I



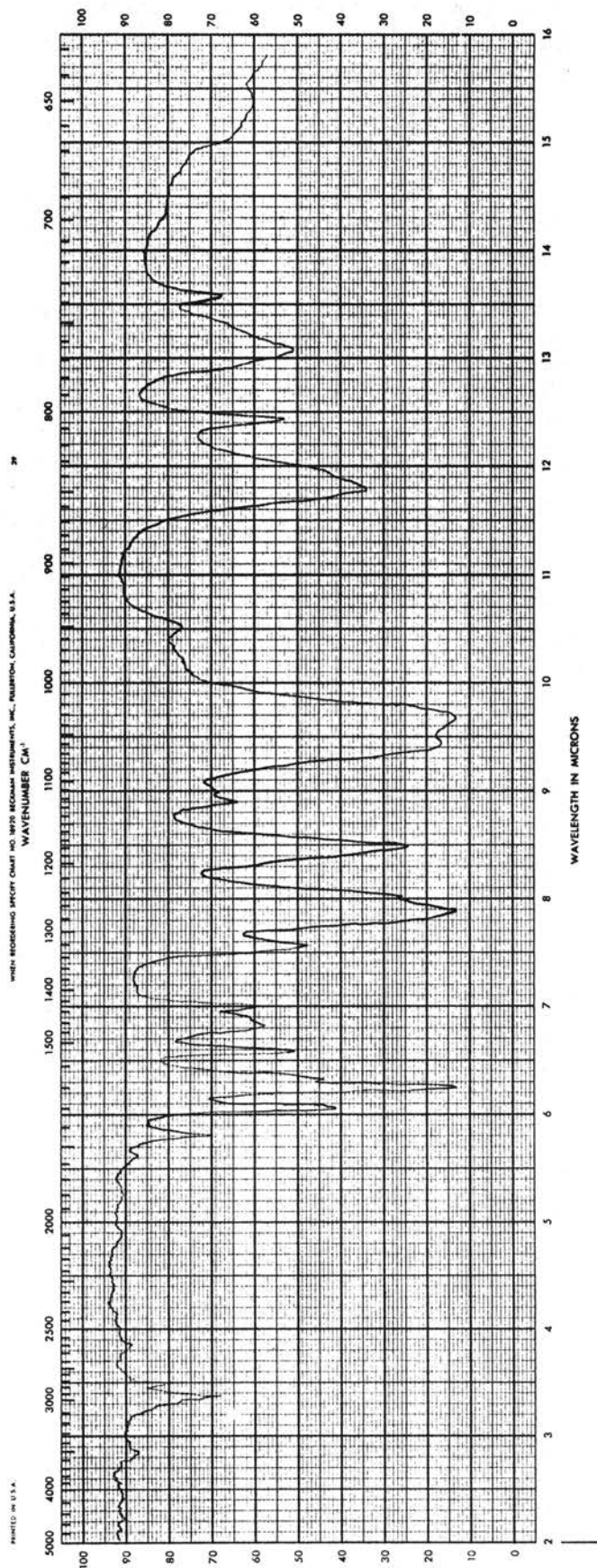
p-Methylcinnamoyl Chloride, Nujol mull.

Plate II



Dimethyl Benzoylphosphonate (IIB)

Plate III



Dimethyl p-Anisoylphosphonate (XXII)

