p-TOLUENESULFONYLCARBAMOYLPHOSPHONATES AND DERIVATIVES

By

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INTRODUCTION

Though dialkyl carbamoylphosphonates have been investigated, in the chemical literature there exists general agreement that most reactions involving dialkyl hydrogenphosphonates utilized the trivalent (dialkyl hydrogen phosphite) form. The reactions went by nucleophilic or electrophilic attack on the substrate. It was the purpose of this study to synthesize, by direct addition, the corresponding dialkyl p-toluenesulfonylcarbamoylphosphonates.

Some of the present methods utilized for the synthesis of carbamoylphosphonates involve high temperatures, which will decompose some of the phosphonates. This may account for the low yields in many of the reported reactions.

Infrared (IR) and nuclear magnetic resonance (NMR) spectral data have been reported for only a few dialkyl carbamoylphosphonates. Consequently, an investigation of similar properties in p-toluenesulfonylcarbamoylphosphonates has been conducted.

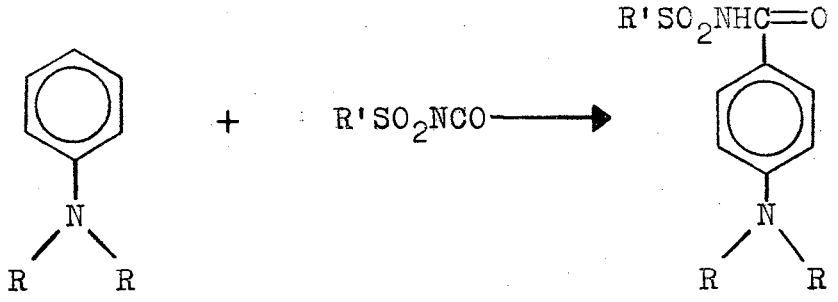
CHAPTER I

HISTORICAL

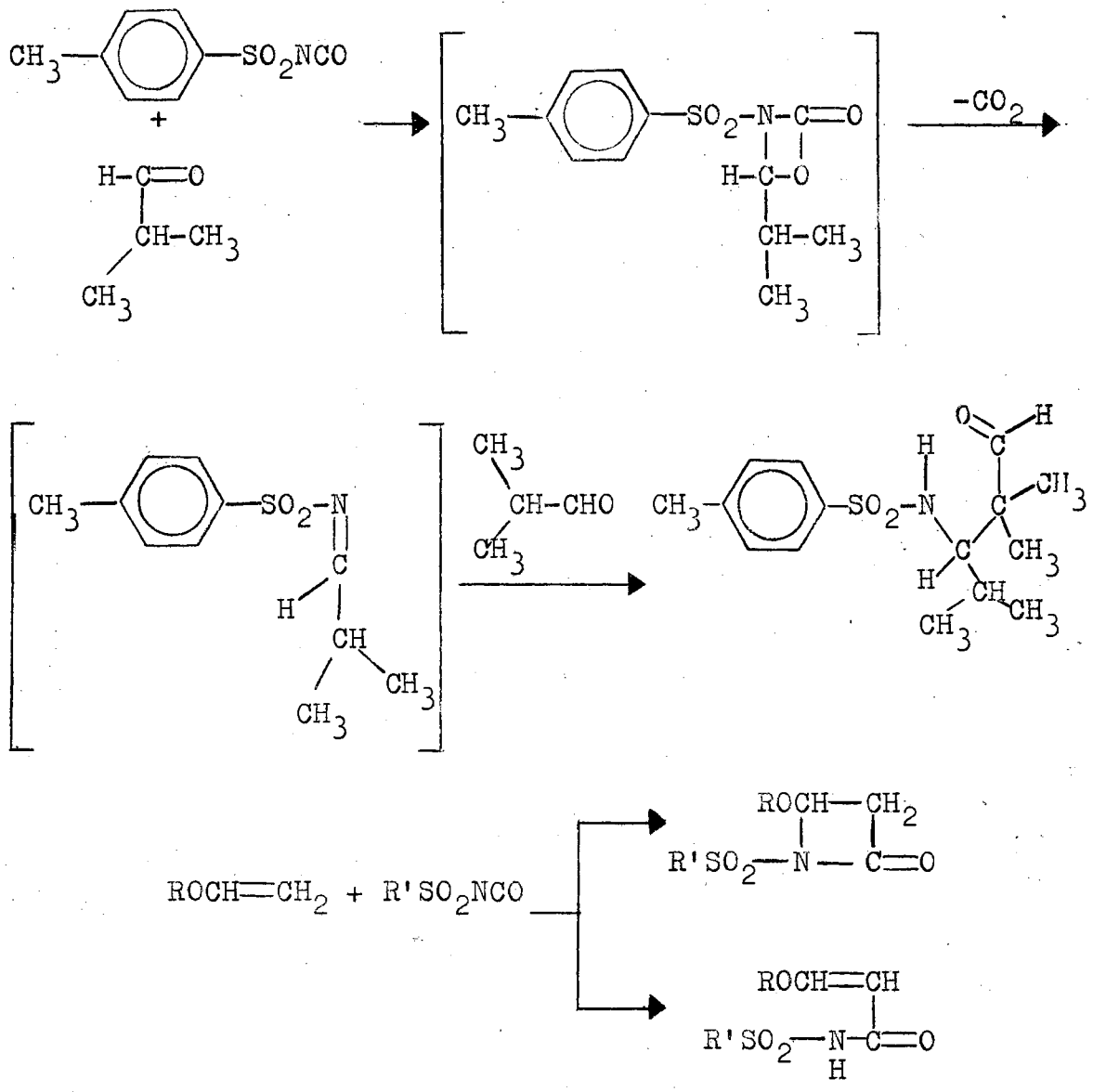
Some Reactions of Sulfonyl Isocyanates

Amines,[9,10,13,14] alcohols,[3,2,36,16] and thiols[53] condensed with sulfonyl isocyanates to give the predicted ureas, urethans and thiourethans, respectively. These reactions proceeded almost instantaneously and needed no catalysis.

The mechanism of the reaction of sulfonyl isocyanates with certain carbon-hydrogen bonds in aromatic systems,[52] aldehydes,[17,22] ketenes[18,19] and vinyl ethers[12] was believed to involve 1,2-dipolar addition. The resulting adducts sometime rearranged with the elimination of carbon dioxide.



$$RSO_2NCO + CH_2{=}C{=}O \longrightarrow RSO_2N(-C{=}O)(C{=}O)CH_2$$



Deviation from the normal urethan formation was investigated by McFarland and coworkers.[33] Triarylmethanols react with isocyanates to give N-(triarylmethyl)sulfonamides and carbon dioxide.

Sulfonyl isocyanates have also been reported to react with Grignard reagents to yield N-sulfonyl amides.[32]

Mechanisms and Reactions of Dialkyl Hydrogenphosphonates

Arbuzov, Batuev and Vinogradova[4] were apparently the first to study the vibrational spectra of dialkyl hydrogen phosphonates; the compounds examined included the dimethyl, diethyl, dipropyl, diisopropyl, dibutyl and diisobutyl hydrogenphosphonates. They found a strong band at 2435 cm^{-1} which was attributed to the P—H bond. The phosphoryl band (P→O) was observed[8] at 1250 - 1300 cm^{-1}.

Dialkyl hydrogenphosphonates undergo typical electrophilic and nucleophilic reactions. It has been proposed by Fox and Venezky[15] that the chief mechanism for the addition to isocyanato groups must involve nucleophilic attack on carbon by dialkyl hydrogenphosphonate or by sodium salt.[11,34]

$$2(RO)_2P(O)H + 2Na \rightleftharpoons 2[(RO)_2P{-}O]^{\ominus}Na^{\oplus} + H_2$$

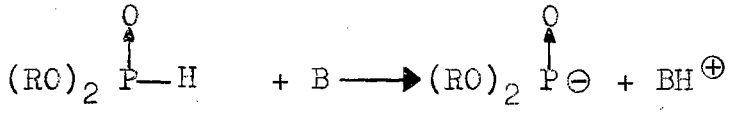
$$RNCO + [(RO)_2P{-}O]^{\ominus}Na^{\oplus} \rightarrow RN{=}C(ONa){-}P(O)(OR)_2$$

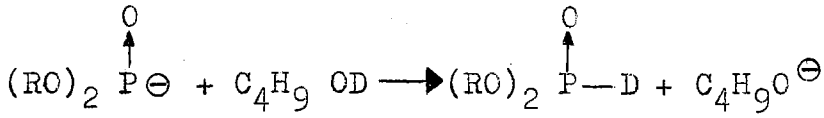
$$RN{=}C(ONa){-}P(O)(OR)_2 + (RO)_2P(O)H \rightarrow [(RO)_2P{-}O]^{\ominus}Na^{\oplus} + RN{=}C(OH){-}P(O)(OR)_2$$

$$RN{=}C(OH){-}P(O)(OR)_2 \rightleftharpoons RNHC(=O){-}P(O)(OR)_2$$

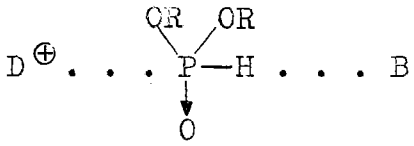
Deuterium exchange[6] between di-n-butyl hydrogenphosphonate and n-butyl alcohol-d was followed by infrared (IR)

measurements in acidic, basic and neutral solutions. It was shown that a prototropic equilibrium exists between the ester and the acidic species in the reaction mixture. The removal of a proton from the hydrogenphosphonate molecule, followed by reaction of the resulting conjugate base with the weaker acid butyl alcohol-d (with both reactions rate-determining), was probably best described by the following mechanism.



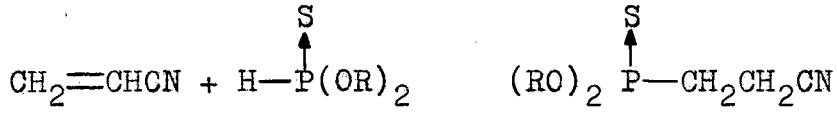


Since the rate of deuterium exchange was dependent on both the concentrations of both base and deuterium, it was believed that a termolecular mechanism in which the deuterium ion attacks phosphorus simultaneously with the removal of the proton by base could not be excluded.

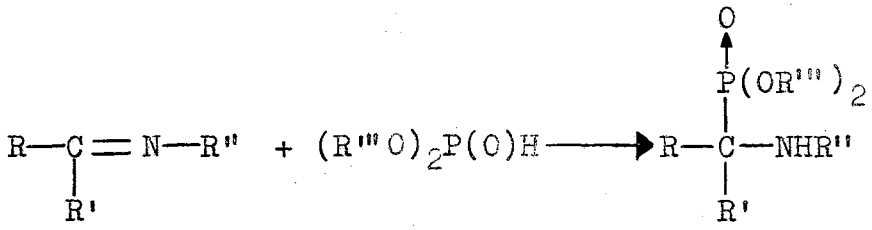


Dialkyl hydrogenphosphonates condensed with ketenes,[31,35] vinyl acetate[43] and unsaturated carboxylic acids.[43] Pudovik and Poloznova[46] have reported the reaction of dialkyl hydrogenphosphonates and dialkyl thiohydrogenphosphonates with acrylonitrile to give the 1,2-adduct of the double bond in

59-74% yields.



McConnell and Coover[30] have investigated anti-Markownikoff addition products to double bonds in the presence of peroxides; the dialkyl hydrogenphosphonates, in the absence of peroxides, gave the normal products. Condensation of dialkyl hydrogenphosphonates, dialkyl hydrogenthiophosphonates and diallyl hydrogenphosphonates have been further investigated by Pudovik and Khlyupina.[42] Activated acetylenes,[40,41] aldehydes, ketones,[47,1] acyl phosphonates[29] and alpha, beta-unsaturated aldehydes were attacked at double bonds by the hydrogenphosphonates. The addition of dialkyl hydrogenphosphonates to imines by Pudovik, et al.[39,44] has resulted in the synthesis of the corresponding α-aminophosphonic acid esters in 67-90% yields.



Synthesis of Carbamoyl and Thiocarbamoylphosphonates

Carbamoylphosphonates may be prepared by utilization of the Arbuzov reaction, the Michaelis reaction, amidation of methyl dialkoxyphosphinylformate or the reaction of a dialkyl hydrogenphosphonate with an isocyanate. Reetz[49,48]

found the Arbuzov reaction to be the most practical and generally applicable.

Reetz[49] described the Arbuzov[5] reaction to be useful in the preparation of diethyl alkyl and diethyl dialkylcarbamoylphosphonates from the corresponding alkyl- and dialkylcarbamoyl chlorides. The monoalkylcarbamoyl chlorides were synthesized by passing the theoretical amount of anhydrous hydrochloric acid into the isocyanate; the chlorides were used without further purification[35] to give 10-80% yields of the carbamates.

$$RR'NC(=O)-Cl + (R''O)_3P \longrightarrow RR'NC(=O)-P(O)(OR'')_2 + R''Cl$$

Esters of thiocarbamoylphosphonates have been obtained in a similar manner by heating equimolar mixtures of diethylcarbamoyl chloride and trialkyl phosphites at 125-38° for two hours.[26] Pudovik, et al.[43] reported an

$$(C_2H_5)_2NC(=S)-Cl + (RO)_3P \longrightarrow (C_2H_5)_2NC(=S)-P(O)(OR)_2 + RCl$$

$R = CH_3$, C_2H_5, $\underline{n}-C_3H_7$, $\underline{i}-C_3H_7$, C_4H_9, $\underline{n}-C_5H_{11}$,

and $\underline{i}-C_5H_{11}$

additional method of synthesis of esters of thiocarbamoylphosphonates in which ethyl isocyanate was condensed with several dialkyl hydrogenphosphonates

$$C_2H_5NCO + (RO)_2P(S)H \longrightarrow C_2H_5NHC(=O)-P(S)(OR)_2$$

In general, the carbamoylphosphonates prepared were more stable thermally than might be expected. However, two exceptions, diethyl phenyl- and cyclohexylcarbamoylphosphonates, gave indications of decomposing upon distillation in vacuo.[49]

Equimolar amounts of RNCO react with $(R'O)_2P(O)H$, $(R'O)_2P(S)H$ and $(R'O)_2PS_2H$.[45] The condensations of these reagents on a steam bath for 20-40 minutes, with or without the addition of dry sodium alkoxide, gave the expected adducts which were distilled or crystallized.

Methyl isocyanate was found to react very slowly in the absence of a catalyst, but found to do so readily with sodium alkoxide. Phenyl isocyanate was more reactive and condensed with dimethyl thiohydrogenphosphonate without a catalyst. The reaction was believed to occur by preliminary attack of the phosphorus atom on the carbon of the isocyanato group. The following compounds were synthesized and have shown toxicity against barn weevil.

$$CH_3NCO + (RO)_2P(O)H \longrightarrow CH_3NH-\overset{\overset{O}{\|}}{C}-\overset{\uparrow O}{P}(OR)_2$$

$$R = CH_3,\ C_2H_5,\ \underline{n}-C_4H_9,\ \underline{i}-C_4H_9$$

$$PhNCO + (CH_3O)_2\overset{\uparrow O(S)}{P}-H \longrightarrow PhNH-\overset{\overset{O}{\|}}{C}-\overset{\uparrow O(S)}{P}(OCH_3)_2$$

Diethyl phenylthiocarbamoylphosphonate has been prepared[27] by the condensation of diethyl hydrogenphosphonate and phenyl isothiocyanate in the presence of triethylamine

on a steam bath for 0.5 hours. This reaction mixture gave, upon molecular distillation, a viscous oil, b.p. 120-8°/ 0.004-0.007 mm, which slowly crystallized in part as $(RO)_2P(O)C(S)NHC_6H_5$, m.p. 57.3-8.0°.

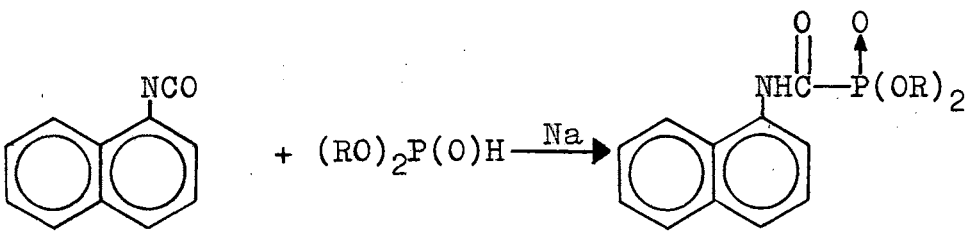
In 1959 Petrov[37] prepared several thiocarbamoylphosphonates by adding (dropwise) a sodium alkoxide to an equimolar mixture of dialkyl hydrogenphosphonate and an isothiocyanate until the exothermic effect terminated. Workup of the reaction mixtures gave the following products.

$$CH_3NCS + (RO)_2P(O)H \longrightarrow CH_3NHC(=S)-P(=O)(OR)_2$$

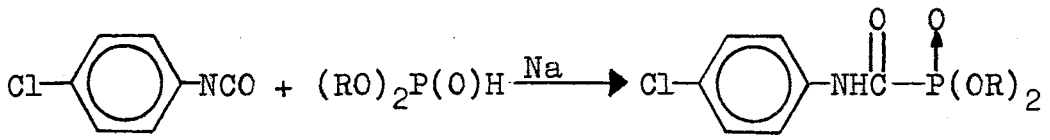
R = C_2H_5, 54.4%; i-C_3H_7, 46.3%; n-C_4H_9, 57.7%; $CH_2{=}CHCH_2$, 47.3%.

Heating diethyl methylthiocarbamoylphosphonate with aqueous hydrochloric acid resulted in hydrolysis to phosphoric acid. Upon treating the phosphonate with phosphorus pentachloride in dry carbon tetrachloride for two hours at 65° (followed by treatment with sulfur dioxide to decompose phosphorus pentachloride), the phosphorus-carbon bond cleaved to give diethyl phosphorochloridate, $(C_2H_5O)_2P(O)Cl$ (59.5%).

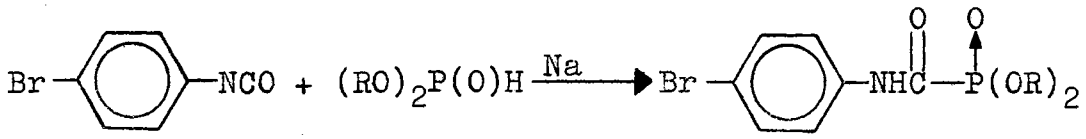
The base-catalyzed reactions of dialkyl hydrogenphosphonates with isocyanates[15] have resulted in the synthesis of the following carbamoylphosphonates.



