SYNTHESIS AND NMR ANALYSIS OF DIISOPROPYL AROYLPHOSPHONATES

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SYNTHESIS AND NMR ANALYSIS OF DIISOPROPYL AROYLPHOSPHONATES

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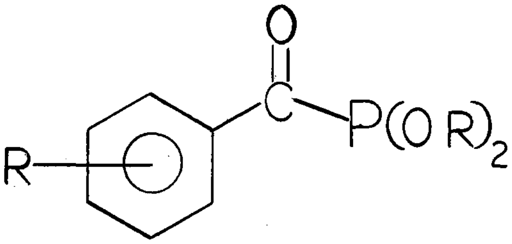
CHAPTER I

HISTORICAL

Acylphosphonates

Since 1964, when the literature on aroylphosphonates was reviewed by Taylor[65], a number of papers on this family have appeared.



The first section of this review is designed to cover the literature published from 1964 to 1971, although a few earlier papers, not included by Taylor, will be cited.

The Michaelis-Arbuzov rearrangement is still the most important method of preparing aroylphosphonates. It was employed by Burger and Wagner[20] to synthesize diethyl benzoylphosphonate and a number of other dialkyl phosphonates. Boiling points, densities, refractive indexes, viscosities, and solubilities in water are tabulated for most compounds. Cade[21] prepared and reported properties of several acylphosphonic esters, among which was dibutyl benzoylphosphonate (1).

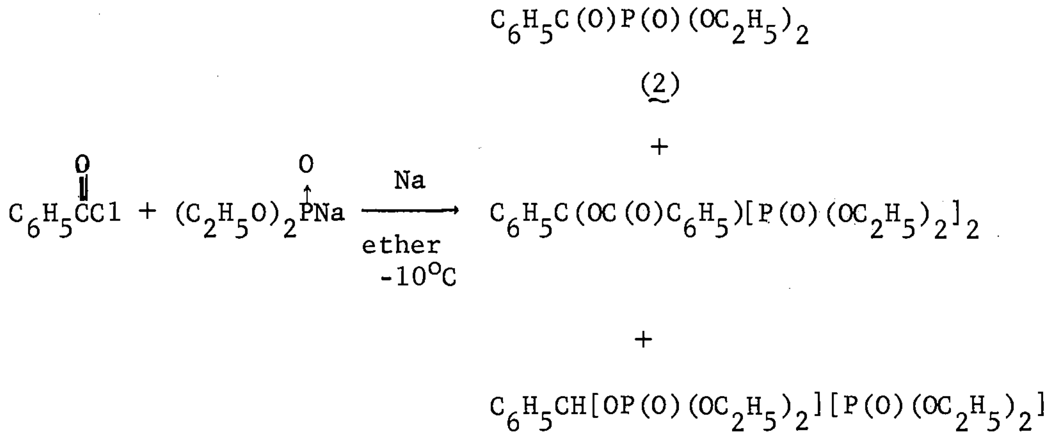
$$C_6H_5C(O)P(O)(O\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3)_2$$

(1)

Kamai and Kukhtin[44] published the synthesis of both diethyl and dimethyl benzoylphosphonate via the reaction of a trialkyl phosphite and benzoic anhydride.[44b]

$$P(OR)_3 + (C_6H_5CO)_2O \longrightarrow C_6H_5C(O)P(O)(OR)_2 + [C_6H_5C(O)P(O)(OR)(OC_6H_5)]$$

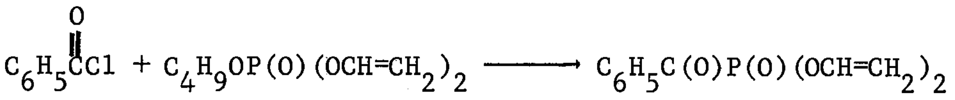
The last product (in brackets) was found only in the case where R=C_2H_5. Diethyl benzoylphosphonate (2) has also been obtained [54] by the following reaction.



$$C_6H_5\overset{O}{\overset{\|}{C}}Cl + (C_2H_5O)_2\overset{O}{\overset{\uparrow}{P}}Na \xrightarrow[\text{ether}\ -10^{\circ}C]{Na} \underset{(2)}{C_6H_5C(O)P(O)(OC_2H_5)_2} + C_6H_5C(OC(O)C_6H_5)[P(O)(OC_2H_5)_2]_2 + C_6H_5CH[OP(O)(OC_2H_5)_2][P(O)(OC_2H_5)_2]$$

The proof of structure of the products rests on boiling points, refractive indexes, and viscosity measurements.