Plate IV

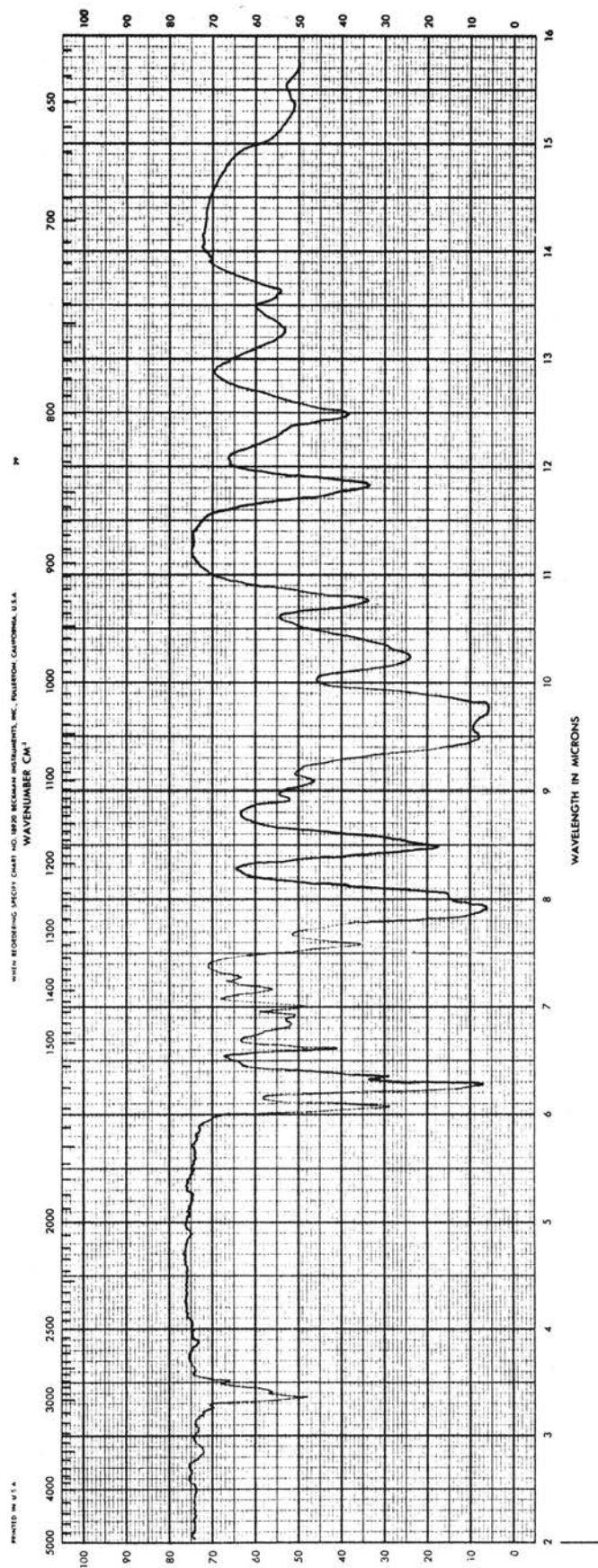
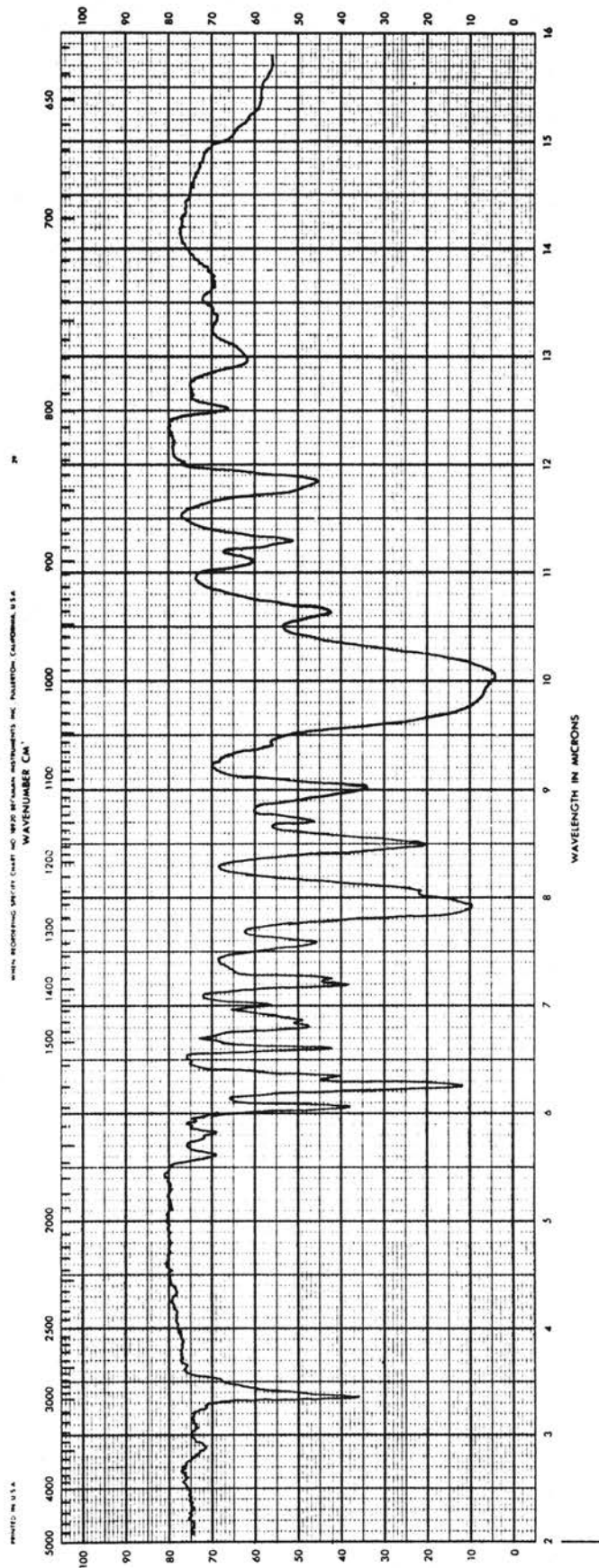
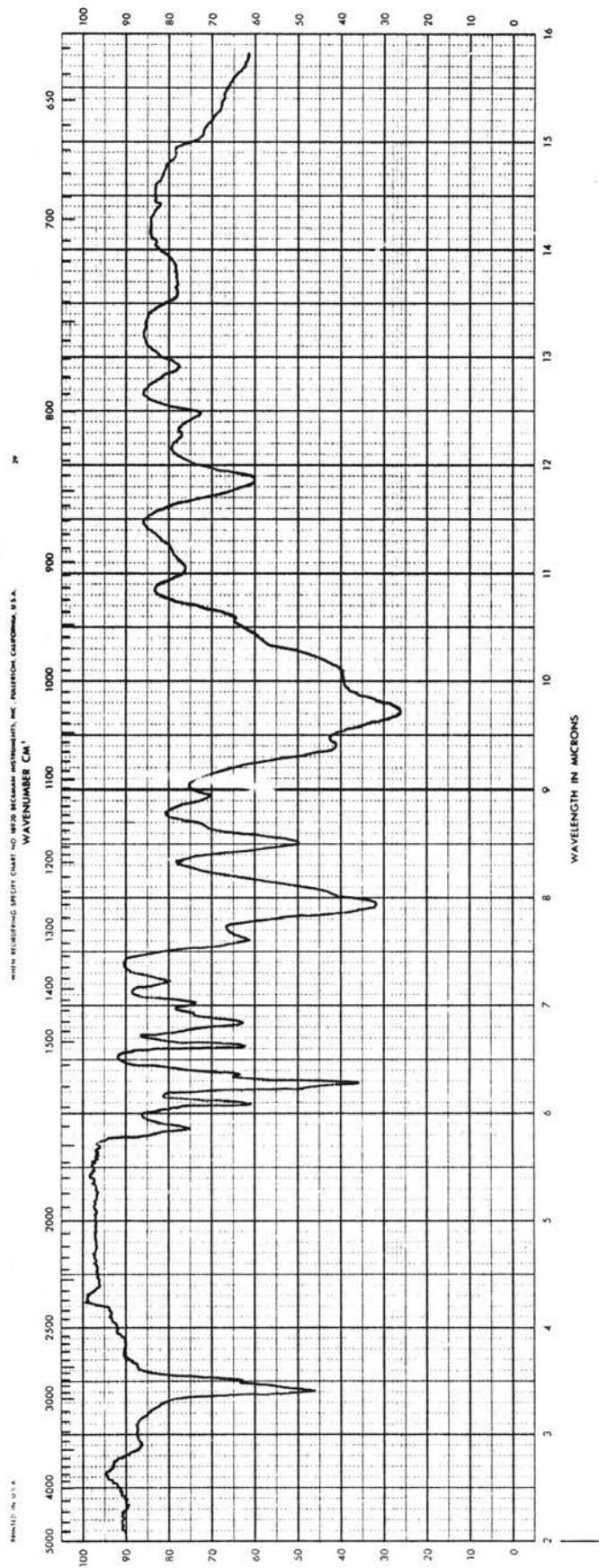
Diethyl *p*-Anisoylphosphonate (XXIII)