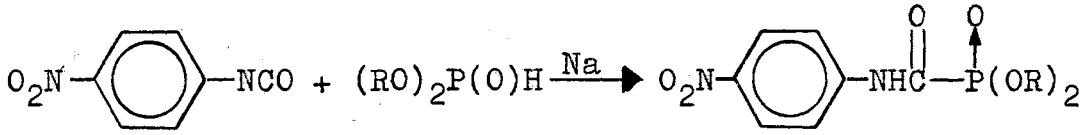
R = CH_3, 96%; C_2H_5, 95%; n-C_3H_7, 61%; i-C_3H_7, 64%; i-C_4H_9, 73%.



R = C_2H_5, 90%; n-C_3H_7, 63%; i-C_3H_7, 69%; i-C_4H_9, 85%.



R = C_2H_5, 77%; n-C_3H_7, 74%; i-C_3H_7, 48%; i-C_4H_9, 59%.



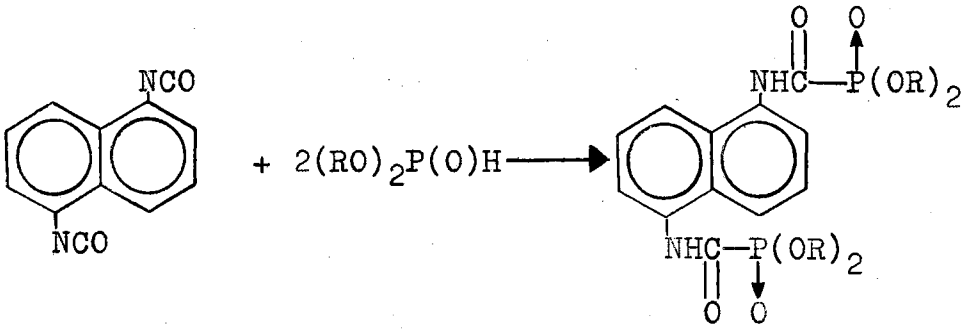
R = CH_3, 51%; C_2H_5, 36%; n-C_3H_7, 39%; i-C_3H_7, 35%;

n-C_4H_9, 41%; C_5H_{11}, 45%.

Both solid and liquid carbamoylphosphonates were obtained. With the exception of ethyl isocyanate, the liquid carbamoylphosphonates could not be distilled even at 1 mm without decomposition to the original reactants at temperatures on the order of 160°.

As reported by Reetz, et al.,[49] the above carbamoylphosphonates were fairly stable toward hydrolysis by water. However, the ease of hydrolysis of the aryl derivatives in acid or base depended upon the substituent on the aromatic

ring. The p-nitro derivatives hydrolyzed to p-nitroaniline, the amide linkage being cleaved. Kuznetsov and Bakhitov[24] found the reactions of 1,5-naphthylene diisocyanate with dialkyl hydrogenphosphonates, in the presence of sodium alkoxide, to proceed at steam-bath temperature to give tetraalkyl 1,5-naphthylenedicarbamoylphosphonates in 80-95% yields.



R = CH_3, C_2H_5, n-C_3H_7, C_4H_9, i-C_3H_7, i-C_4H_9,

i-C_5H_{11}, $CH_2{=}CHCH_2$.

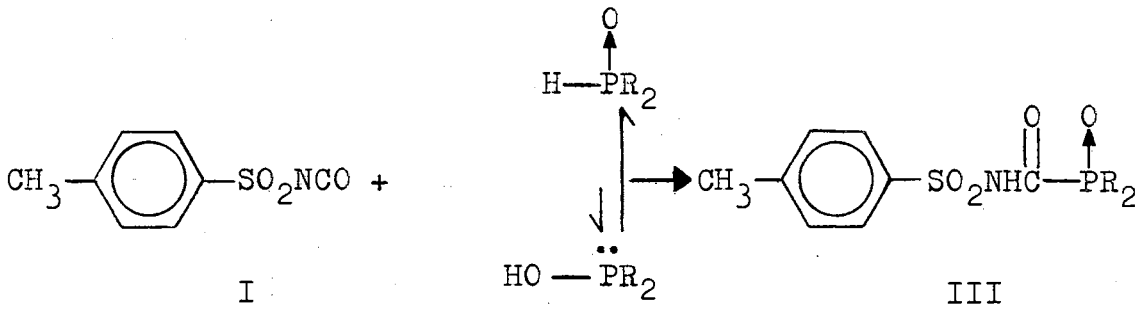
Under similar conditions, Kuznetsov and Bakhitov[25] conducted the reaction of hexamethylene diisocyanates with dialkyl hydrogenphosphonates. These reactions gave the expected adducts which were block-polymerized with methyl metacrylate, in the presence of 0.2% benzoyl peroxide. These polymers as adjuvants reduced the flammability of other material.

Dialkyl (carbamoylmethyl)phosphonates[57] have been patented as plasticizers, plastics, flameproofing and extreme-pressure additives and as insecticides and rodenticides.

CHAPTER II

DISCUSSION AND RESULTS

A series of disubstituted carbamoylphosphonates has been synthesized. The general equation for preparation of the products is illustrated.



I II III

R

a, CH_3O-

b, C_2H_5O-

c, n-C_3H_7O-

d, i-C_3H_7O-

e, n-C_4H_9O-

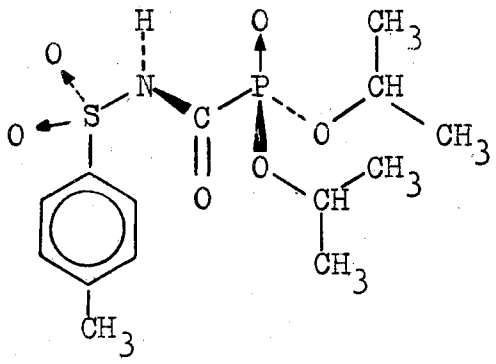
f, n-$C_8H_{17}O$-

g, $CH_2{=}CHCH_2O$-

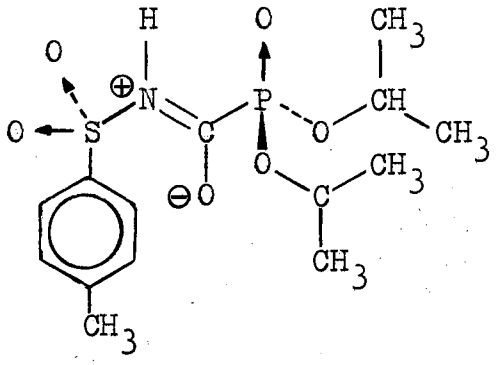
h, C_6H_5O-

i, C_6H_5-

Several members of this new class of compounds, p-toluenesulfonylcarbamoylphosphonates (72-97%), were synthesized by the addition of p-toluenesulfonyl isocyanate I to dialkyl (or aryl) hydrogenphosphonates II. A derivative, diphenyl-p-toluenesulfonylcarbamoylphosphine oxide, was prepared in 36% yield by a slightly modified procedure. NMR, IR and elemental analyses supported the structures of the products; physical properties are listed in Tables I, II and III. All the compounds investigated were acidic to sodium bicarbonate and the labile amide hydrogen was easily removed by deuterium oxide. $^{31}P - {}^{1}H$ splitting was observed in the NMR spectra of dialkyl derivatives and was attributed to $J_{P-O-C-H}$ coupling (0.5 - 11.0 c.p.s.). No long-range phosphorus splitting ($J_{P-O-C-C-H}$), as reported by Hellwege[21] for some systems, was observed for the compounds studied. However, a case of magnetic nonequivalence of methyl substituents of isopropyl groups was observed; a similar case was reported by Siddall and Prohaska.[55] Siddall[54] explained the magnetic nonequivalence of protons in several phosphorus esters and organonitrogen compounds in terms of symmetry properties. Slow rotation around the carbonyl-to-nitrogen bond in amides reduced the probability of a symmetrical system and the attached groups are therefore nonequivalent at room temperature. A difference in the environments of the methyl groups due to restricted rotation is believed to account for the nonequivalence of the methyl groups at room temperature in IIId.



IIId



Similar to the resonance forms usually written to show the double bond character of the C-N bond in amides, resonance forms for the carbamoylphosphonates may be written as shown. In IIId, rotation of the large isopropyl groups is probably slow, causing a nonequivalence of the two sets of geminal methyl groups.

The aromatic ring protons gave an A_2B_2 pattern with peaks at δ 7.34 - 7.45 and δ 7.81 - 8.04, J = 8 c.p.s. The A_2B_2 splitting pattern (ν_o = 29.5 - 33 c.p.s.) was observed for the p-toluenesulfonylcarbamoylphosphonates. The methyl group on the aromatic ring appears as a singlet at δ 2.28 - 2.46 in members of the series. A broad

multiplet at ca. δ 9.57-11.41 appeared for the NH proton of the amide linkage [δ 16.41 was observed for the diphenyl p-toluenesulfonylcarbamoylphosphonate (IIIh) amide proton in pyridine-d_5]. The methyl, methylene or methine proton adjacent to the corresponding alkoxy group showed a splitting pattern (~ 0.5 - 11 c.p.s.) which has been attributed to $^{31}P - {}^{1}H$ coupling. Protons alpha to oxygen in the alkoxy group gave coupling constants ~ 6.0 - 6.4 c.p.s. Terminal methyl protons of the alkoxy groups bonded to phosphorus appeared as a triplet (J ~ 5.0 - 6.8 c.p.s.). Decoupling of the alkoxyl group has not been attempted for the products III; therefore, the J values are approximate but probably not in error by more than 1-2 c.p.s. The remaining peaks appeared at δ values according to classical predictions.

The IR data for the dialkyl (and diaryl) p-toluenesulfonylcarbamoylphosphonates listed in Table II (Plates I-X) showed amide absorption at 3289-3333 cm^{-1}. Carbonyl frequencies were observed at 1686 - 1751 cm^{-1} and phosphoryl absorptions were found in the range of 1188 - 1276 cm^{-1}. The aliphatic P-O-C stretching frequencies were observed at 980 - 1060 cm^{-1}. Sulfonyl stretching frequencies were 1355 - 1366 cm^{-1} (asym.) and 1145 - 1188 cm^{-1} (sym.).

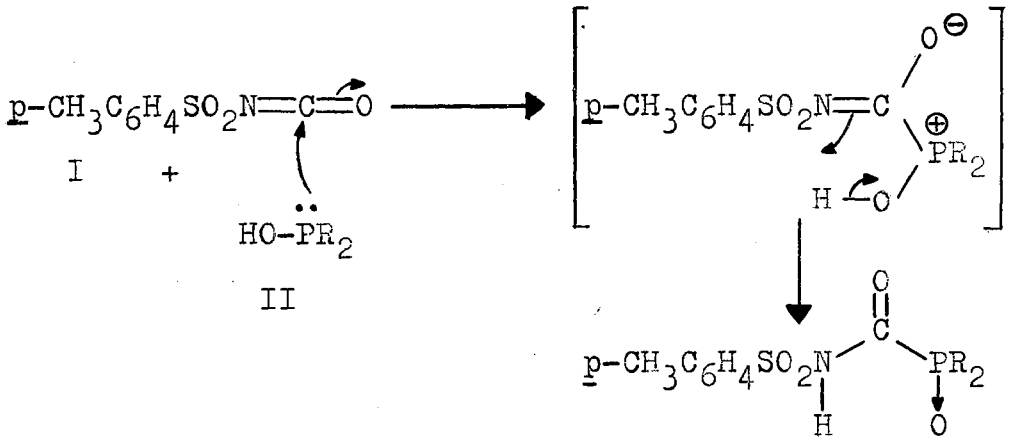
The value of the synthetic procedure was found in the formation of products at a low temperature. Unlike the method used by previous authors,[15,26,43,45,49] the reaction discovered in this work involved no catalyst. The increase in reactivity of I compared to isocyanates may be attributed

to the influence of the polar sulfonyl group adjacent to the isocyanato group. This arrangement greatly enhanced the electrophilicity of the isocyanato group and rendered it increasingly vulnerable to nucleophilic attack.

Tautomeric equilibrium (keto-enol forms) of dialkyl hydrogenphosphonates has been clarified in recent years by kinetic studies.[6,50,51] A mechanism involving nucleophilic attack by phosphorus has been proposed by Grayson, et al.[20] to account for the cleavage of the disulfide bond in diphenyl disulfide.

$$(\underline{p}\text{-}CH_3C_6H_4)_2P(O)H + C_6H_5SSC_6H_5 \longrightarrow (\underline{p}\text{-}CH_3C_6H_4)_2P(O)SC_6H_5 + C_6H_5SH$$

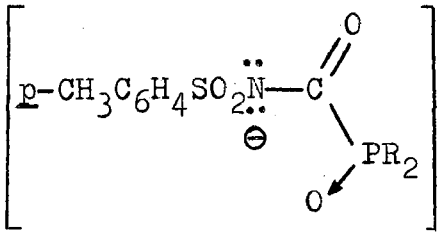
The reaction of I and II may proceed by nucleophilic attack of II (the trivalent-phosphorus form) on the isocyanato group followed by rearrangement of a suspected intermediate to give III.

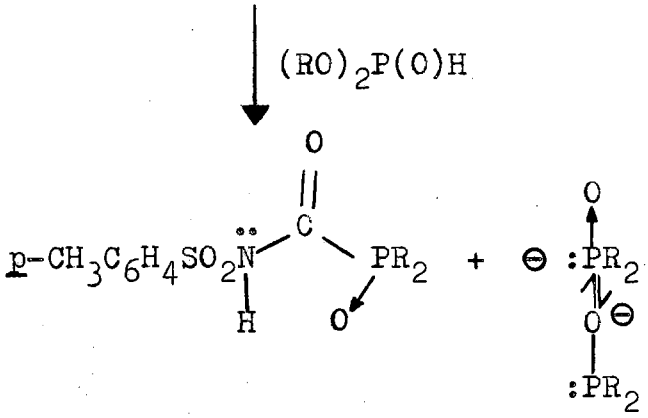


III

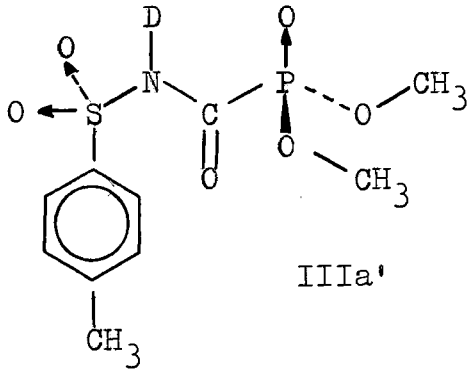
An alternate mechanism for the formation of product (after a probable intermediate is formed) could involve formation

of a phosphonate anion which propagate the reaction.





Compound IIIa was prepared by the addition of dimethyl hydrogenphosphonate (IIa) to p-toluenesulfonyl isocyanate (I). An amide band was observed in the IR spectrum (chloroform solution, Plate II) at 3300cm^{-1}; a broad multiplet appeared at ca. δ 11.18 in the NMR spectrum for the amide NH. Aromatic ring protons gave a typical A_2B_2 pattern, ν_0 = 30 c.p.s. (other data in Tables II and III). Treatment of a sample of IIIa with deuterium oxide caused the amide peak to disappear at δ 11.18 to give IIIa' (Plate XVI).



IIIa'

The sulfonyl stretching frequencies appeared at 1355 cm^{-1} and 1179 cm^{-1}, respectively. The phosphoryl bands appeared at 1274 and 1256 cm^{-1} when the IR was taken as KBr pellet; the chloroform solution gave a single band at 1266 cm^{-1}. The position of the phosphoryl band indicated the P→O group was unassociated.[7] The NMR spectrum of IIIa suggested the amide proton was highly deshielded; as might be suspected, this proton was acidic to sodium bicarbonate.

Compound IIIb under similar conditions gave, in addition to the expected NMR aromatic pattern, a pseudo quintet (overlapping of two quartets) at δ 4.19, J = ca. 6.4 c.p.s. The amide proton of IIIb was considerably more shielded, appeared at ca. δ 9.57. Methyl protons of the ethoxy group appeared as a triplet at δ 1.30 with a coupling constant of 6.4 c.p.s. The IR data, as given in Table II, showed an amide hydrogen at 3311 cm^{-1}, a carbonyl absorption at 1692 cm^{-1}, phosphoryl at 1267 cm^{-1} and the SO_2 stretching frequencies at 1355 and 1183 cm^{-1}.

In the phosphonate IIIc, IR bands for the amide, carbonyl and phosphoryl appeared at 3333, 1686 and 1264 cm^{-1},

respectively (data is in Table II). NMR analysis showed the expected triplet at δ 0.89 (J = 6.8 c.p.s.) for the methyl group in the propyl function. A sextet appeared for the CH_2 protons of this function with a coupling constant of 6.4 c.p.s. The aromatic A_2B_2 pattern (ν_o = 31.5 c.p.s.), appeared in positions given in Table III. The amide proton appeared as a broad multiplet ca. δ 11.37. For IIIc $J_{P-O-C-H}$ was approximately 7.4 c.p.s. for the methylene protons ($O\underline{CH_2}CH_2CH_3$) attached to oxygen.

A case of magnetic nonequivalence for the methyl proton (which has been attributed to restricted rotation around the amide bond) is observed for the diisopropyl ester IIId, which has signals appearing as two overlapping doublets at δ 1.32 and δ 1.27 (field separation of 3.0 c.p.s.). The expected heptet was observed for the methine protons with indications of $J_{P-O-C-H}$ splitting. However, the coupling constants could not be interpreted without spin-spin decoupling of the methyl groups. Characteristic IR bands are observed for compound IIId as indicated in Table II. A shoulder at 1239 cm^{-1} came in the hydrogen-bonding region for phosphoryl groups. Asymmetric and symmetric stretch appeared at 1356 and 1179 cm^{-1} for SO_2.

NMR data on compound IIIe contained an A_2B_2 pattern (ν_o = 32 c.p.s.) and a $J_{P-O-C-H}$ = ca. 7.8 c.p.s. (Table III). A shoulder appeared at 1751 cm^{-1} in addition to the carbonyl band at 1695 cm^{-1}. The SO_2 bands appeared at 1355 and 1179 cm^{-1} due to asymmetric and symmetric stretching

frequencies. Other frequencies are given in Table II.