Divinyl benzoylphosphonate[49] (3) was produced by the following reaction.



$$C_6H_5\overset{O}{\overset{\|}{C}}Cl + C_4H_9OP(O)(OCH{=}CH_2)_2 \longrightarrow C_6H_5C(O)P(O)(OCH{=}CH_2)_2$$

(3)

The mixed ester $C_6H_5C(O)P(O)(O\text{-}\underline{n}\text{-}C_3H_7)(OCH{=}CH_2)$ was also prepared by this general route. It is interesting to note that there was no reported loss of the vinyl group in either case. However, little proof of structure was offered.

In a series of papers from this Laboratory[6-9] the synthesis and physical and spectral properties were reported for several acylphosphonates. In 1956 Van Wazer[69] and co-workers tabulated a number of ^{31}P chemical shifts of organophosphorus compounds. Among the compounds was diethyl benzoylphosphonate (2), which had a chemical shift of 2(±1) Hz relative to 85% orthophosphoric acid. Cornell and Birum[23] patented a process for the separation of close-boiling hydrocarbons using an extractive distillation technique. The extracting agent was a dialkyl(C_{1-10}) aroylphosphonate or dialkyl alkylphosphonate.

The ultraviolet spectra of a number of dialkyl aroylphosphonates were described by Terauchi and Sakurai[67] (Table I). They considered the strong absorption band (258-295 mμ) to result from a π-π^* transition; the much weaker band (373-385 mμ) was attributed to a n-π^* transition involving the carbonyl group. It is postulated that interaction of the π bond of the carbonyl group with the phosphorus $\underline{d}$ orbitals is responsible for a red shift (bathochromic) in the π-π^* transition relative to that of the correspondingly substituted benzaldehydes. The same rationalization is employed to account for the increase in the extinction coefficients for the aroylphosphonates as compared to the benzaldehyde analogs. The authors also noted a correlation of wavelengths of the most intense n-π* bands with the Hammett σ constants.

TABLE I

ULTRAVIOLET SPECTRAL DATA FOR AROYLPHOSPHONATES

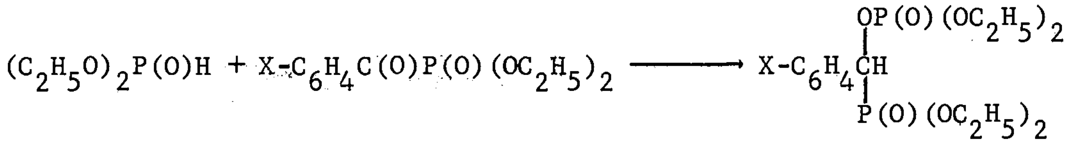
$R\text{-}C_6H_4C(O)P(O)(OR')_2$		Transition	
		$\pi\text{-}\pi^*$ γ max, mμ ($\log\epsilon_{max}$)	$n\text{-}\pi^*$ γ max, mμ ($\log\epsilon_{max}$)
R	R'		
H	C_2H_5	258 (4.05)	379 (1.92)
H	$\underline{i}\text{-}C_3H_7$	258 (4.11)	379 (1.91)
H	$\underline{n}\text{-}C_4H_9$	259 (4.11)	380 (2.01)

Studies on reactions of aroylphosphonates make up a significant portion of the recent literature on aroylphosphonates. In 1967 Pudovik[53a] and co-workers discovered the following reaction.

$$X\text{-}C_6H_4C(O)P(O)(OR)_2 + (R'O)_3P \xrightarrow{CO_2} X\text{-}C_6H_4C(OR')[OP(O)(OR')_2]P(O)(OR)_2$$

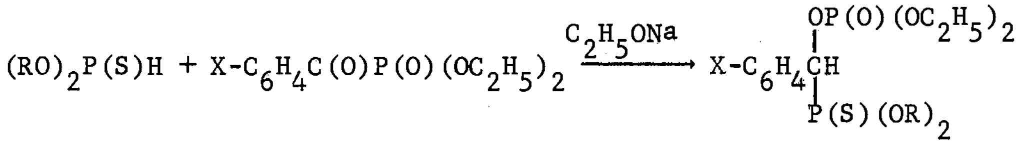
X	R	R'
H	C_2H_5	C_2H_5
H	$n\text{-}C_3H_7$	$n\text{-}C_3H_7$
H	$n\text{-}C_4H_9$	$n\text{-}C_4H_9$
p-Br	C_2H_5	C_2H_5
p-Br	$n\text{-}C_3H_7$	C_2H_5
p-Br	$n\text{-}C_4H_9$	C_2H_5
o-Cl	C_2H_5	C_2H_5
o-Cl	$n\text{-}C_3H_7$	C_2H_5
o-Cl	$n\text{-}C_4H_9$	C_2H_5

The structures of the products were based on identification of $(C_2H_5O)_3P(O)$ and $C_2H_5ONa\text{-}C_2H_5OH$, which were formed upon prolonged heating of diethyl benzoylphosphonate (2). The Russian authors also studied[53b,53c] the reaction of phosphorus, ethylphosphonic and thiophosphorus acid esters with dialkyl aroylphosphosphonates.