Plate V



Di-2-propyl p-Anisoylphosphonate (XXIV)

Plate VI



Di-n-butyl p-Anisoylphosphonate (XXV)

Plate VII

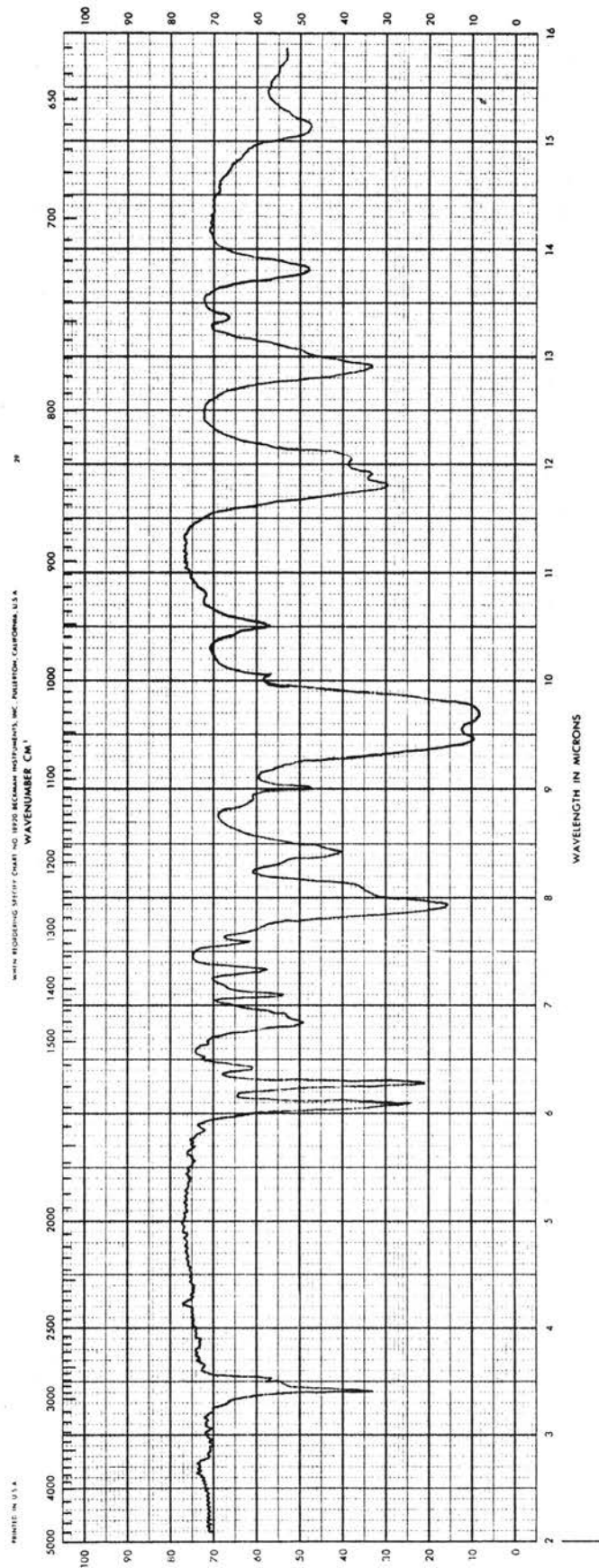
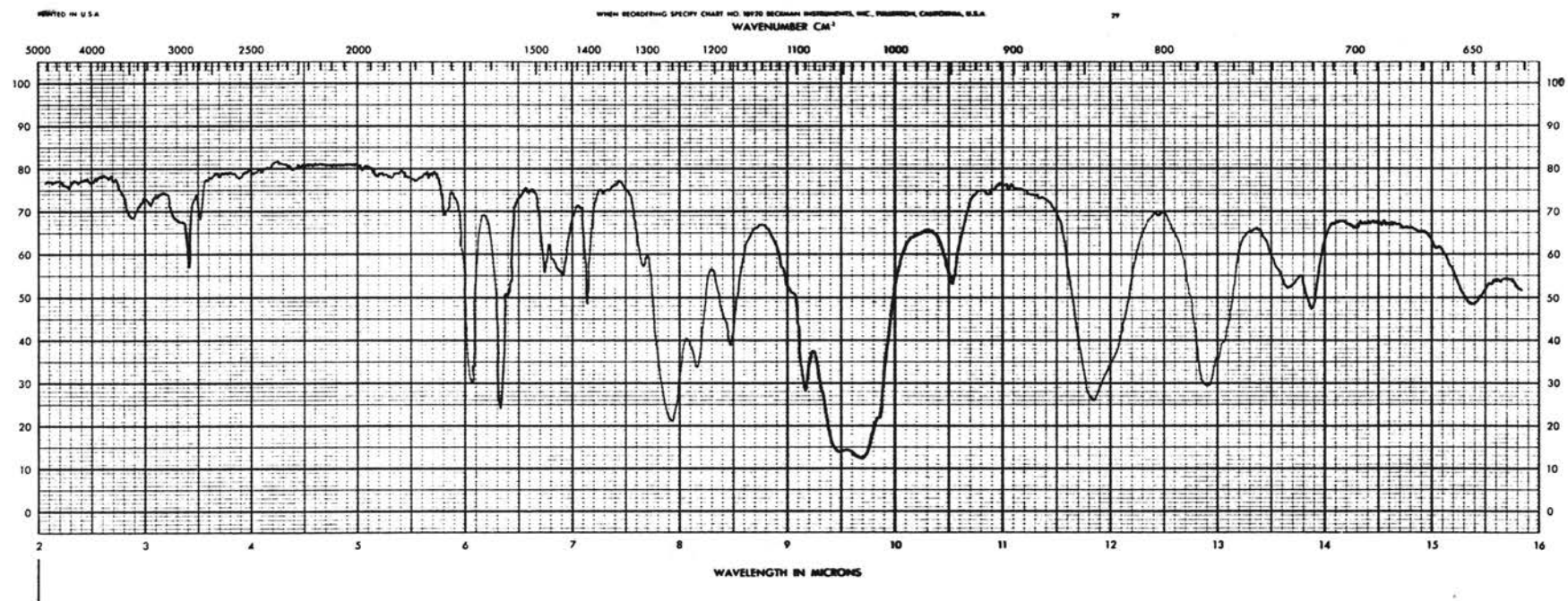
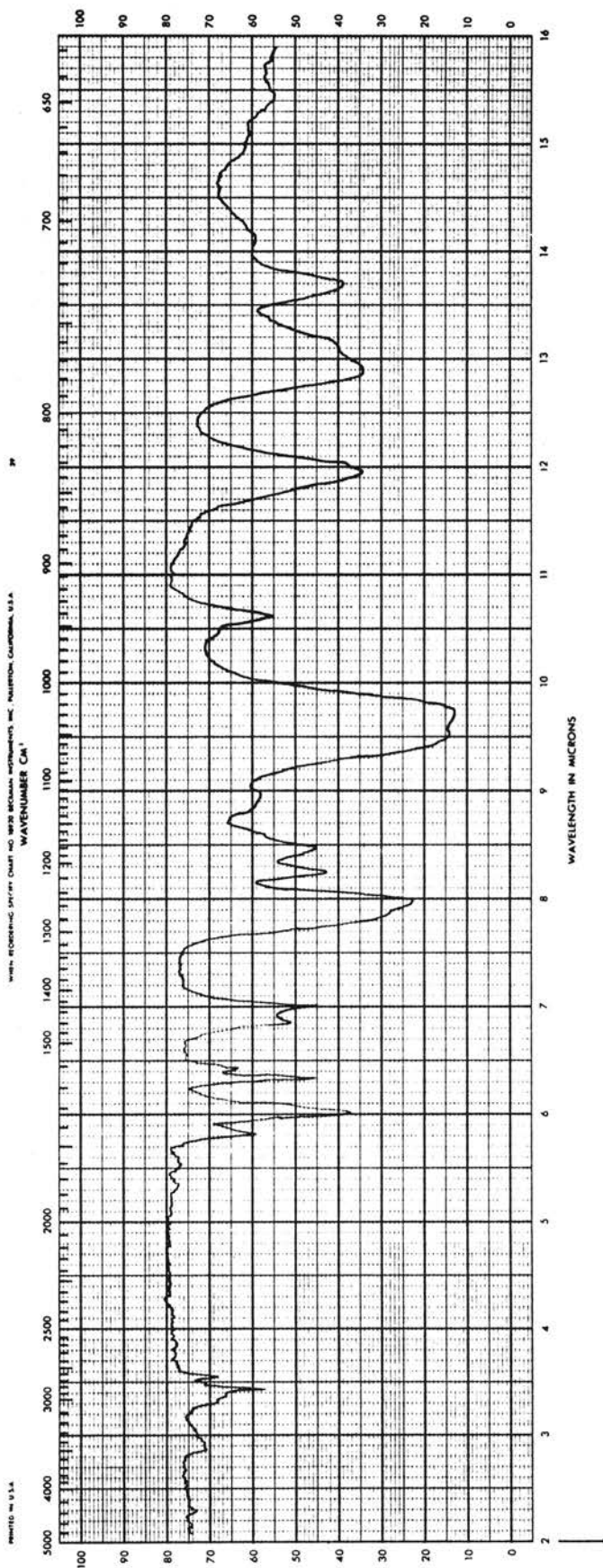
Dimethyl (p-tert-Butylbenzoyl)phosphonate (XXX)

Plate VIII



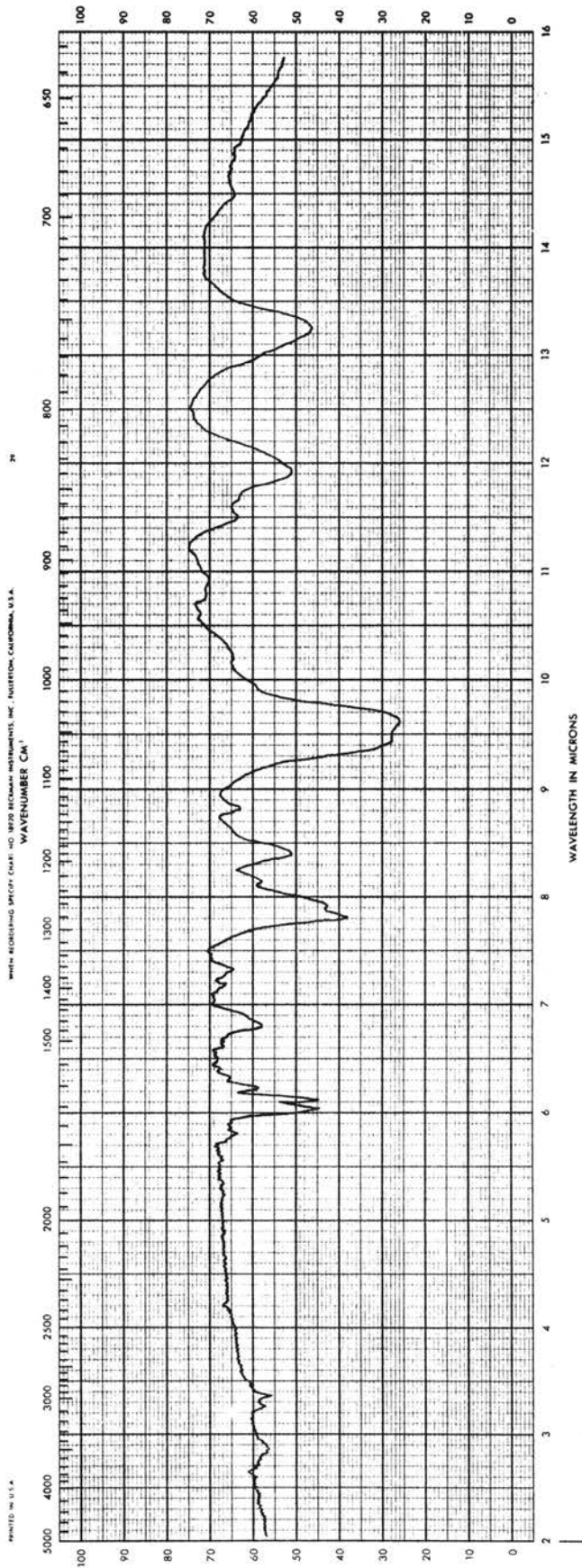
Dimethyl (p-Chlorobenzoyl)phosphonate (XXVIII)