Compound IIIf has a shoulder at 1748 cm^{-1} in addition to the carbonyl band at 1692 cm^{-1}. The bands at 1355 cm^{-1} and 1177 cm^{-1} were due to asymmetric and symmetric stretching of the SO_2 group. The NMR spectrum IIIf showed a triplet at δ 0.88 (J = 5.0 c.p.s.), two overlapping triplets at δ 4.12 (J = ca. 6.2 c.p.s.) and $^{31}P - {}^{1}H$ splitting of ca. 7.6 c.p.s.; a multiplet was observed at δ 10.61 and attributed to the NH proton. The A_2B_2 pattern for the aromatic proton has a ν_o = 33 c.p.s. (Tables II and III).

Carbonyl absorption for IIIg appeared at 1704 cm^{-1} while the SO_2 asymmetric stretching band absorbs at 1359 cm^{-1} and the symmetric stretching band appeared at 1182 cm^{-1}. The phosphoryl band was shifted toward longer wave length (1248 cm^{-1}) [compared to the saturated compounds] owed to conjugation of the alkoxy group with the allyl group. NMR signals for this compound gave a complex splitting pattern due to cis-trans coupling of the allyl protons and $^{31}P - {}^{1}H$ splitting. The centers of the multiplet patterns are given in Table III.

The usual absorptions for the amide, carbonyl and phosphoryl bands appeared at 3322, 1704 and 1276 cm^{-1}, respectively, for compound IIIh. NMR analysis showed a complex multiplet centered at δ 7.12; aromatic protons adjacent to the sulfonyl group gave a doublet at δ 8.30 (J = 8.0 c.p.s.). The NH peak (in tetramethylurea) appeared at δ 10.85 (the same peak in pyridine-d_5 appeared at δ 16.14).

Compound IIIi had absorption bands appearing at a lower frequency than the carbamoylphosphonates IIIa-h. The decreased frequencies of the amide, carbonyl and phosphoryl bands at 3289, 1686 and 1188 cm^{-1}, respectively, may be attributed to the direct conjugation of the benzene ring with the phosphoryl moiety.[56] Other significant absorption bands are shown in Table II. NMR signals for this compound included a complex multiplet centered at δ 7.57; the aromatic methyl appeared as a singlet at δ 2.39 and the amide peak as a broad multiplet at ca. δ 10.61.

Thus, a new class of compounds, p-toluenesulfonyl-carbamoylphosphonates, have been prepared in good yields by the addition of p-toluenesulfonyl isocyanate to dialkyl or diaryl hydrogenphosphonates. Attempts to distill liquid products, even under high vacuum (10^{-3} mm), resulted in extensive decomposition. Purification of members IIIe and IIIf by careful washing with a mixture of solvents gave samples from which the data was recorded in the Tables.

The most novel feature observed for this class of compound was the highly deshielded character and acidity of the amide proton. These compounds were also found to be unusually stable toward aqueous hydrolysis.

IR and NMR spectra have been recorded and used to characterize the carbamoylphosphonates.

TABLE I

PHYSICAL PROPERTIES OF PRODUCTS

Compound	M.p., °C	Yield, %	Analysis, %					
			N		P		S	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
IIIa	126-127	72	4.56	4.79	10.08	10.22	10.44	10.52
IIIb[a]	70.5-71.5	95.6[b]	4.18	---	9.24	10.01	9.56	10.28
IIIc	73-74	90	3.86	---	8.52	8.43	8.82	8.78
IIId	92.5-93.5	87.5	3.86	3.72	8.52	8.50	8.82	8.92
IIIe[a]	---	77.5	3.58	---	7.91	---	8.19	---
IIIf[a]	---	97.7	3.64	---	6.15	---	6.37	---
IIIg	87.5-88.5	97.0	3.87	---	8.62	8.51	8.89	8.72
IIIh	139.5-41.5	83.5	3.25	3.36	7.18	7.52	7.43	7.83
IIIi	133.5-34.5(dec.)	36.1	3.51	3.39	7.76	7.80	8.02	8.15

[a]Refractive indices of compounds IIIb, IIIe and IIIf were n_D^{26} 1.5130, n_D^{27} 1.5060, n_D^{27} 1.4806, respectively. These compound were undistillable oils which were purified by petroleum ether extraction.

[b]Compound crystallized in part from petroleum ether to give 1.40% solid and remaining per cent viscous liquid.

TABLE II

INFRARED ABSORPTION BANDS (cm^{-1}) OF PRODUCTS[a,b]

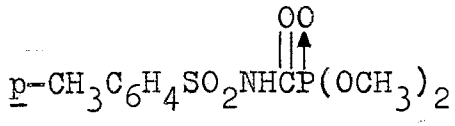
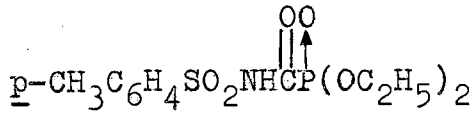
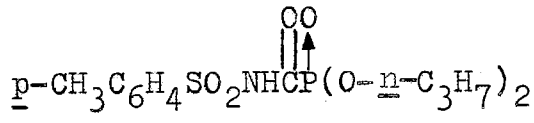
Compound	Amide[c]	C=O	P→O	Additional Bands
 IIIa	3300	1686	1274,1256	1464,1355,1197, 1179,1151,1053
 IIIb	3311	1692	1267	1451,1356,1196, 1183,1154,1024
 IIIc	3333	1686	1264	1451,1356,1193, 1184,1156,1036, 1008

TABLE II (CONTINUED)

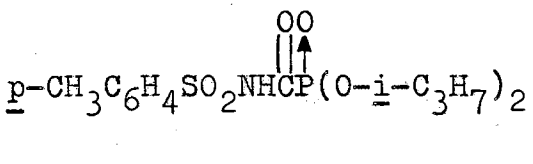
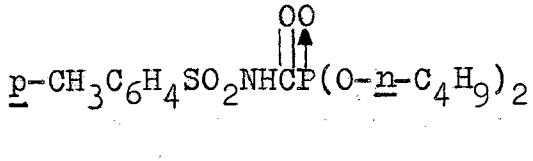
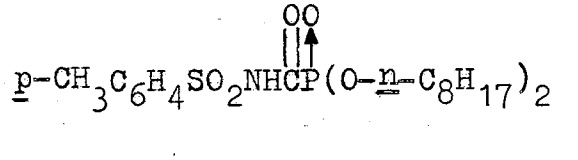
Compound	Amide	C=O	P→O	Additional Bands
 IIId	3322	1692	1261 (shoulder at 1239)	1460,1356,1194 1179,1156,1007
 IIIe	3333	1751, 1695	1250	1456,1355,1194, 1179,1162,1028
 IIIf	3333	1692 (shoulder at 1748)	1252	1451,1355,1193, 1177,1158,1018

TABLE II (CONTINUED)

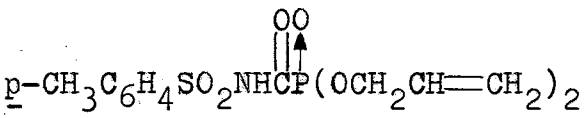
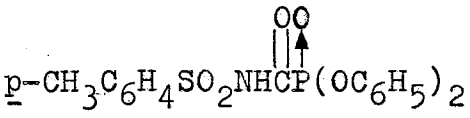
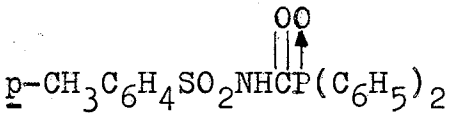
Compound	Amide	C=O	P→O	Additional Bands
 IIIg	3311	1704	1248	1451,1359,1195, 1182,1147,990
 IIIh	3322	1704	1276	1488,1366,1196, 1188,1161
 IIIi	3289	1686	1188	1355,1192,1145, 1086,767

TABLE II (CONTINUED)

[a]Spectra of IIIa, IIIb, IIIc, IIId, IIIg, IIIh and IIIi were determined in KBr pellets.

[b]Compounds IIIe and IIIf were observed as films on NaCl plates.

[c]All amide bands were observed in chloroform solutions obtained by using a rock salt cell having a film thickness of 0.1 mm. The solvent absorptions were balanced in the spectra by adjustment of a variable-path wedge rock salt cell which opposed the second solution- (or solvent-) containing cell. Both cells were obtained from Barnes Engineering Company, Stamford, Conn.

TABLE III

NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS OF PRODUCTS

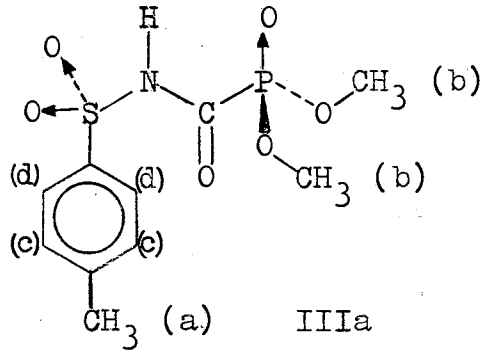
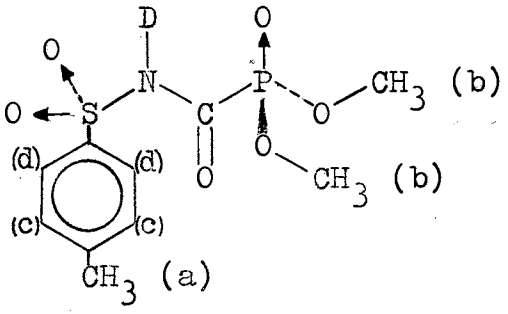
Compound	Plate	Solvent	δ(values) (p.p.m.)[a,b]	J(c.p.s.)	Assignment
 IIIa	XV	$CDCl_3$	2.44s	- - -	CH_3 (a)
			3.86d	11.0	CH_3 (b)
			7.38d	8.0	C_6H_4 (c)
			7.88d	8.0	C_6H_4 (d)
			11.18m(broad)	- - -	NH
	XVI	$CDCl_3$	2.45s	- - -	CH_3 (a)
			3.85d	11.C	CH_3 (b)
			7.42d	8.0	C_6H_4 (c)
			7.91d	8.0	C_6H_4 (d)

TABLE III (CONTINUED)

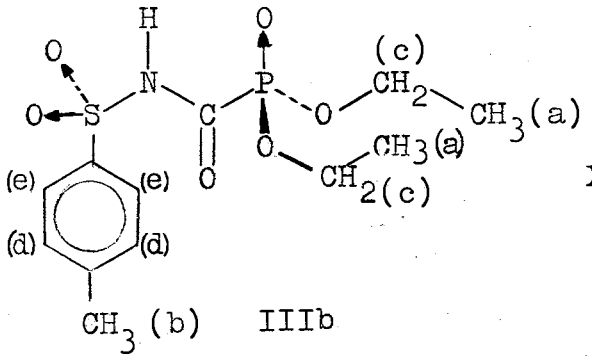
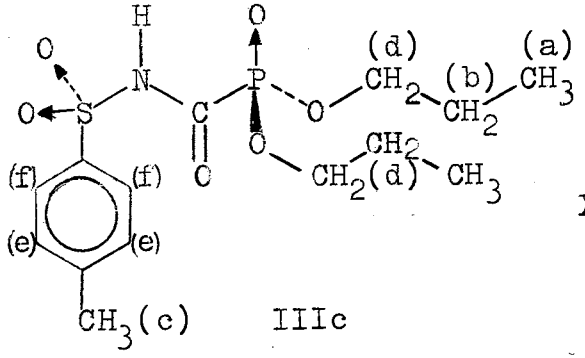
Compound	Plate	Solvent	δ(values) (p.p.m.)[a,b]	J(c.p.s.)	Assignment
 IIIb	XVII	$CDCl_3$	1.30t	6.4	CH_3 (a)
			2.42s	- - -	CH_3 (b)
			4.23m	6.4	CH_2 (c)
			7.39d	8.0	C_6H_4 (d)
			7.91d	8.0	C_6H_4 (e)
			ca. 9.57(broad)	- - -	NH
 IIIc	XVIII	$CDCl_3$	0.89t	6.8	CH_3 (a)
			1.69s'	6.4	CH_2 (b)
			2.46s	- - -	CH_3 (c)
			4.10,423dt[c]	6.4,7.4	CH_2 (d)
			7.45d	8.0	C_6H_4 (e)
			7.84d	8.0	C_6H_4 (f)
			ca.11.37(broad)	- - -	NH

TABLE III (CONTINUED)

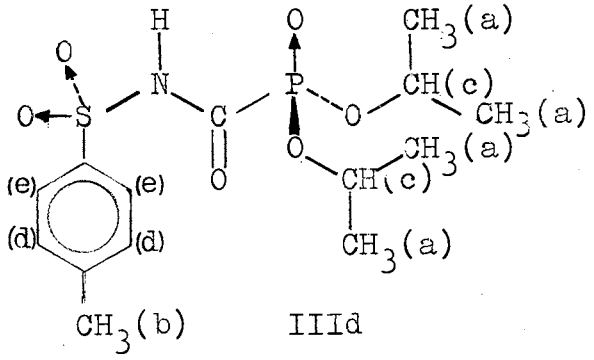
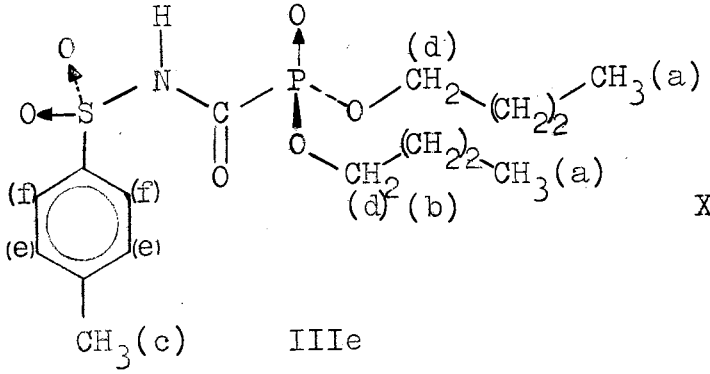
Compound	Plate	Solvent	δ(values) (p.p.m.)[a,b]	J(c.p.s.)	Assignment
 IIId	XIX	$CDCl_3$	1.27,1.32dd[d]	6.0	CH_3 (a)
			2.43s	---	CH_3 (b)
			4.82m	6.2	CH (c)
			7.38d	8.0	C_6H_4 (d)
			7.90d	8.0	C_6H_4 (e)
			11.27(broad)	---	NH
 IIIe	XX	$CDCl_3$	0.86t	6.0	CH_3 (a)
			1.49m	---	CH_2 (b)
			2.38s	---	CH_3 (c)
			4.08,4.20dt[e]	6.0,7.8	CH_2 (d)
			7.34d	8.0	C_6H_4 (e)
			7.87d	8.0	C_6H_4 (f)
			ca.11.06(broad)	---	NH

TABLE III (CONTINUED)

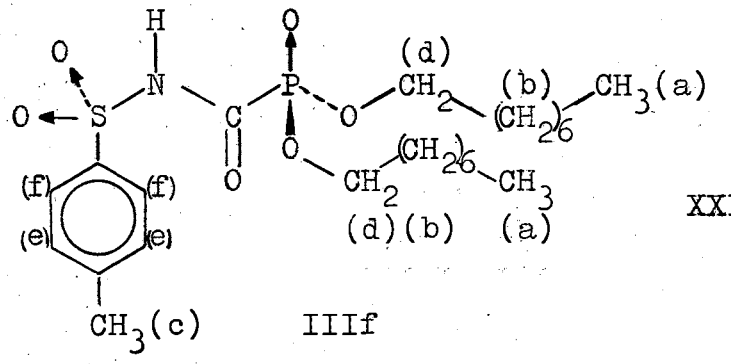
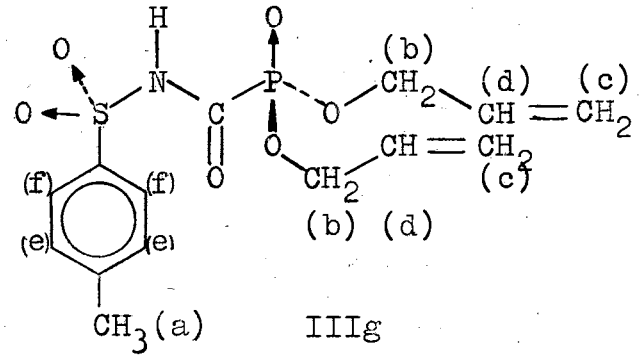
Compound	Plate	Solvent	δ(values) (p.p.m.)[a,b]	J(c.p.s.)	Assignment
 IIIf	XXI	$CDCl_3$	0.88t	5.0	CH_3 (a)
			1.26m	---	CH_2 (b)
			2.43s	---	CH_3 (c)
			4.08,4.22dt[f]	6.2,7.6	CH_2 (d)
			7.39d	8.0	C_6H_4 (e)
			7.81d	8.0	C_6H_4 (f)
			ca.10.61(broad)	---	NH
 IIIg	XXII	$CDCl_3$	2.43s	---	CH_3 (a)
			4.70m	---	CH_2 (b)
			5.47,5.30,5.17m	---	CH_2 (c)
			5.97m	4.6	CH (d)
			7.35d	8.0	C_6H_4 (e)
			8.04d	8.0	C_6H_4 (f)
			11.41(broad)	---	NH

TABLE III (CONTINUED)

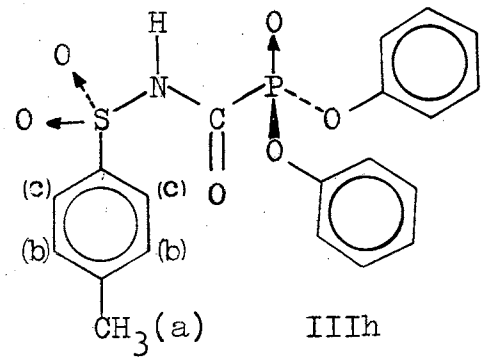
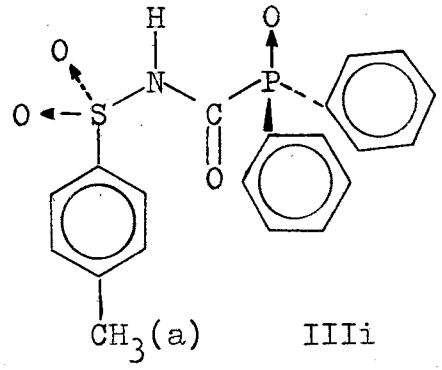
Compound	Plate	Solvent	δ(values) (p.p.m.)[a,b]	J(c.p.s.)	Assignment
 IIIh	XXIII	pyridine-d_5	2.21s	---	CH_3 (a)
			7.12m	---	C_6H_4, C_6H_5 (b)
			8.30d	8.0	C_6H_4 (c)
			16.14, 10.85[g]	---	NH
 IIIi	XXIV	$CDCl_3$	2.39s	---	CH_3 (a)
			7.57m	---	C_6H_4, C_6H_5
			10.61(broad)	---	NH

TABLE III (CONTINUED)

[a]All spectra were run at a sweep width of 1000 c.p.s. and all chemical shifts are reported at sweep widths of 500 c.p.s.

[b]The multiplicity of each peak is indicated as follows: singlet, s; doublet, d; triplet, t; quartet, q; sextet, s'; multiplet, m; doublet of doublets, dd; and doublet of triplets, dt.

[c]Two overlapping triplets were observed at the field positions indicated due to $^{31}P-^{1}H$ splitting.

[d]Magnetically nonequivalent methyl groups were observed at the field positions above.

[e]Overlapping triplets were observed due to $^{31}P-^{1}H$ splitting.

[f]$^{31}P-^{1}H$ splitting gave two overlapping triplets with the chemical shifts indicated.

[g]This NH field position was observed in tetramethylurea.

CHAPTER III

EXPERIMENTAL[a-d]

Starting Materials. The following chemical reagents were purchased: p-toluenesulfonyl isocyanate, n_D^{20} 1.5357, Aldrich Chemical Co., Inc.; dimethyl hydrogenphosphonate, n_D^{27} 1.3989 [lit.[23], b.p. 56.5°/8mm, n_D^{20} 1.4036], diethyl hydrogenphosphonate, n_D^{27} 1.4066 [lit.[23], b.p. 72-3°/9mm, n_D^{20} 1.4073], dibutyl hydrogenphosphonate, n_D^{27} 1.4193 [lit.[23], b.p. 116-7°/8mm, n_D^{20} 1.4240], Virginia-Carolina Chemical Corporation; diphenyl hydrogenphosphonate, n_D^{28} 1.5531 [lit.[23], b.p. 218-9°/25mm]; triisopropyl phosphite, n_D^{28} 1.4079 b.p. 60-1°/8-10mm[23], Virginia-Carolina Chemical Corporation; triallyl phosphite, n_D^{28} 1.4552, Hooker Chemical Corporation; diphenylphosphinous chloride, b.p. 178-80°/18mm, Columbia Organic Chemical Co., Incorporated.

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[a] All melting points are corrected; all boiling points are uncorrected. Skelly solvent F and petroleum ether boiled 30-60°.

[b] The infrared spectra were determined on a Beckman IR-5A as films on sodium chloride cells or as potassium bromide pellets unless otherwise specified.

[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.

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

Preparation of Dimethyl p-Toluenesulfonylcarbamoylphosphonate (IIIa). A 50-ml., one-neck, round-bottom flask fitted with a drying tube (3A molecular sieve), magnetic stirring bar and nitrogen inlet was charged by dropwise addition of 3.32 g. (0.0169 mole) of p-toluenesulfonyl isocyanate to 1.80 g. (0.0164 mole) of dimethyl hydrogenphosphonate dissolved in 25 ml. of anhydrous diethyl ether at -5°. The resulting mixture was allowed to warm to room temperature with stirring over an 11-hour period. A white, crystalline precipitate formed and the ether was decanted. The compound was washed with ether (10 ml.) 10 times; weight 3.74 g (72%), m.p. 124.5-26°. A sample recrystallized from aqueous methanol gave the physical properties indicated in Tables I, II and III.

Preparation of Diethyl p-Toluenesulfonylcarbamoylphosphonate (IIIb). p-Toluenesulfonyl isocyanate (6.11g., 0.031 mole) was added dropwise to 4.28 g. (0.0310 mole) of diethyl hydrogenphosphonate (in a flask equipped as described in the previous preparation) dissolved in 15 ml. of anhydrous diethyl ether at -5° and the reaction mixture was allowed to warm to room temperature with stirring for 11 hours. The ether was evaporated under aspirator pressure and there was obtained an undistillable, viscous liquid which was extracted with petroleum ether-methylene chloride solution. The residual oil weighed 10.0 g. (95.6%), n_D^{26} 1.5130. The extract was concentrated and cooled to give 0.15 g. (1.4%) of a sample having the properties indicated

in the Tables.

Preparation of Di-n-propyl p-Toluenesulfonylcarbamoylphosphonate (IIIc). A system equipped in the usual manner was charged by the dropwise addition of 6.18 g. (0.03135 mole) of p-toluenesulfonyl isocyanate to 5.21 g. (0.03135 mole) of di-n-propyl hydrogenphosphonate[28] dissolved in 15 ml. of anhydrous diethyl ether at -5°. The reacting mixture was stirred for 11 hours, and the ether was evaporated under aspirator pressure; a white crystalline compound (10.23 g., 90%), m.p. 61-4°(hexane), formed. Recrystallization from aqueous ethanol gave a solid with the properties indicated in Tables I, II and III.

Preparation of Diisopropyl p-Toluenesulfonylcarbamoylphosphonate (IIId). To a flask (equipped as in previous preparations) containing 5.15 g. (0.0309 mole) of diisopropyl hydrogenphosphonate[38], dissolved in 15 ml. of anhydrous diethyl ether at -5°, was added 6.10 g. (0.0309 mole) of p-toluenesulfonyl isocyanate. The resulting mixture was allowed to warm with stirring as usual and the ether removed under aspirator pressure to give 9.80 g. (87.5%) of a white crystalline solid, m.p. 82-92°(hexane). A sample was recrystallized from aqueous ethanol to give material with the properties indicated in the Tables.

Preparation of Di-n-butyl p-Toluenesulfonylcarbamoylphosphonate (IIIe). Dibutyl hydrogenphosphonate (6.04 g., 0.0311 mole) in 5 ml. of anhydrous diethyl ether at 25° was placed in a 50-ml. flask equipped as described in previous

preparations. p-Toluenesulfonyl isocyanate (6.12 g., 0.0310 mole) was added dropwise and the reagents were stirred for 11 hours. Evaporation of the ether, in the usual manner, gave a viscous liquid which was extracted with 10 15-ml. portions of petroleum ether. The product obtained, n_D^{27} 1.5060, weighed 9.40 g. (77.5%). Spectral data is found in the Tables.

Preparation of Di-n-Octyl p-Toluenesulfonylcarbamoylphosphonate (IIIf). p-Toluenesulfonyl isocyanate (3.49 g., 0.0177 mole) was added dropwise to 5.41 g. (0.0177 mole) of di-n-octyl hydrogenphosphonate[28], in 15 ml. of anhydrous ether, in a system assembled as in previous experiments at -5°. The stirred reagents were allowed to warm over an 11-hour period and the ether was evaporated in the usual manner. Upon extracting the residual oil with petroleum ether, at acetone-dry ice bath temperature, there was obtained a liquid weighing 8.7 g. (97.7%), n_D^{27} 1.4806. The Tables contain pertinent spectra data.

Preparation of Diallyl p-Toluenesulfonylcarbamoylphosphonate (III g). To a solution of diallyl hydrogenphosphonate[38] (5.02 g., 0.0309 mole) in 15 ml. of anhydrous diethyl ether at -5°, was added 6.10 g. (0.0309 mole) of p-toluenesulfonyl isocyanate as specified in previous preparations. After a reaction time of 11 hours, the ether was evaporated to give 10.79 g. (97%) of product. Recrystallization of a sample from a petroleum ether-chloroform solution gave m.p. 87.5-8.5°. The data shown in Tables I,

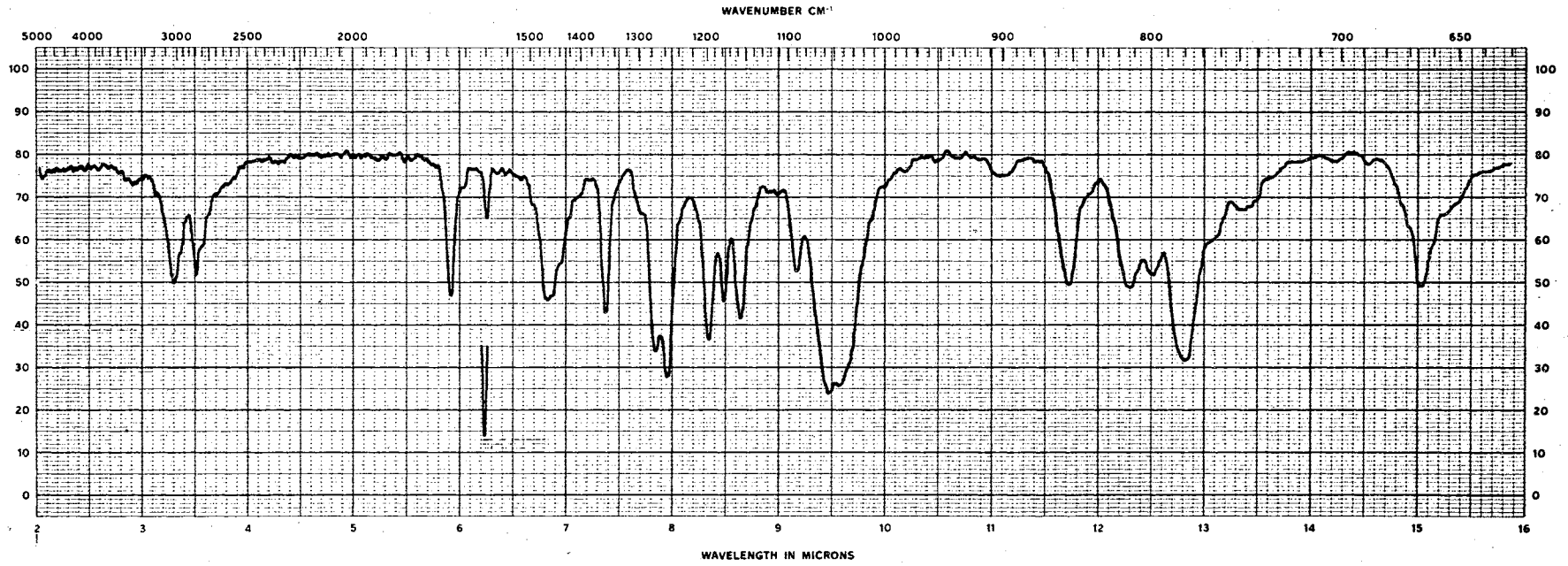
II and III indicated that the predicted product was indeed obtained.

Preparation of Diphenyl p-Toluenesulfonylcarbamoylphosphonate (IIIh). p-Toluenesulfonyl isocyanate (6.13 g., 0.0310 mole) was added to 7.29 g. (0.0310 mole) of diphenyl hydrogenphosphonate dissolved in 25 ml. of diethyl ether at -5°. After a reaction time of 11 hours under conditions similar to those in previous preparations, a white crystalline solid was obtained and the ether was decanted. The product was washed with ether (10 ml.) ten times, weight 11.18 g. (83.5%), m.p. 139-41°. Recrystallization from aqueous methanol gave a sample with the properties indicated in Tables I, II and III.

Preparation of Diphenyl-p-toluenesulfonylcarbamoylphosphine Oxide (IIIi). To a 50-ml. flask, equipped in the usual manner, was added 0.820 g. (0.0456 mole) of water to 10.03 g. (0.0456 mole) diphenylphosphinous chloride dissolved in 20 ml. of anhydrous diethyl ether. An insoluble, white, crystalline product [presumably $(C_6H_5)_2P(O)H$] formed after 0.5 hour; this immediately absorbed water when a small sample was exposed to the atmosphere. To the ether suspension was added dropwise at 0°, 9.52 g. (0.0484 mole) of p-toluenesulfonyl isocyanate. The reaction mixture was allowed to warm to room temperature, with stirring for 11 hours. There was obtained 6.56 g. (36.1% based on phosphinous chloride) of a white, insoluble product; a m.p. 133.5-4.5°(dec.) was obtained after washing the solid with

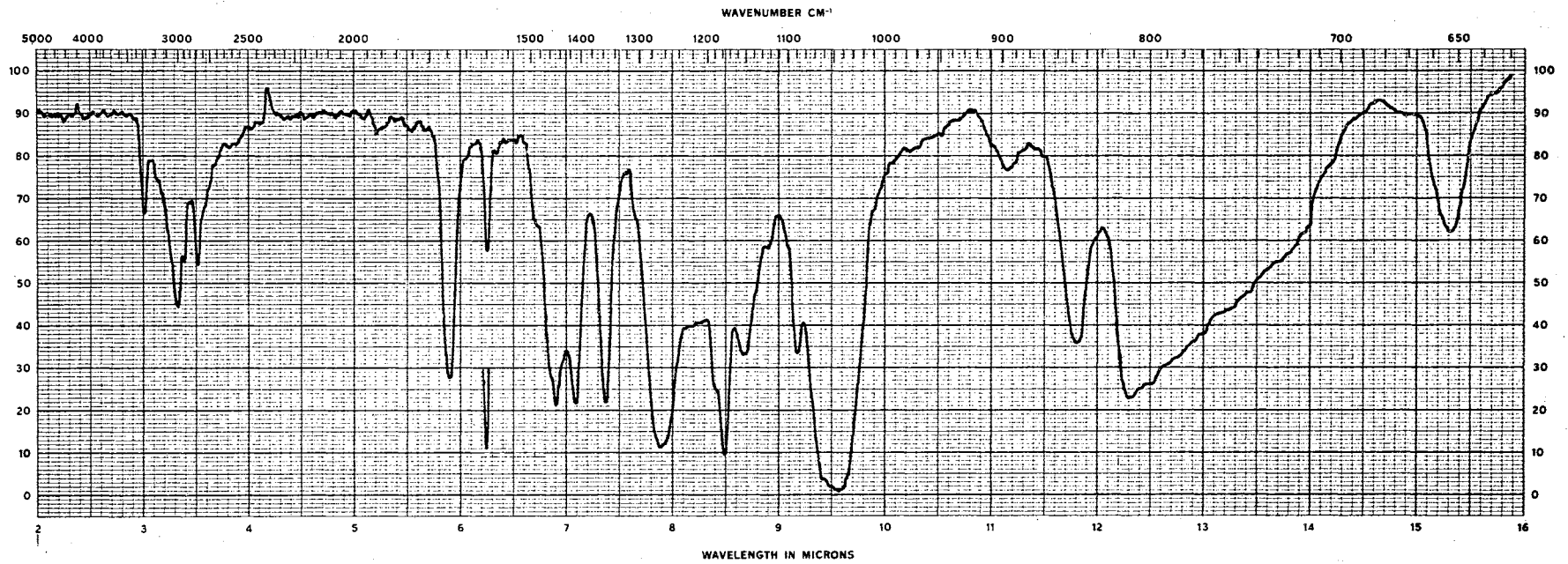
ten 20-ml. portions of anhydrous diethyl ether.

Plate I



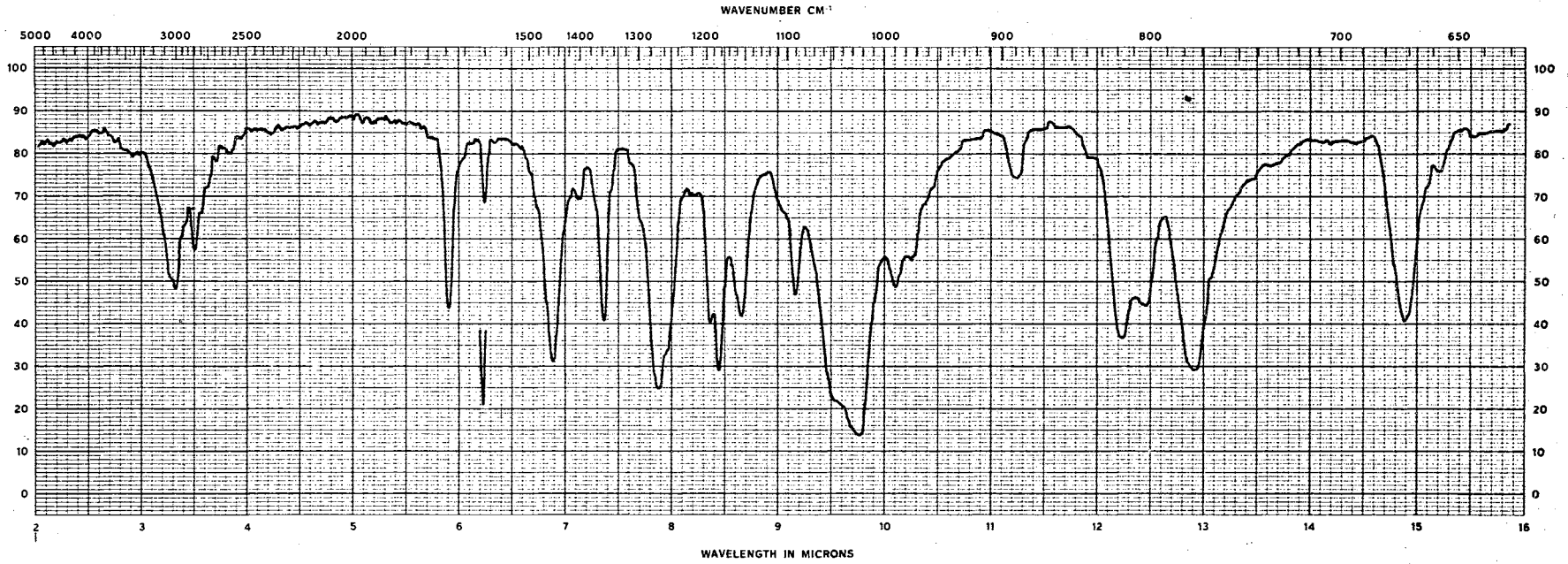
Dimethyl p-Toluenesulfonylcarbamoylphosphonate (IIIa), KBr Pellet