Plate IX



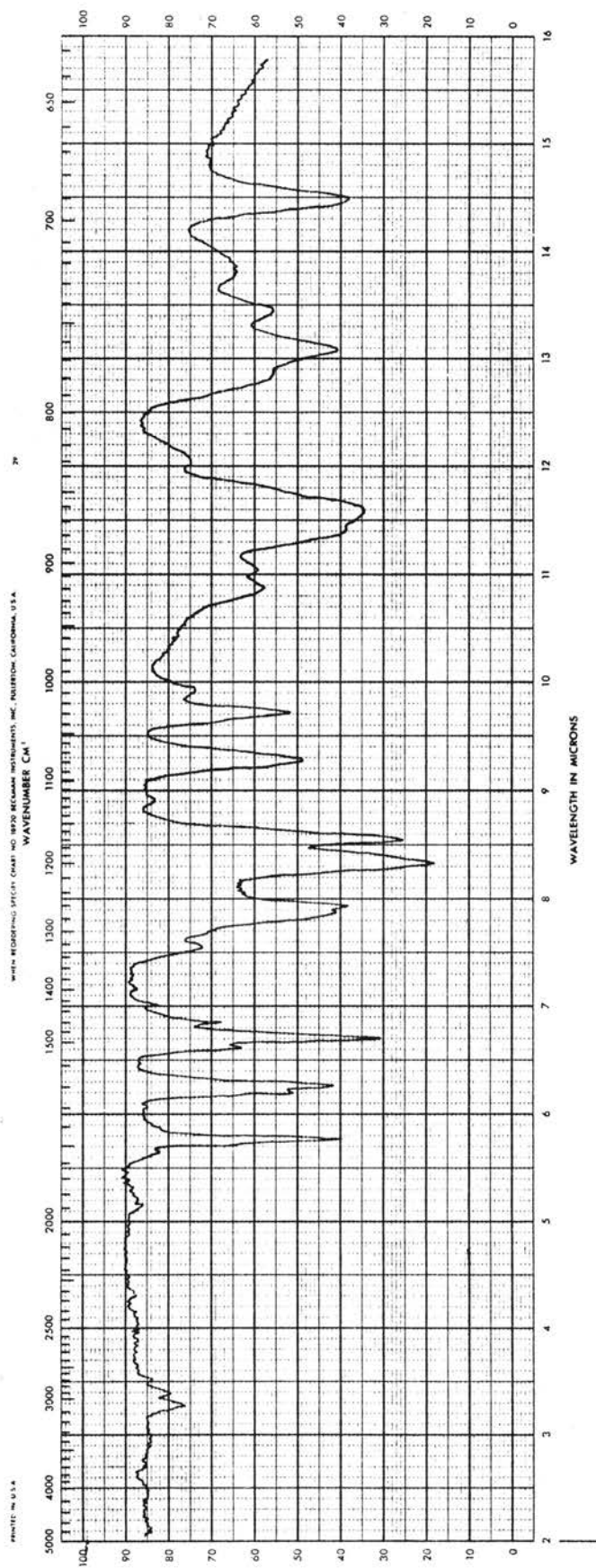
Dimethyl (*o*-Chlorobenzoyl)phosphonate (XXIX)

Plate X



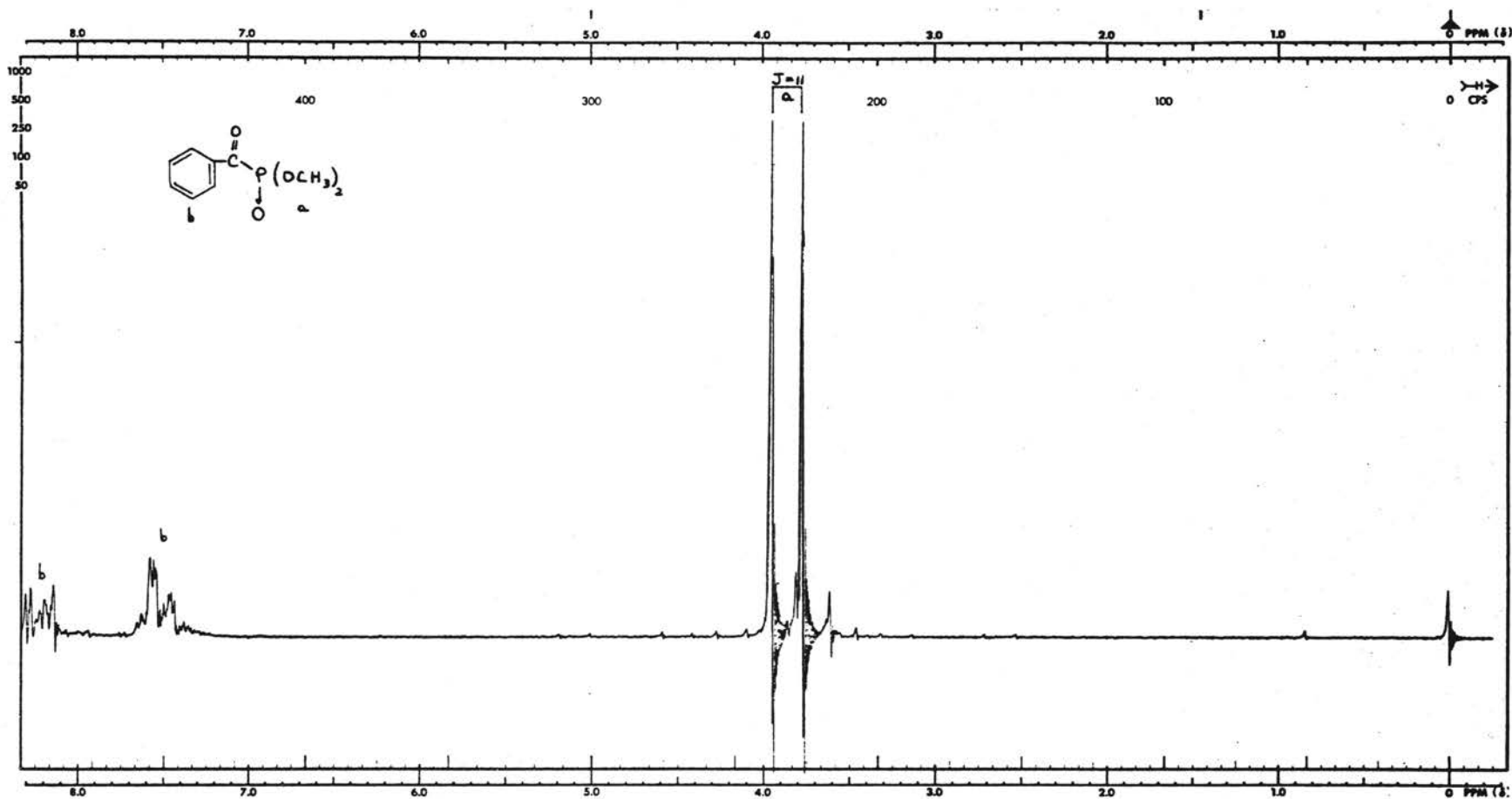
Dimethyl 2-Naphthoylphosphonate (XXXII)

Plate XI



Diphenyl p-Anisoylphosphonate (XXVII)

Plate XII



Dimethyl Benzoylphosphonate (IIb)