Plate II



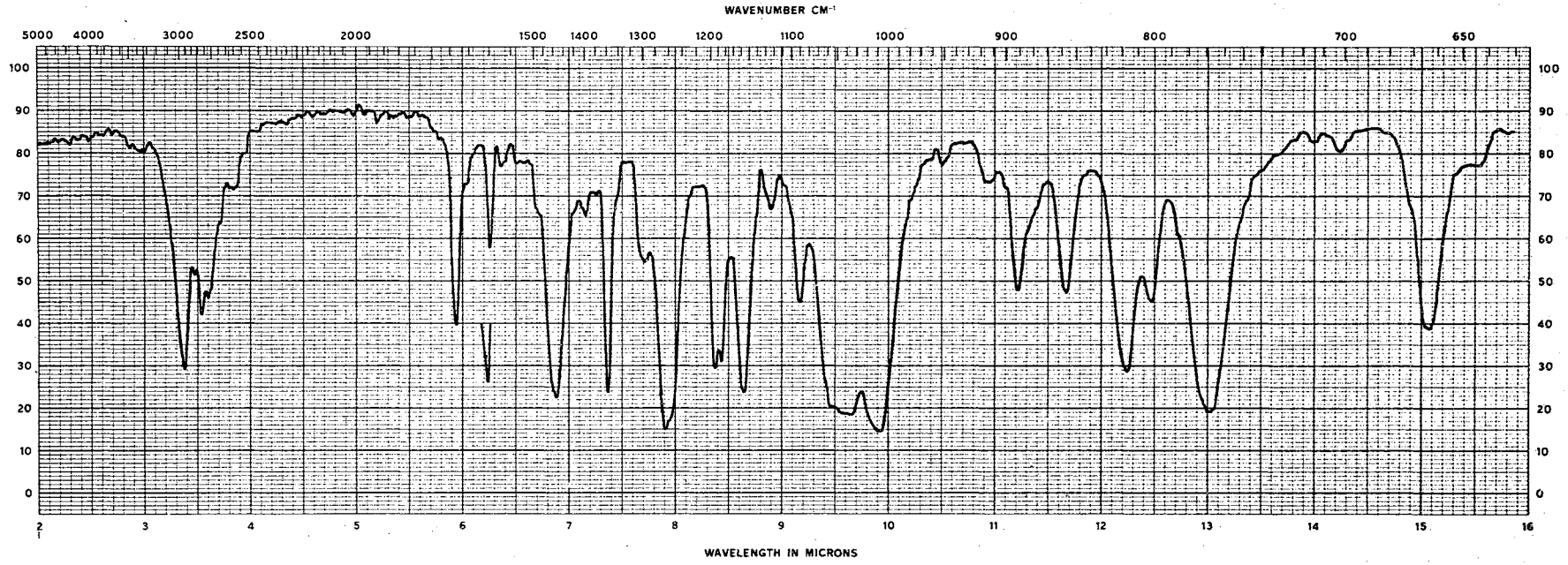
Dimethyl p-Toluenesulfonylcarbamoylphosphonate (IIIa), Chloroform Solution

Plate III



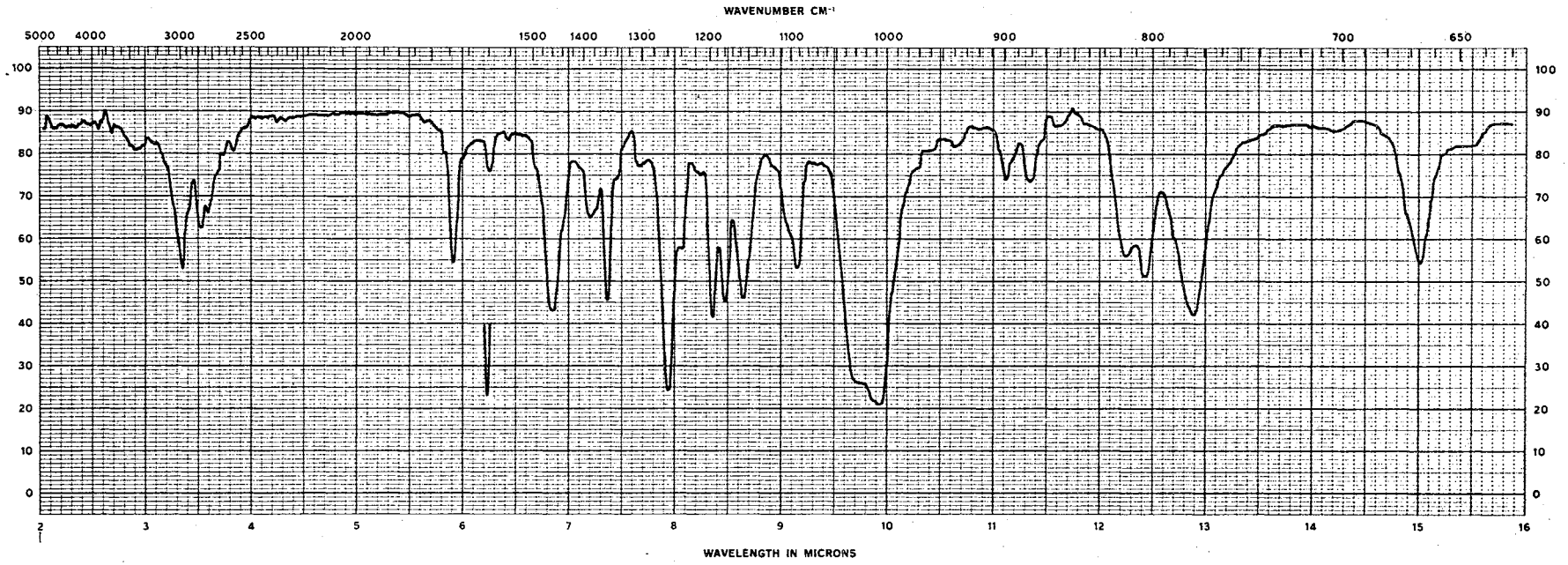
Diethyl p-Toluenesulfonylcarbamoylphosphonate (IIIb), KBr Pellet

Plate IV



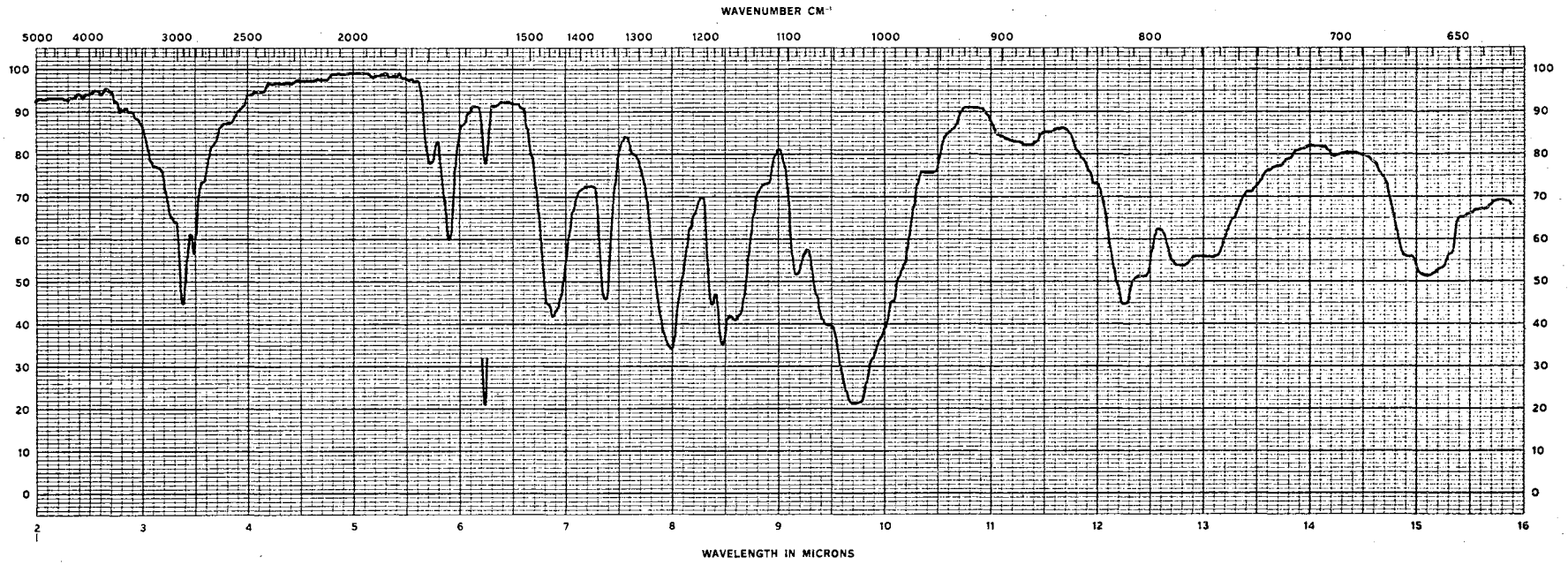
Di-n-propyl p-Toluenesulfonylcarbamoylphosphonate (IIIc), KBr Pellet

Plate V



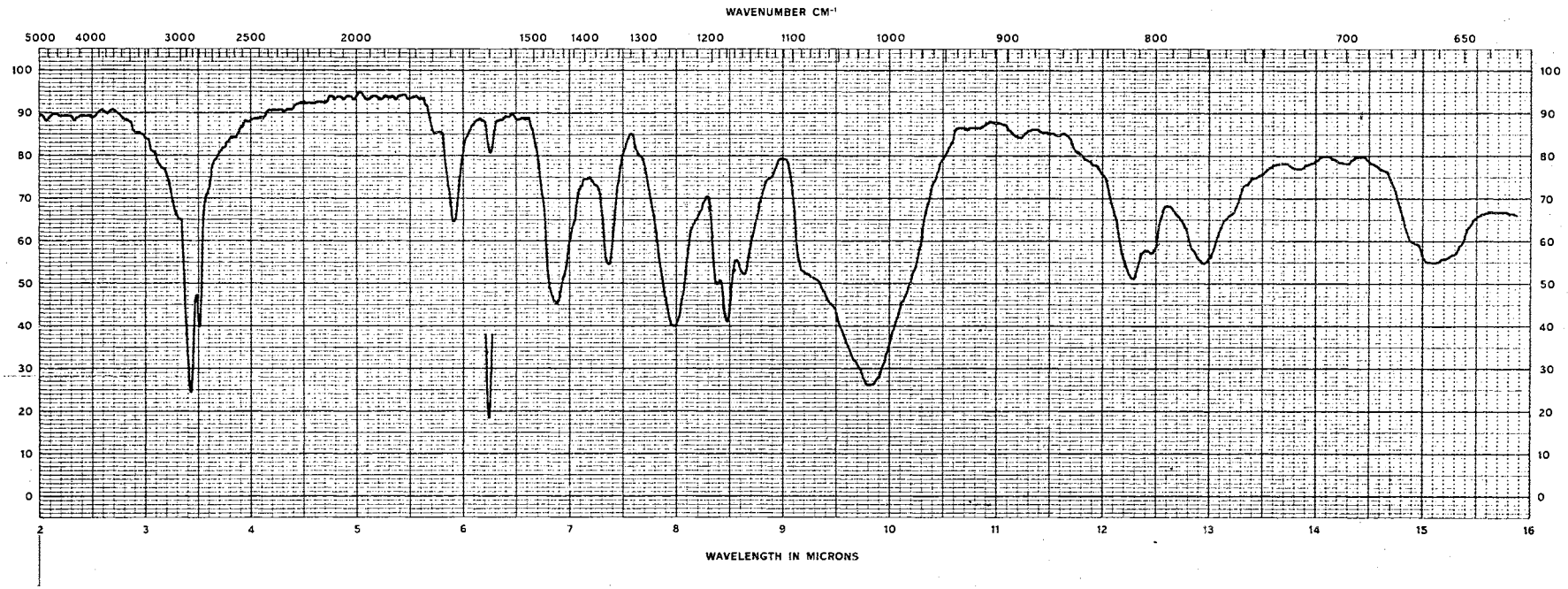
Diisopropyl p-Toluenesulfonylcarbamoylphosphonate (IIId), KBr Pellet

Plate VI



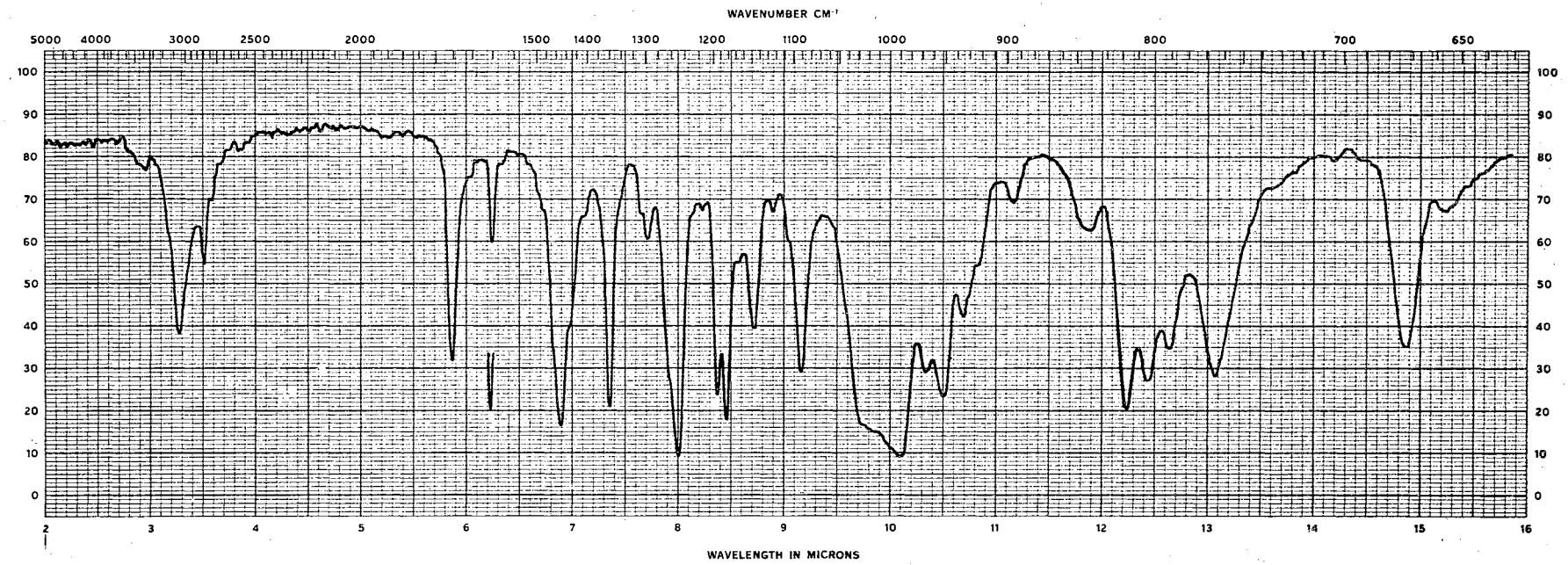
Di-n-butyl p-Toluenesulfonylcarbamoylphosphonate (IIIe), Film on NaCl Plates

Plate VII



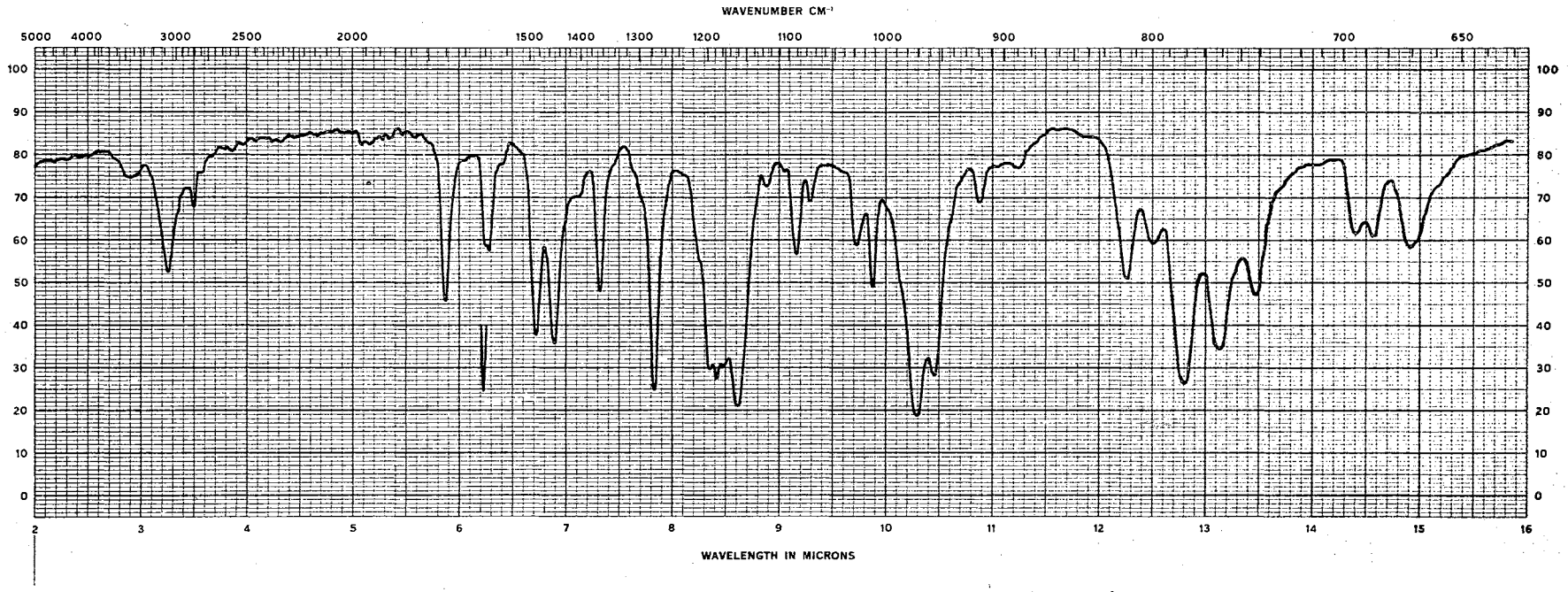
Di-n-octyl p-Toluenesulfonylcarbamoylphosphonate (IIIf), Film on NaCl Plates

Plate VIII



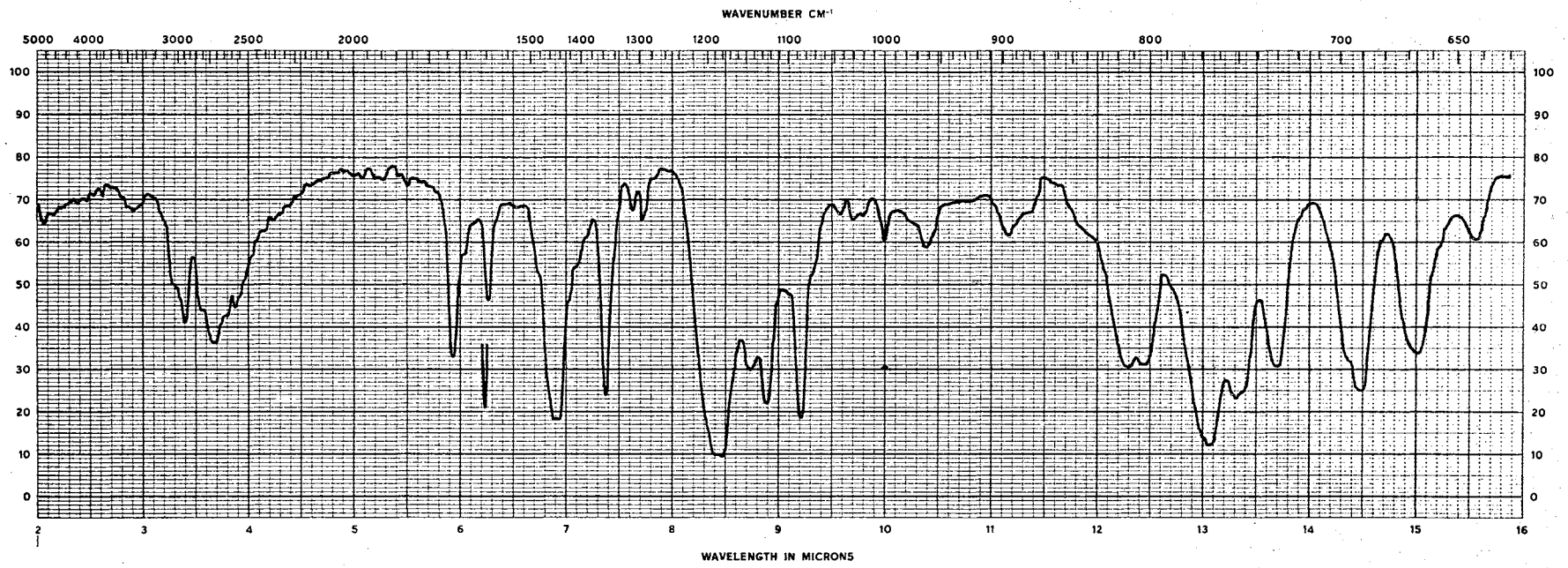
Diallyl p-Toluenesulfonylcarbamoylphosphonate (IIIg), KBr Pellet

Plate IX



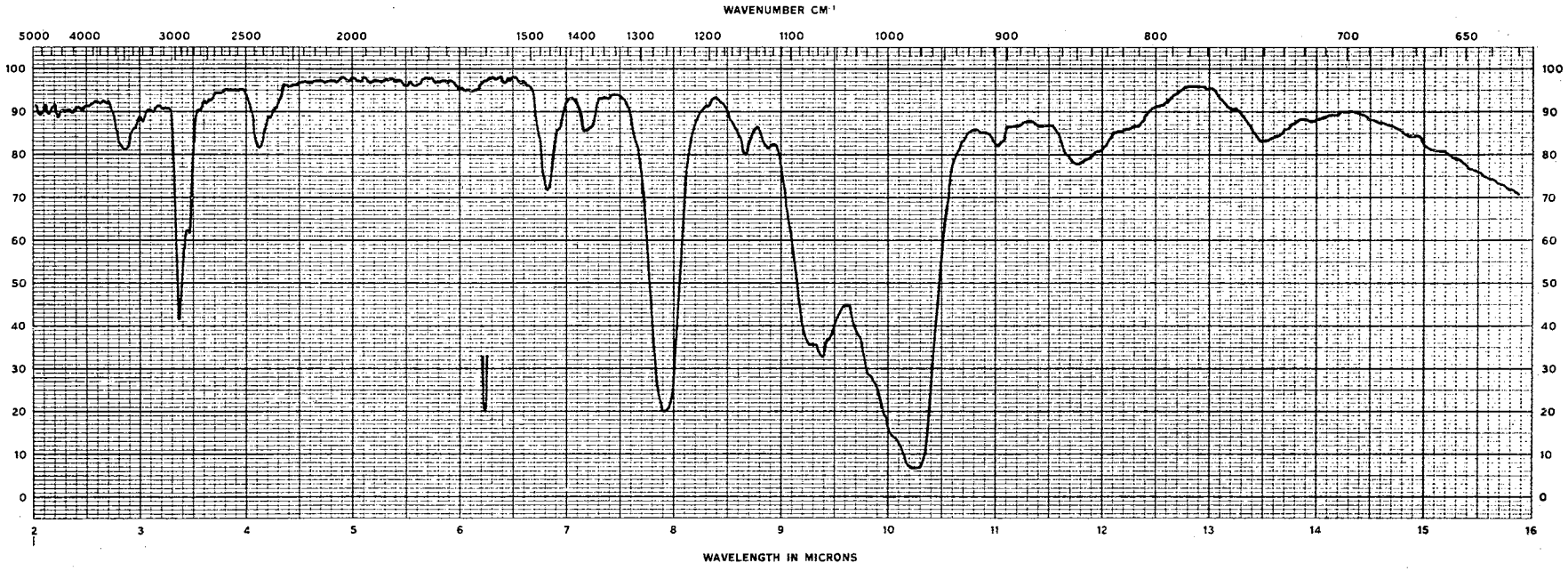
Diphenyl p-Toluenesulfonylcarbamoylphosphonate (IIIh), KBr Pellet

Plate X



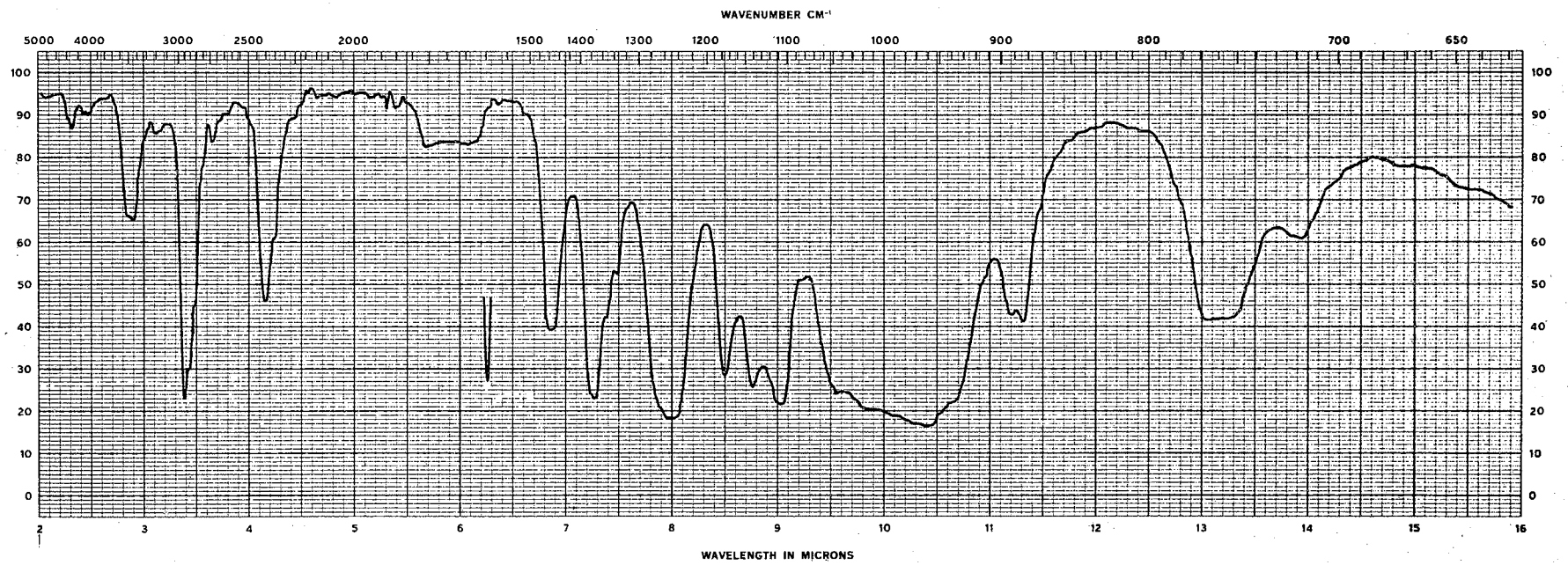
Diphenyl-p-toluenesulfonylcarbamoylphosphine Oxide (IIIi), KBr Pellet

Plate XI



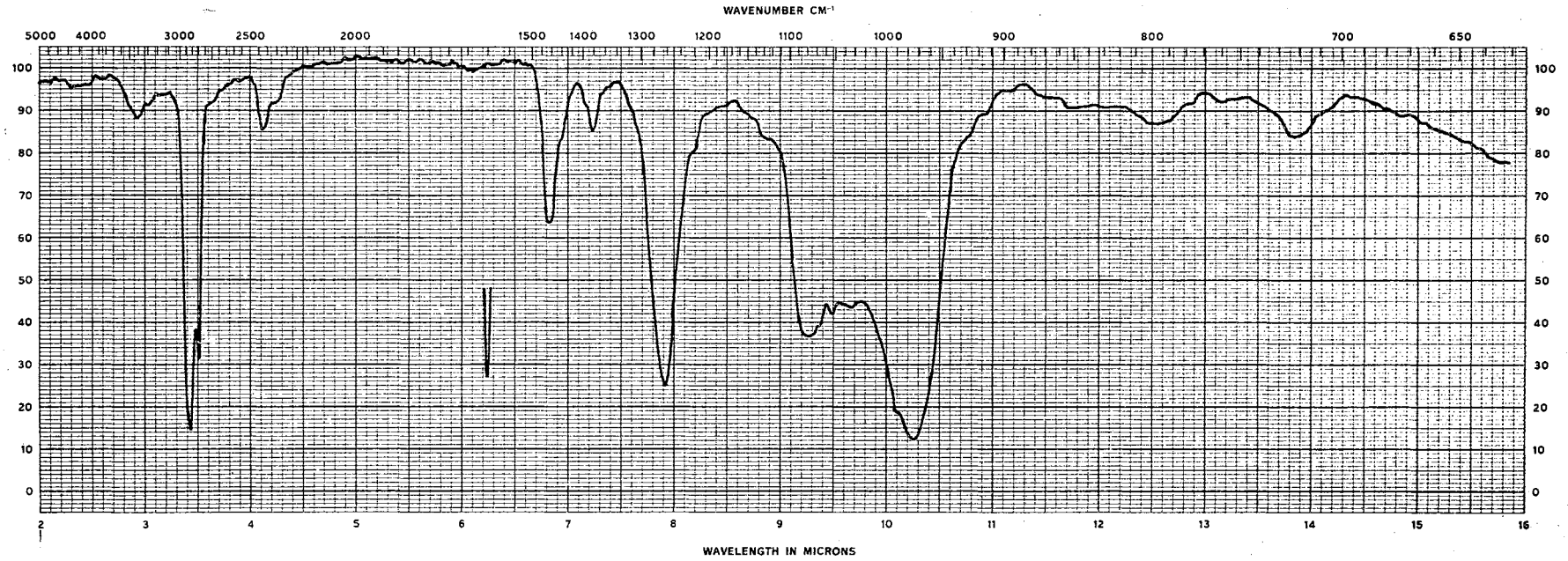
Di-n-propyl Hydrogenphosphonate (IIc), Film on NaCl Plates

Plate XII



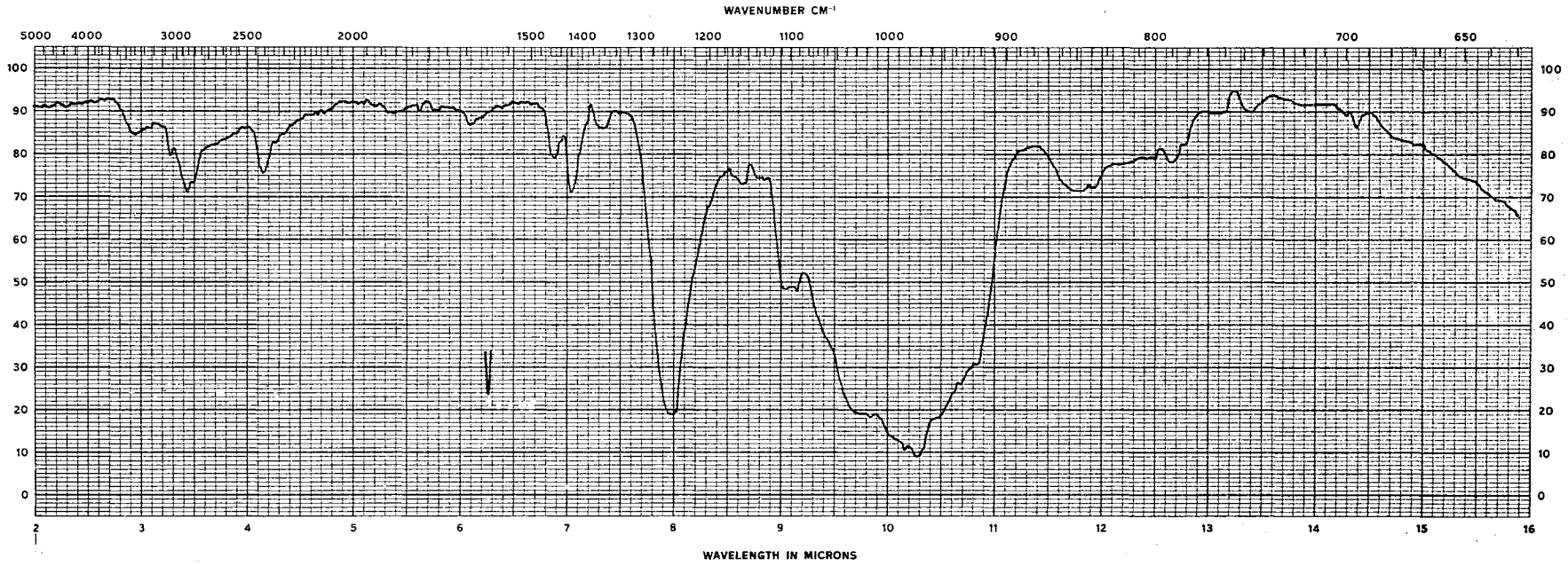
Diisopropyl Hydrogenphosphonate (IId), Film on NaCl Plates

Plate XIII



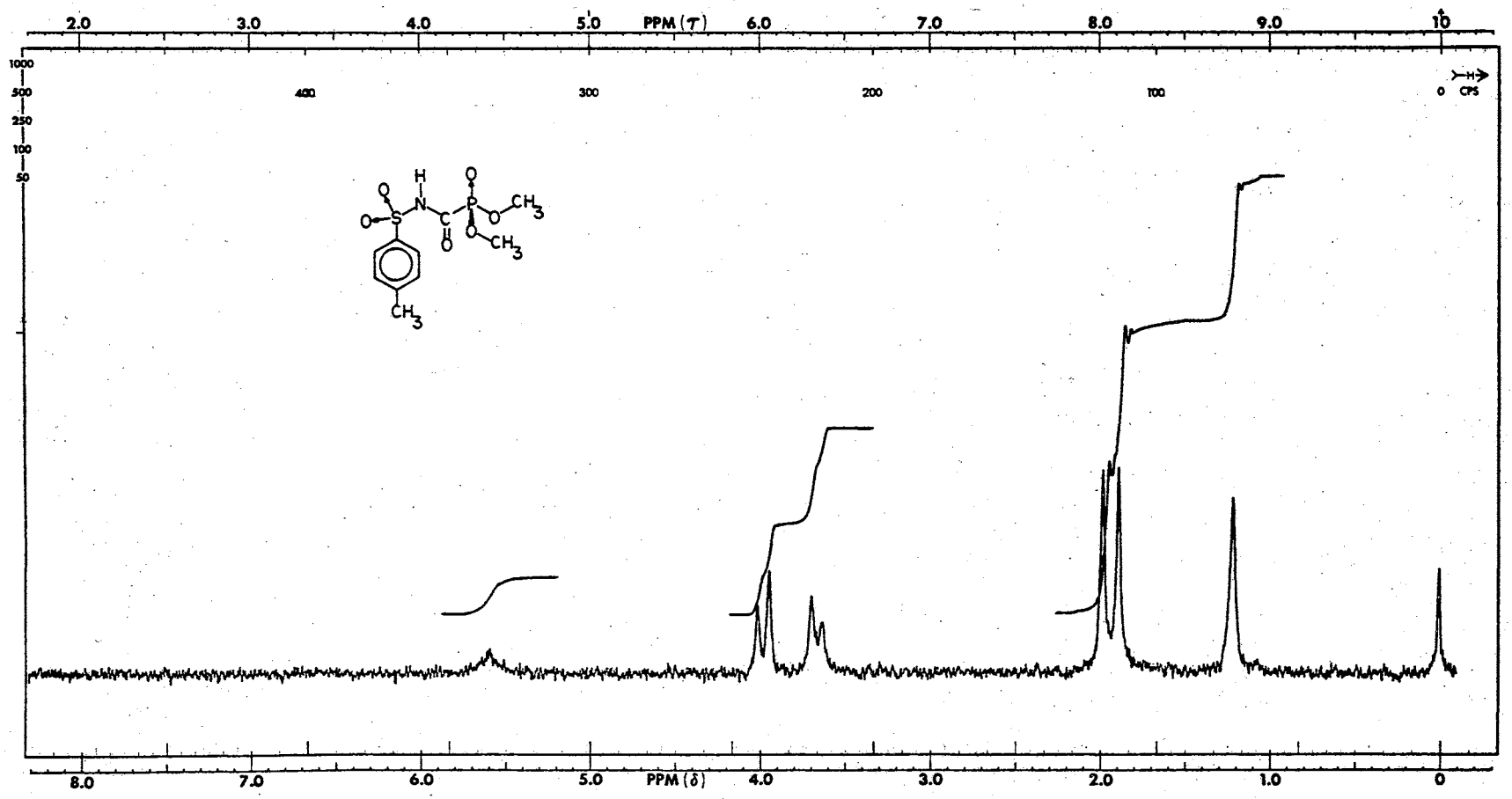
Di-n-octyl Hydrogenphosphonate (IIf), Film on NaCl Plates