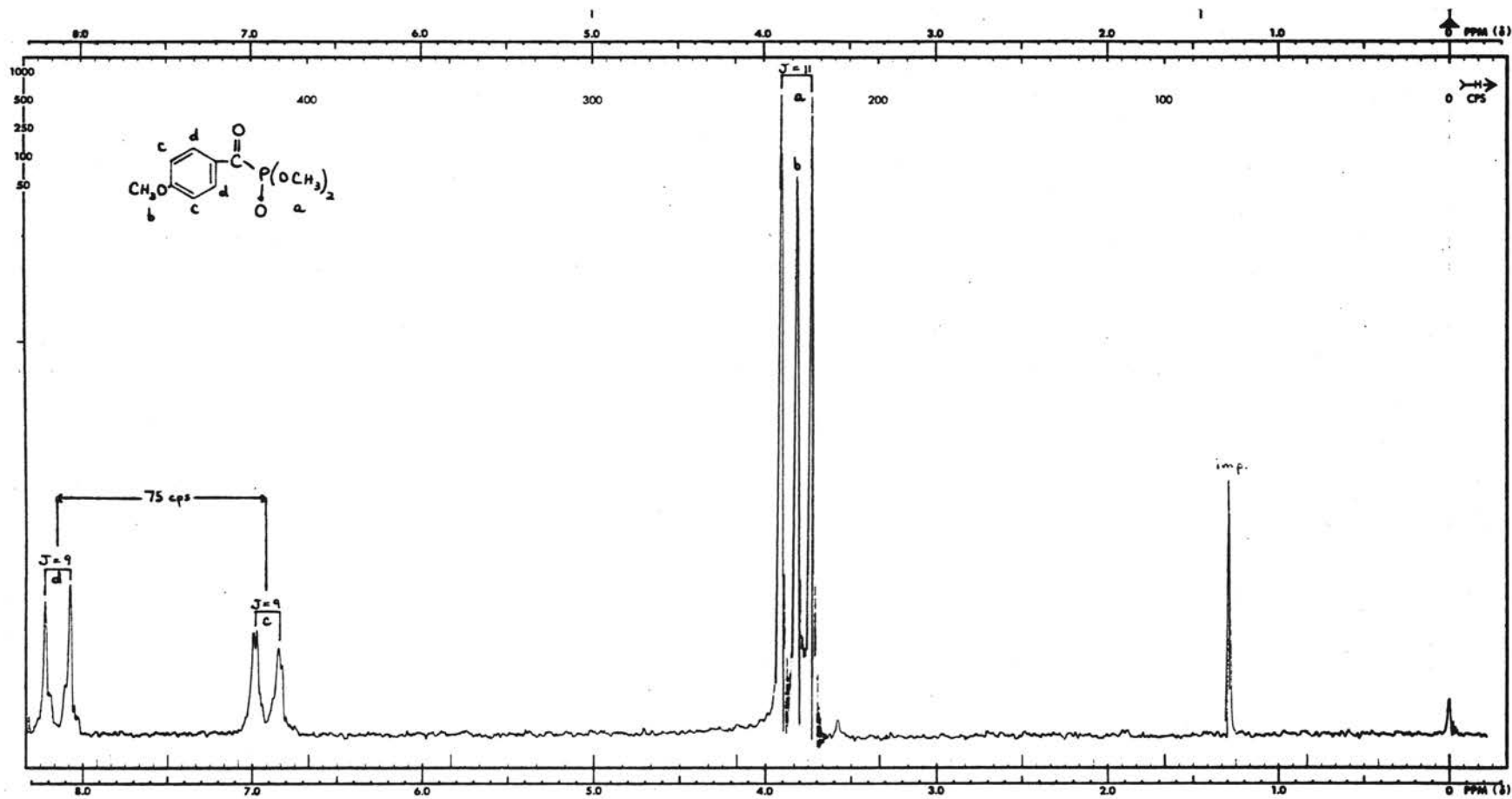
Solvent.....CCl₄
 F.B.4.0 cps

R.F. Field.....0.2 mG
 S.T.500 sec

S.W.500 cps
 S.O.000 cps

S.A.1.0
 I.A.off

Plate XIII



Dimethyl p-Anisoylphosphonate (XXII)

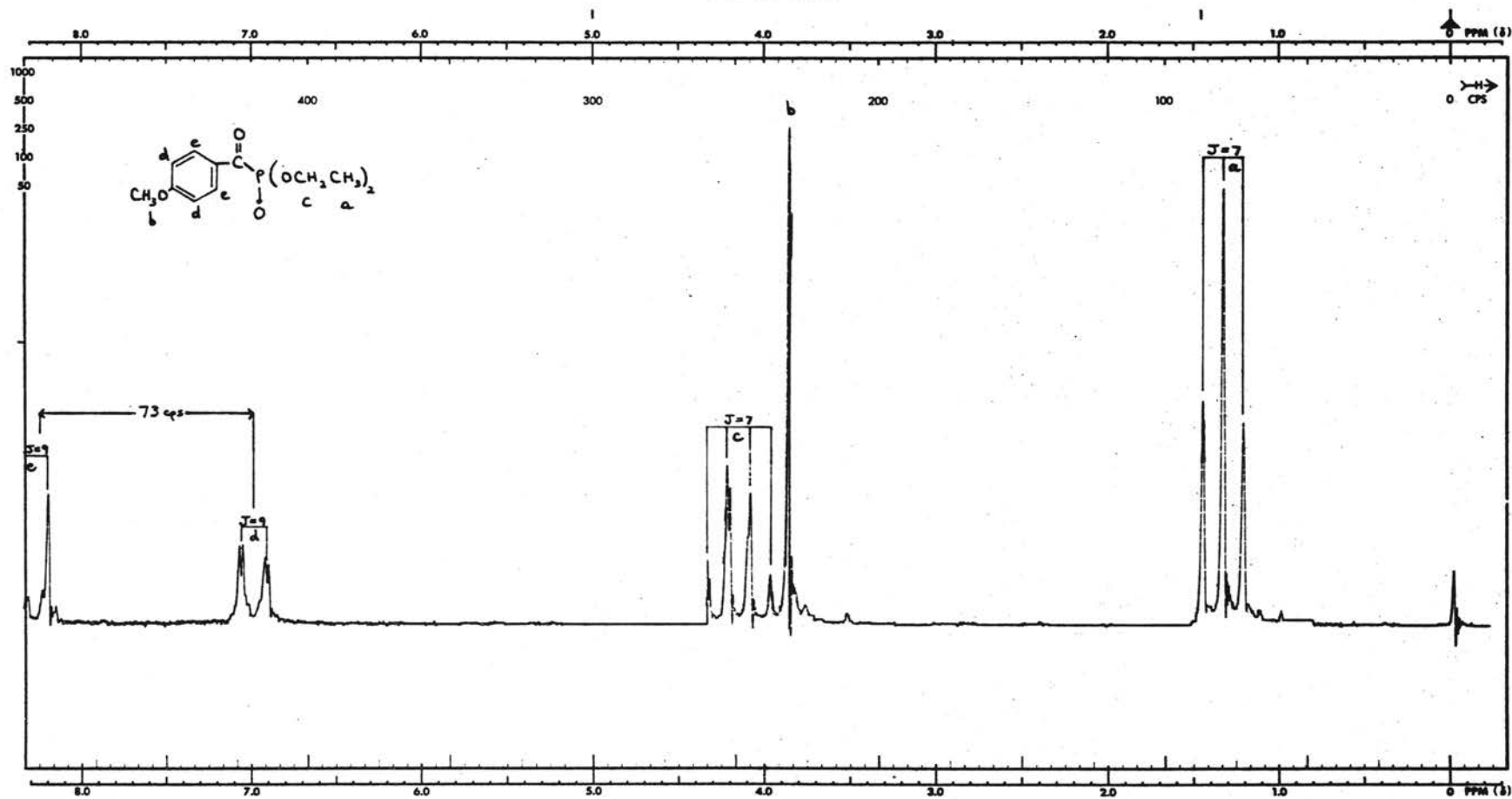
Solvent..... CCl_4
 F.B.1.0 cps

R.F. Field.....0.3 mG
 S.T.250 sec

S.W.500 cps
 S.O.000 cps

S.A.16
 I.A.off

Plate XIV



Diethyl p-Anisoylphosphonate (XXIII)

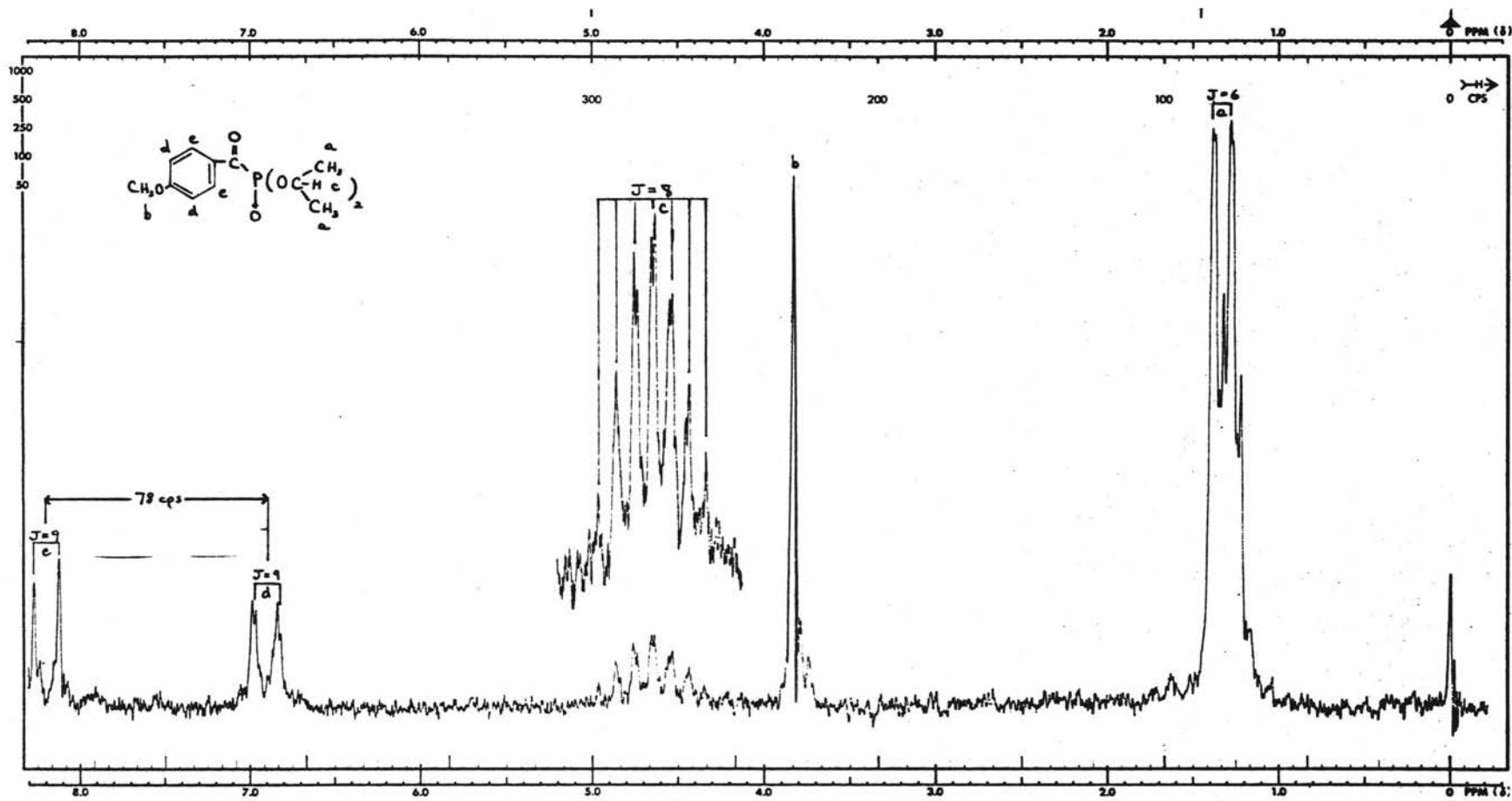
Solvent.....CCl₄
 F.B.4.0 cps

R.F. Field.....0.2 mG
 S.T.500 sec

S.W.500 cps
 S.O.000 cps

S.A.2.5
 I.A.off

Plate XV



Di-2-propyl p-Anisoylphosphonate (XXIV)

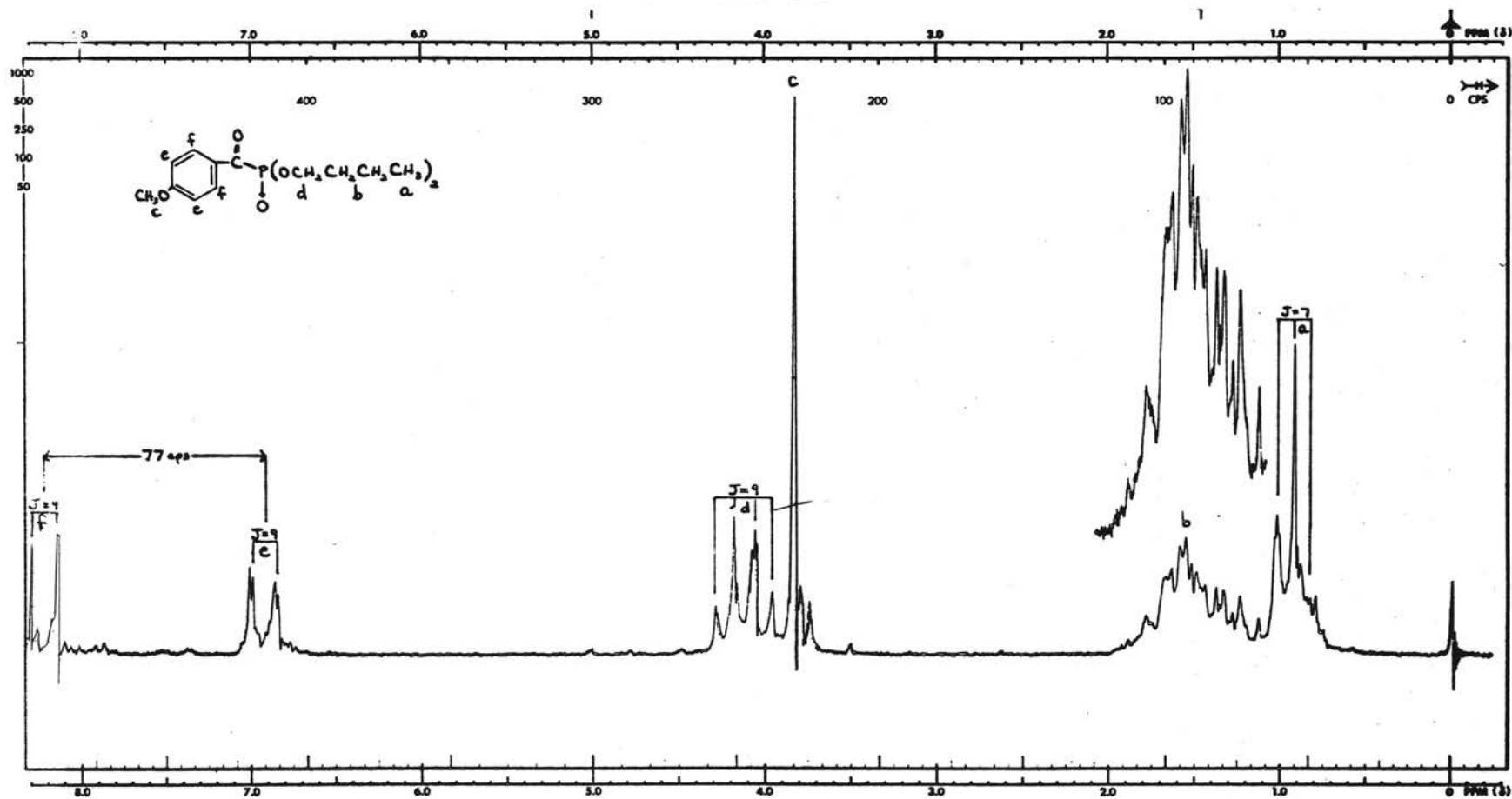
Solvent.....CCl₄
 F.B.2.0 cps

R.F. Field.....0.3 mG
 S.T.250 sec

S.W.500 cps
 S.O.000 cps

S.A.40
 I.A.off

Plate XVI



Di-n-butyl p-Anisoylphosphonate (XXV)