Plate XIV



Diallyl Hydrogenphosphonate (IIg), Film on NaCl Plates

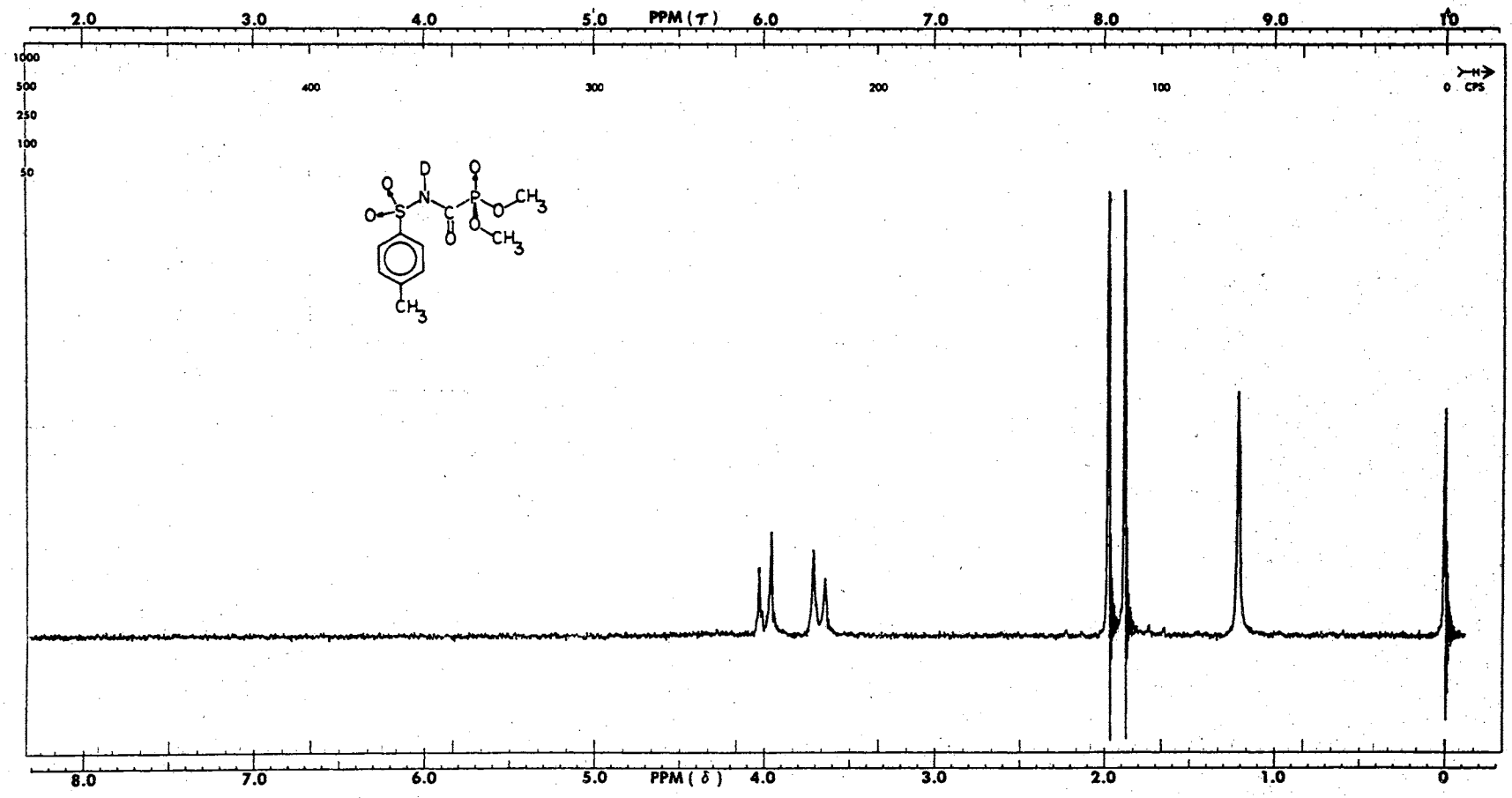
Plate XV



Dimethyl p-Toluenesulfonylcarbamoylphosphonate (IIIa)

Solvent.....$CDCl_3$ F.B.....2 cps S.W.....1000 cps S.A.....8.0
R.F. Field...0.05 mG S.T.....250 sec S.O.....63 cps I.A.....80

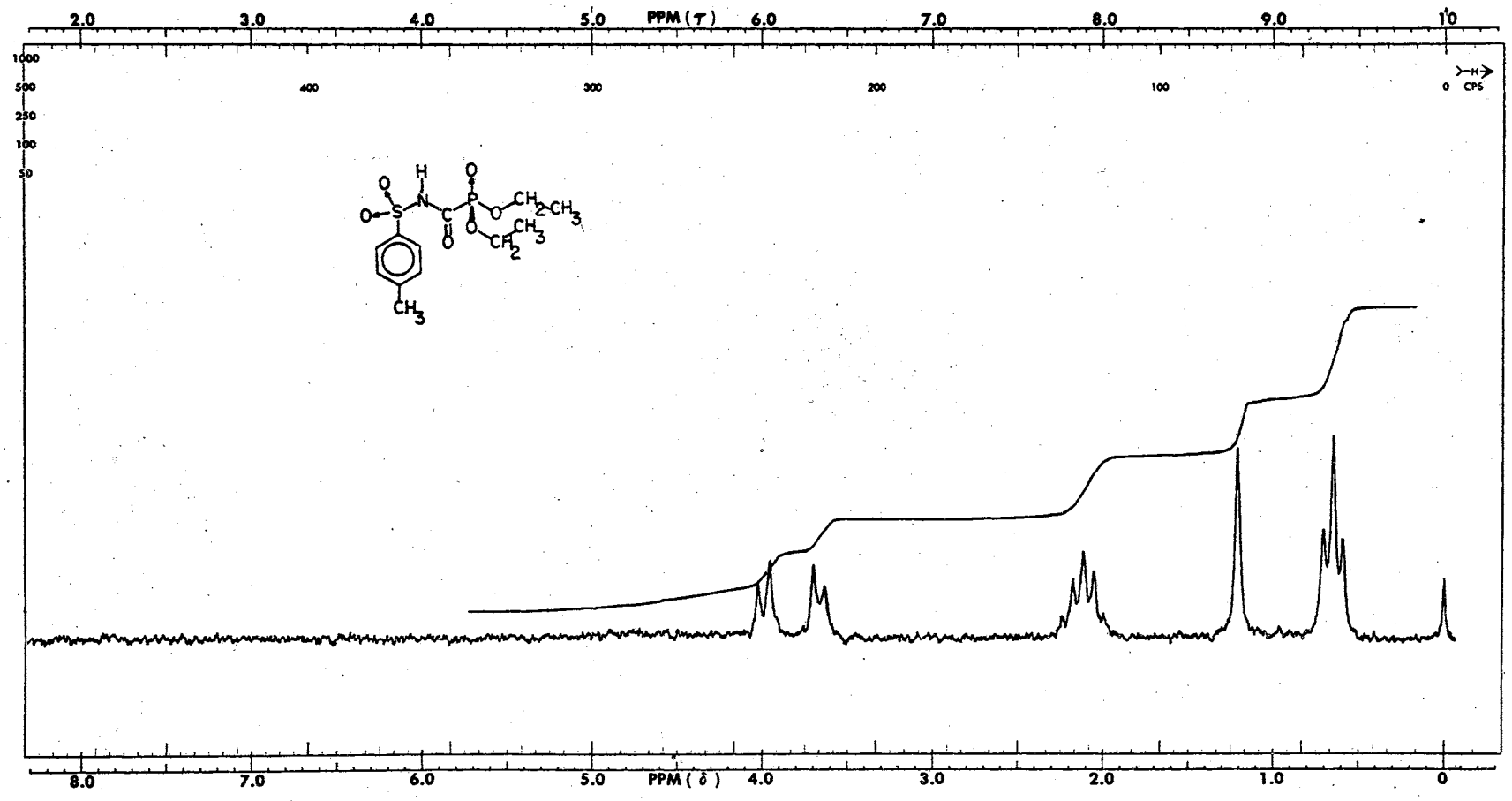
Plate XVI



Dimethyl (p-Toluenesulfonylcarbamoyl-d) phosphonate (IIIa')

Solvent.....$CDCl_3$ F.B.....2 cps S.W.....1000 cps S.A.....4.0
R.F. Field.....0.05 mG S.T.....500 sec S.O.....70 cps I.A.....off

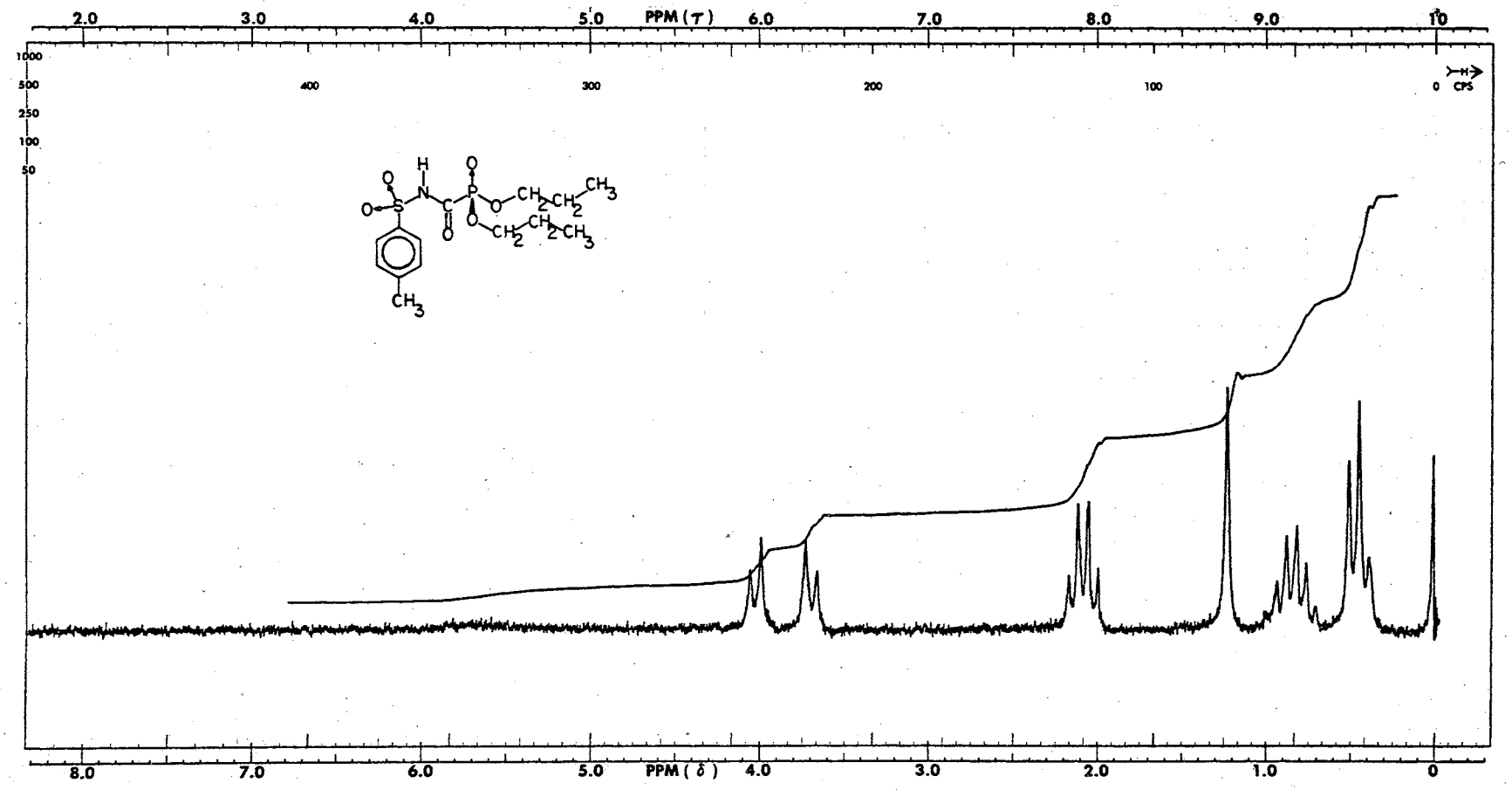
Plate XVII



Diethyl p-Toluenesulfonylcarbamoylphosphonate (IIIb)

Solvent.....$CDCl_3$ F.B.....1 cps S.W.....1000 cps S.A.....8.0
R.F. Field.....0.05 mG S.T.....250 sec S.O.....0 cps I.A.....63

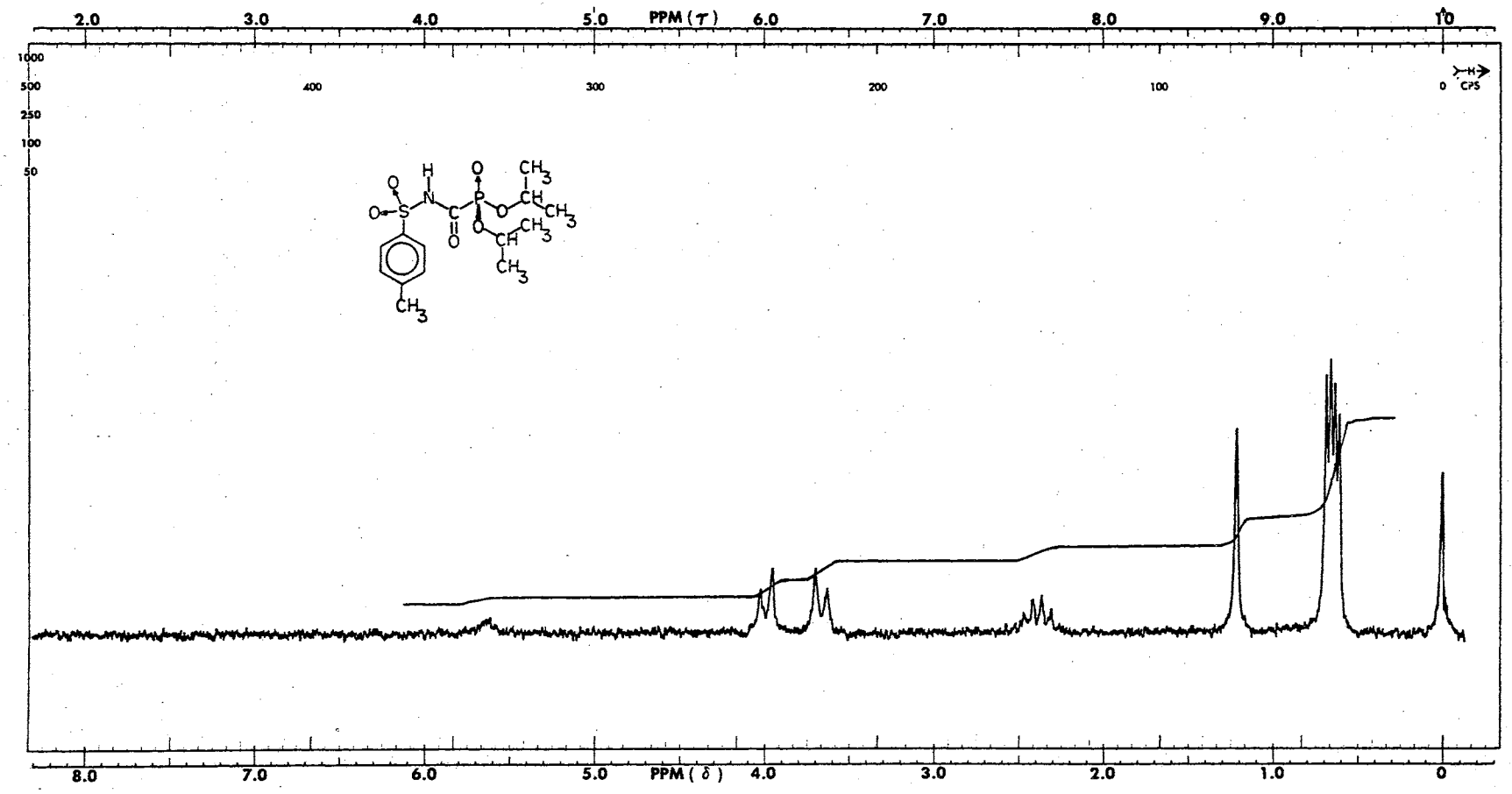
Plate XVIII



Di-n-propyl p-Toluenesulfonylcarbamoylphosphonate (IIIc)

Solvent.....$CDCl_3$ F.B.....2 cps S.W.....1000 cps S.A.....8.0
R.F. Field.....0.05 mG S.T.....500 sec S.O.....35 cps I.A.....63

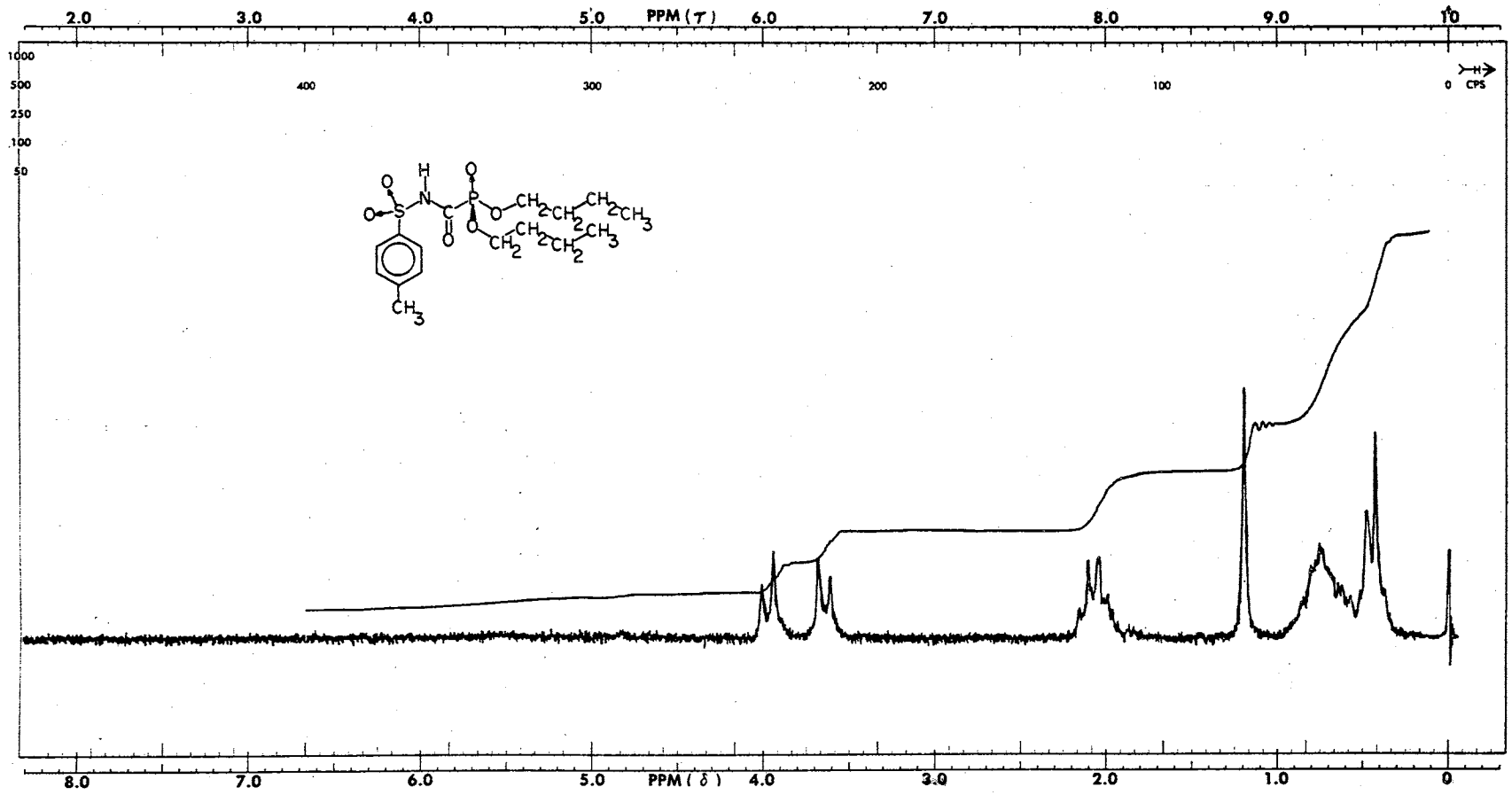
Plate XIX



Diisopropyl p-Toluenesulfonylcarbamoylphosphonate (IIId)