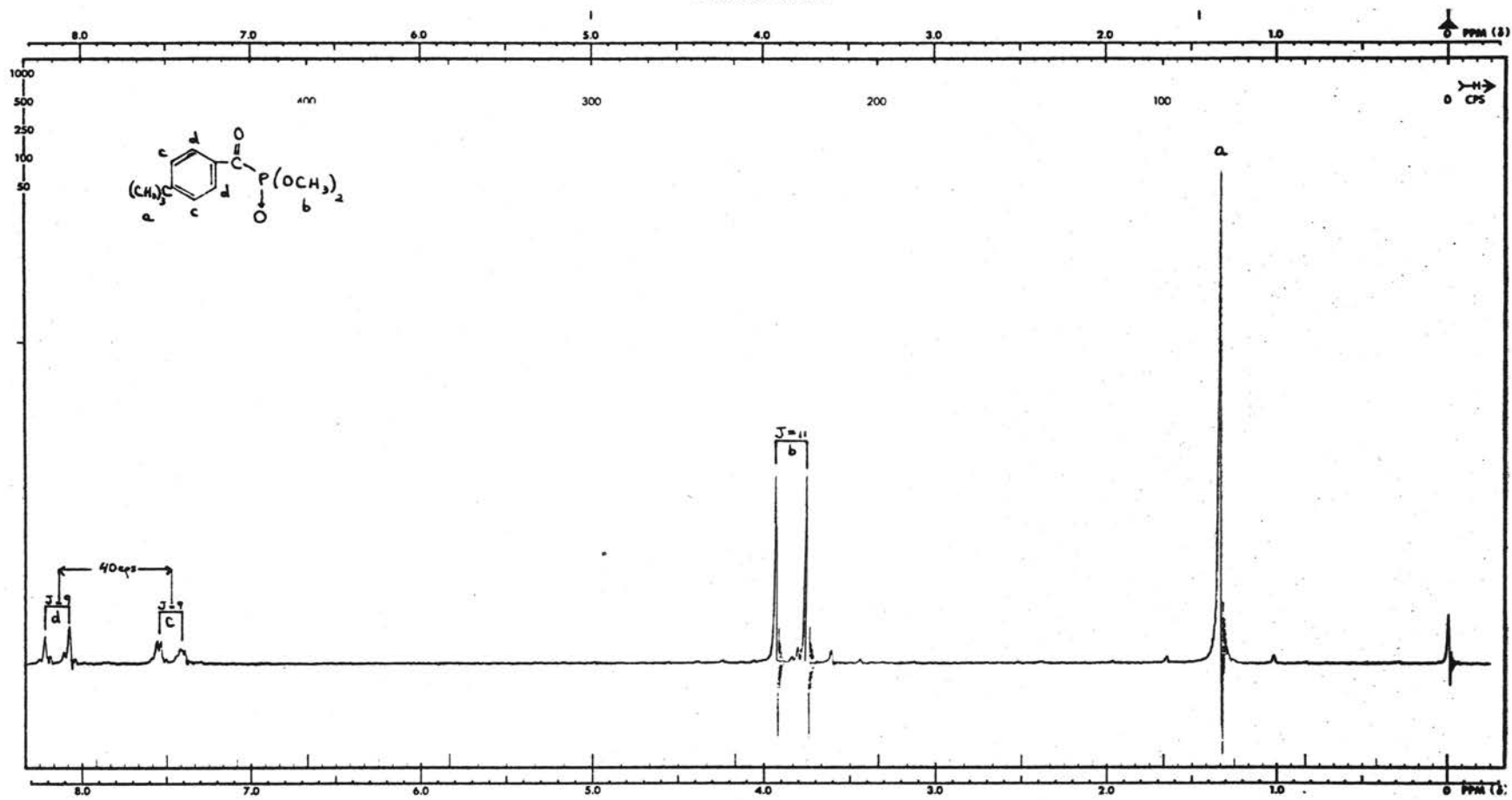
Solvent..... CCl_4
 F.B.4.0 cps

R.F. Field.....0.2 mG
 S.T.500 sec

S.W.500 cps
 S.O.000 cps

S.A.1.6
 I.A.off

Plate XVII



Dimethyl (p-tert-Butylbenzoyl)phosphonate (XXX)

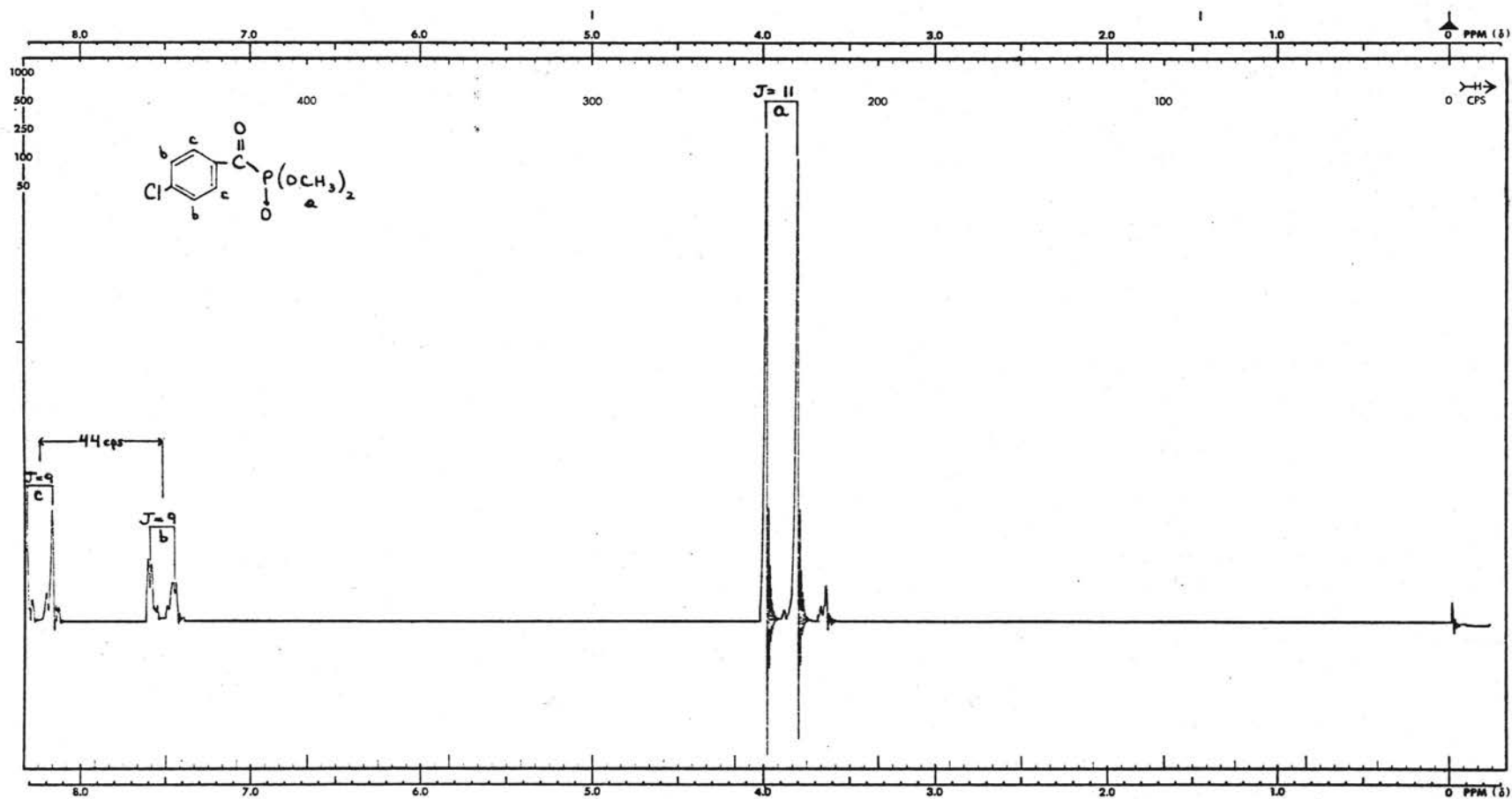
Solvent..... CCl_4
 F.B.4.0 cps

R.F. Field.....0.2 mG
 S.T.500 sec

S.W.500 cps
 S.O.000 cps

S.A.0.8
 I.A.off

Plate XVIII



Dimethyl (*p*-Chlorobenzoyl)phosphonate (XXVIII)

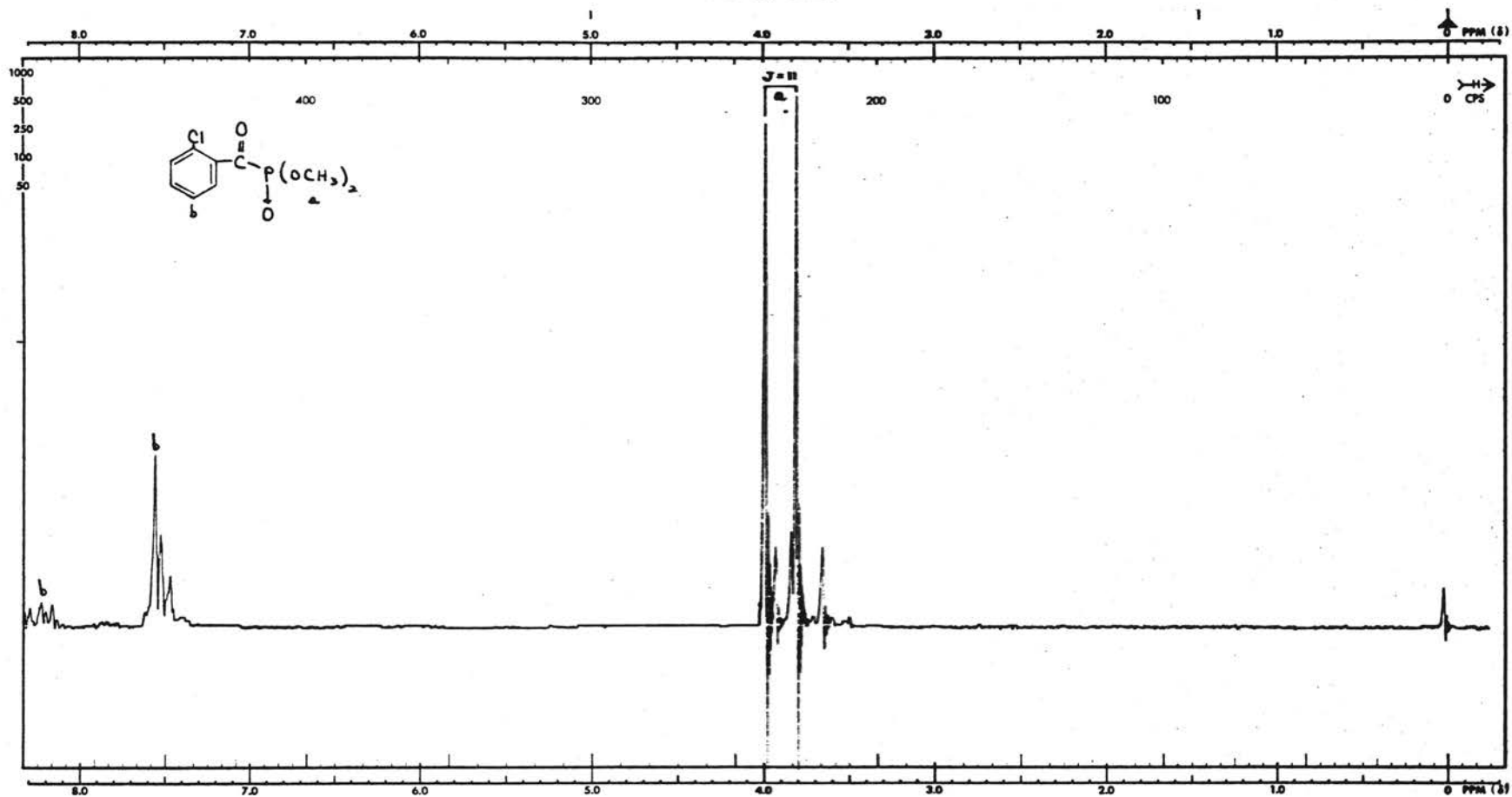
Solvent..... CCl_4
 F.B.4.0 cps

R.F. Field.....0.2 mG
 S.T.500 sec

S.W.500 cps
 S.O.000 cps

S.A.1.2
 I.A.off

Plate XIX



Dimethyl (o-Chlorobenzoyl)phosphonate (XXIX)

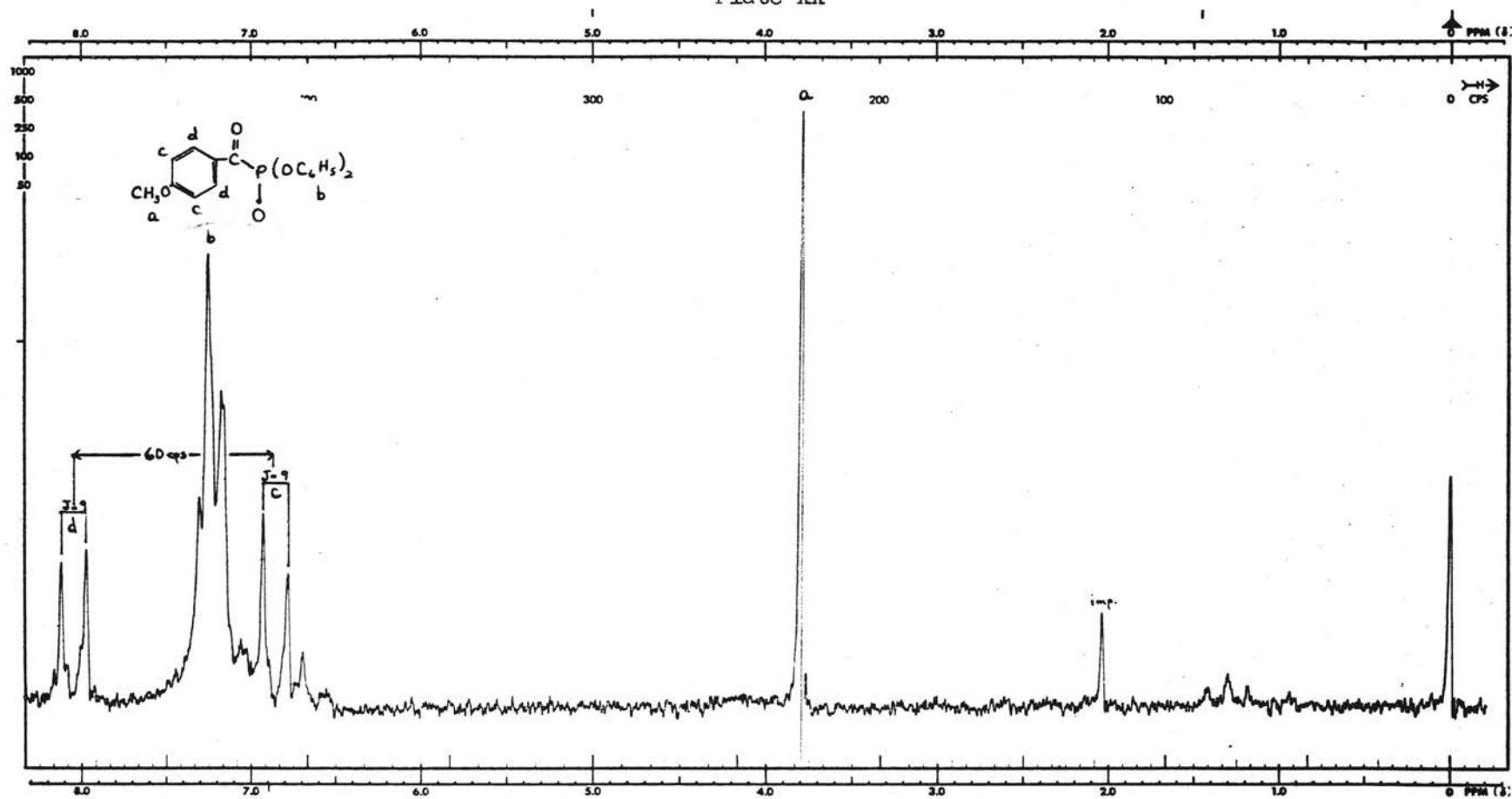
Solvent..... CCl_4
 F.B.4.0 cps

R.F. Field.....0.2 mG
 S.T.500 sec

S.W.500 cps
 S.O.000 cps

S.A.2.0
 I.A.off

Plate XX



Diphenyl *p*-Anisoylphosphonate (XXVII)

Solvent..... CCl_4
 F.B.2.0 cps

R.F. Field.....0.3 mG
 S.T.250 sec

S.W.500 cps
 S.O.000cps

S.A.32
 I.A.off

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Master of Science

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