Solvent.....$CDCl_3$ F.B.....2 cps S.W.....1000 cps S.A.....8.0
R.F. Field.....0.075 mG S.T.....250 sec S.O.....0 cps I.A.....50

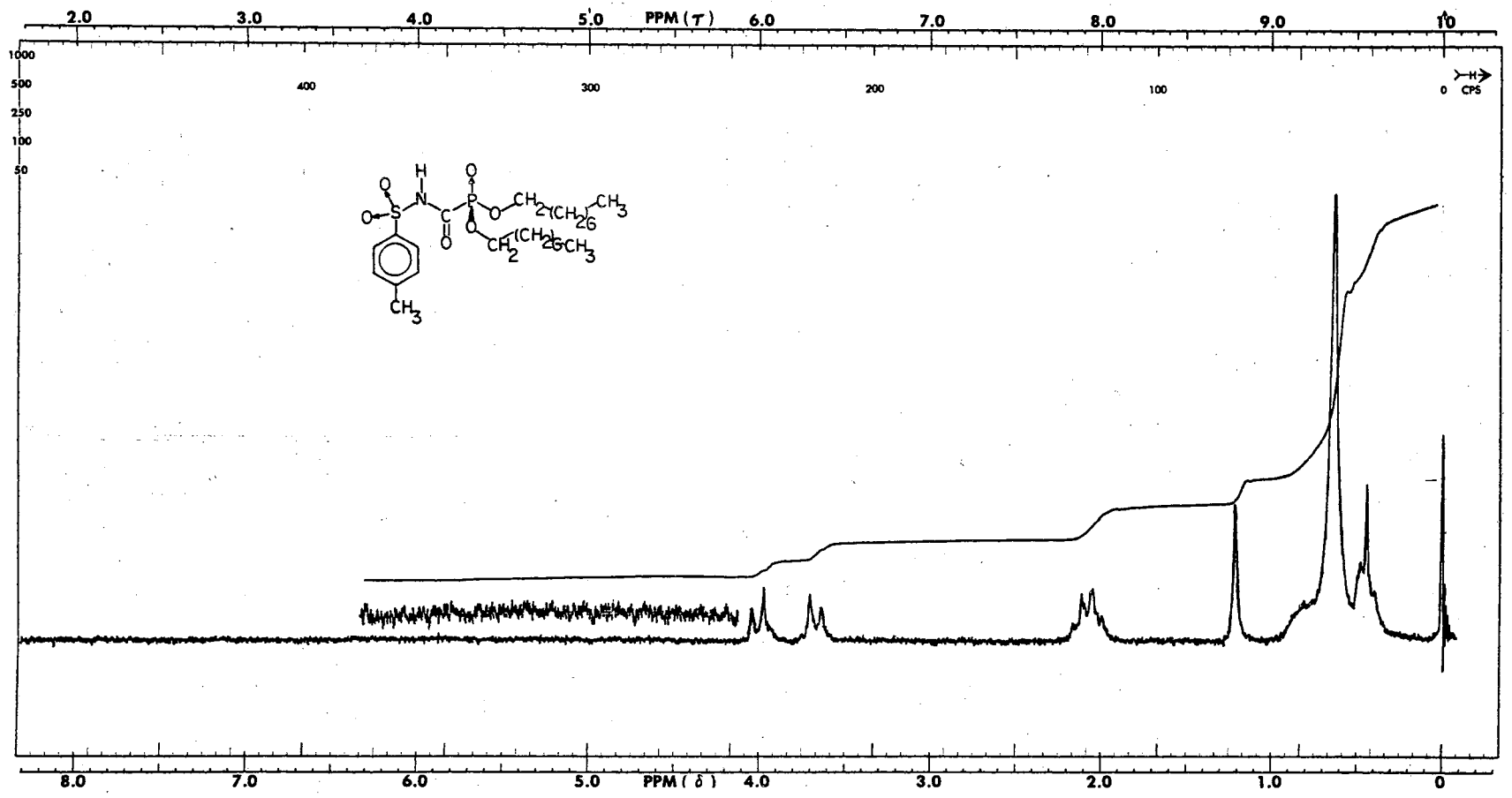
Plate XX



Di-n-butyl p-Toluenesulfonylcarbamoylphosphonate (IIIe)

Solvent.....$CDCl_3$ F.B.....2 cps S.W.....1000 cps S.A.....5.0
R.F. Field.....0.05 mG S.T.....500 sec S.O.....56 cps I.A.....63

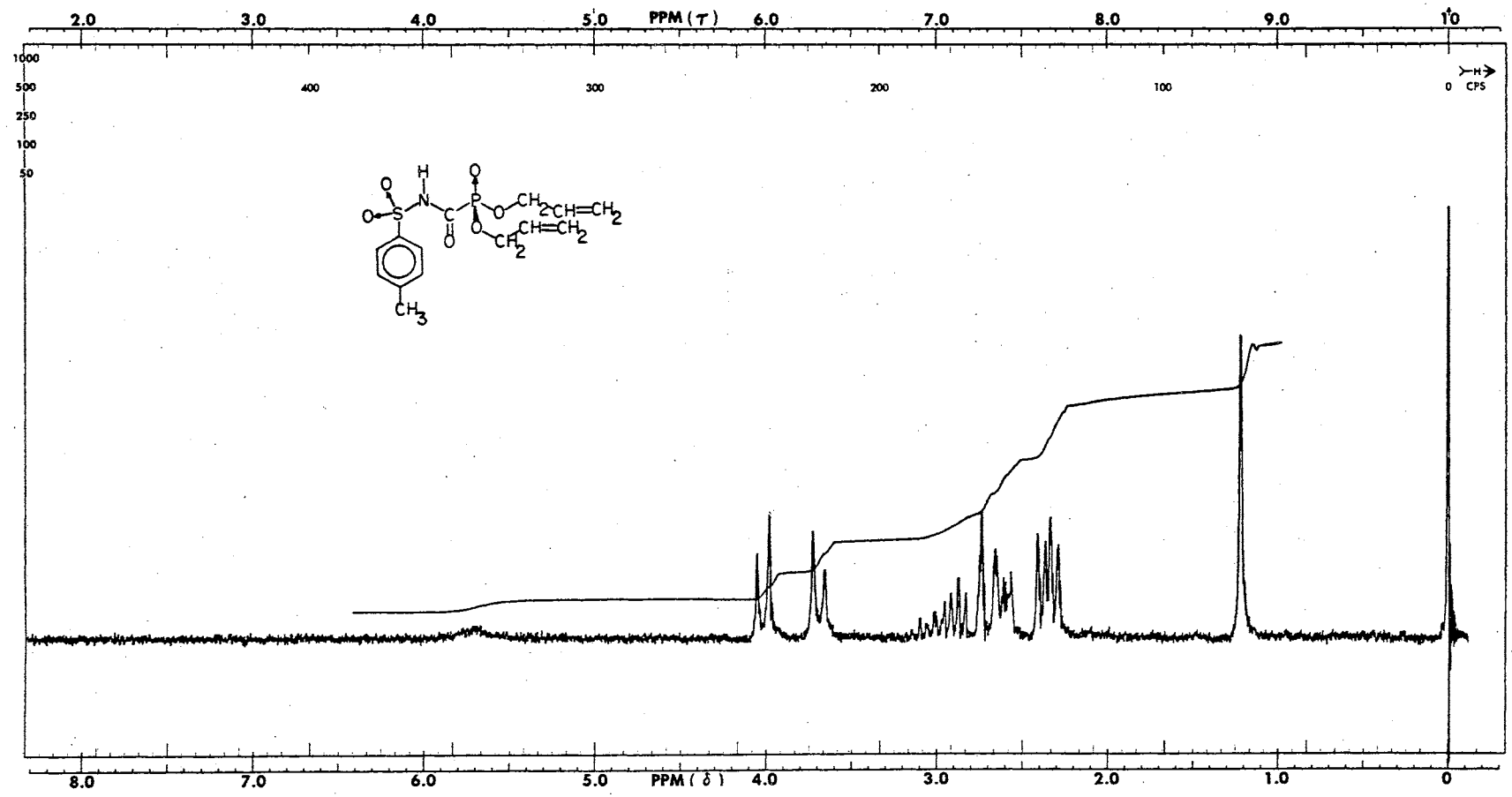
Plate XXI



Di-n-octyl p-Toluenesulfonylcarbamoylphosphonate (IIIf)

Solvent.....$CDCl_3$ F.B.....2,1 cps S.W.....1000 cps S.A.....5,20
R.F. Field.....0.05 mG S.T.....500 sec S.O.....0 cps I.A.....63

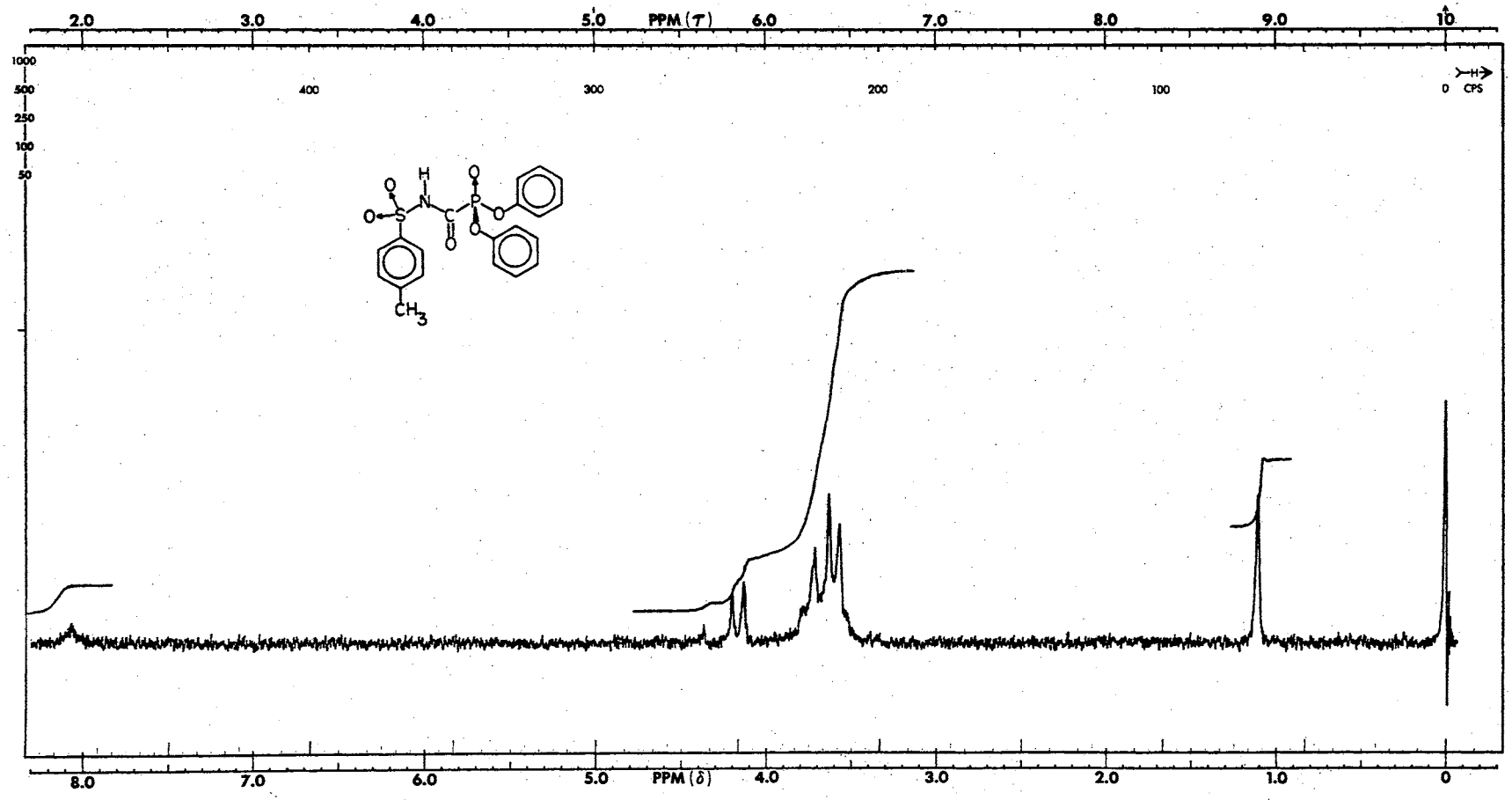
Plate XXII



Diallyl p-Toluenesulfonylcarbamoylphosphonate (IIIg)

Solvent	$CDCl_3$	F.B.	4 cps	S.W.	1000 cps	S.A.	5.0
R.F. Field	0.05 mG	S.T.	500 sec	S.O.	40 cps	I.A.	80

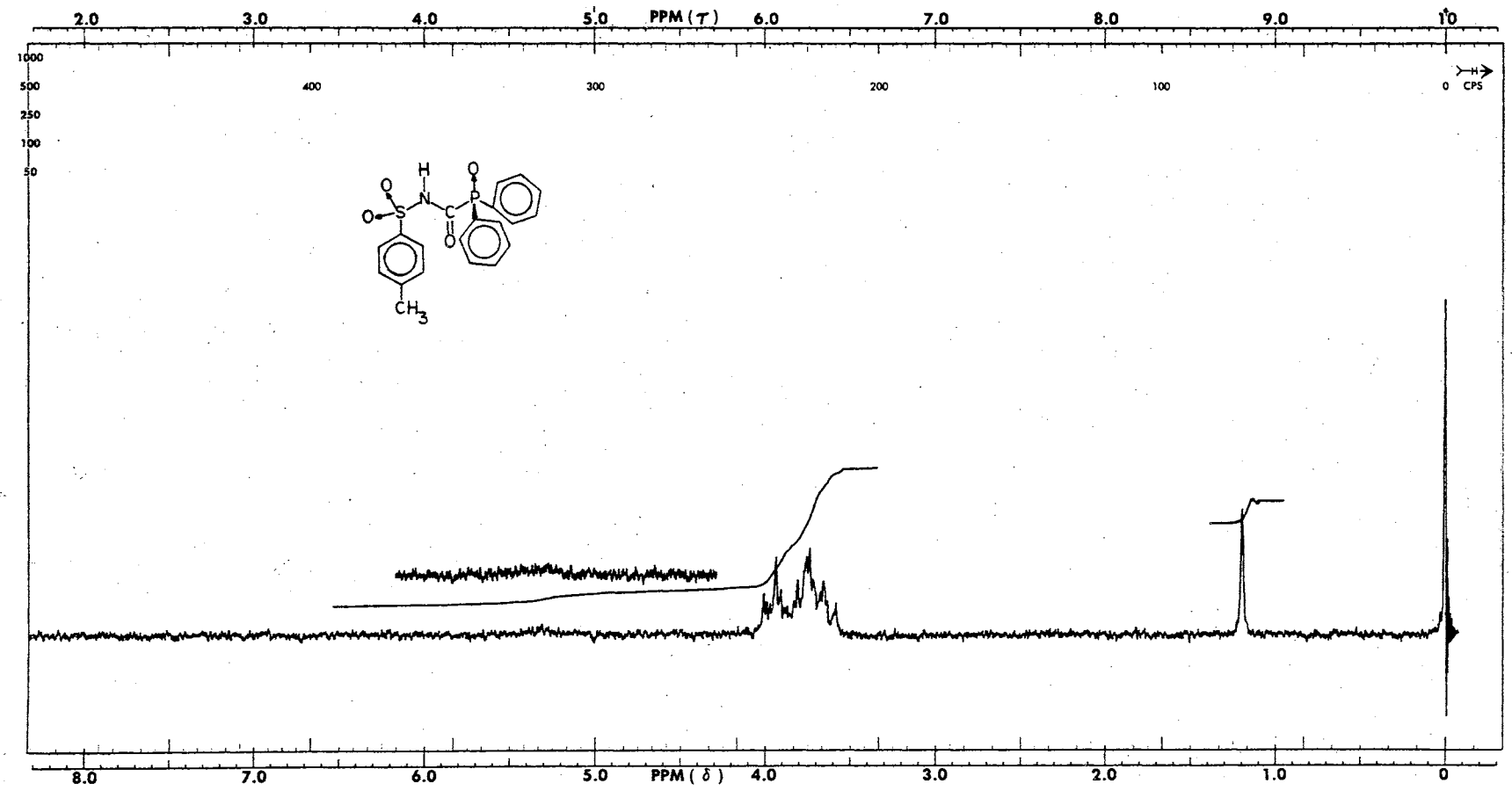
Plate XXIII



Diphenyl p-Toluenesulfonylcarbamoylphosphonate (IIIh)

Solvent.....C_5D_5N F.B.....4 cps S.W.....1000 cps S.A.....6.3
R.F. Field.....0.05 mG S.T.....250 sec S.O.....486 cps I.A.....80

Plate XXIV



Diphenyl-p-toluenesulfonylcarbamoylphosphine Oxide (IIIi)

Solvent.....$CDCl_3$ F.B.....1 cps S.W.....1000 cps S.A.....10,16
R.F. Field.....0.075 mG S.T.....500 sec S.O.....0 cps I.A.....80

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