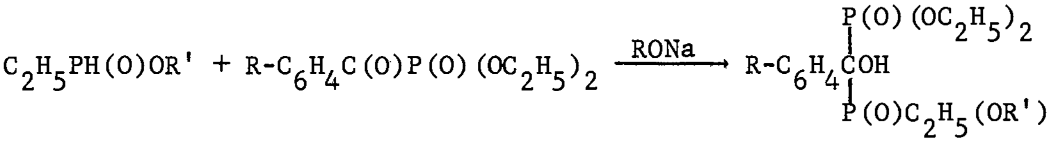
$$(C_2H_5O)_2P(O)H + X\text{-}C_6H_4C(O)P(O)(OC_2H_5)_2 \longrightarrow X\text{-}C_6H_4\underset{\displaystyle P(O)(OC_2H_5)_2}{\overset{\displaystyle OP(O)(OC_2H_5)_2}{CH}}$$

X = p-Br, o-Cl



$$(RO)_2P(S)H + X\text{-}C_6H_4C(O)P(O)(OC_2H_5)_2 \xrightarrow{C_2H_5ONa} X\text{-}C_6H_4\underset{\displaystyle P(S)(OR)_2}{\overset{\displaystyle OP(O)(OC_2H_5)_2}{CH}}$$

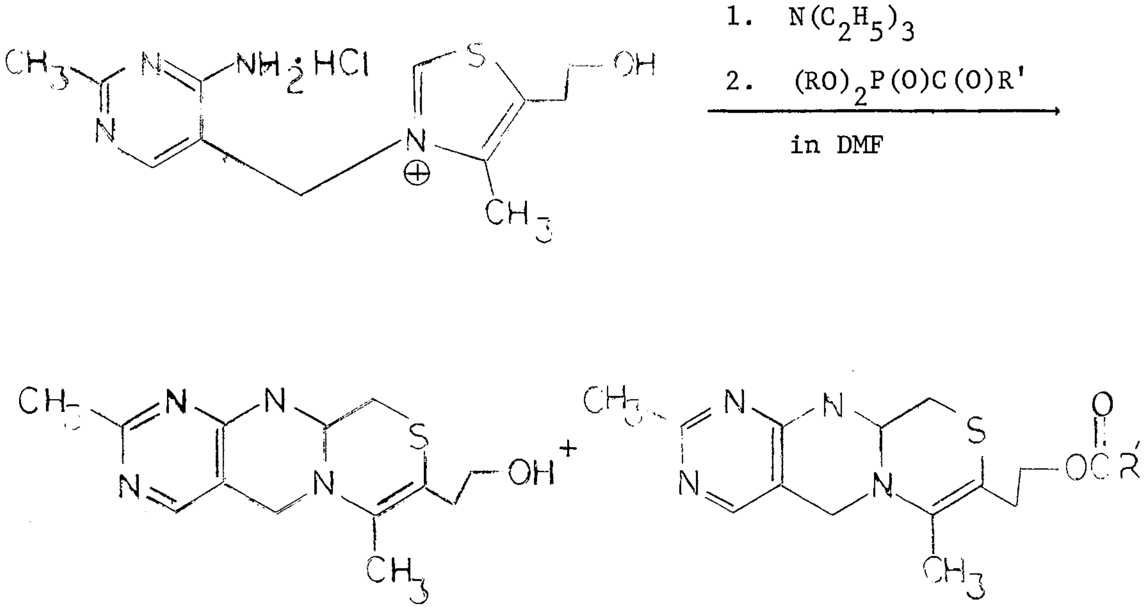
X	R'
p-Br	C_2H_5
o-Cl	$n\text{-}C_3H_7$



$$C_2H_5PH(O)OR' + R\text{-}C_6H_4C(O)P(O)(OC_2H_5)_2 \xrightarrow{RONa} R\text{-}C_6H_4\underset{\displaystyle P(O)C_2H_5(OR')}{\overset{\displaystyle P(O)(OC_2H_5)_2}{COH}}$$

R	R'
p-Br	C_2H_5
p-Br	n-C_4H_9
o-Cl	C_2H_5
p-OCH_3	C_2H_5
p-OCH_3	n-C_3H_7

Takamizawa has studied the reaction of pyrimidine derivatives[64a,64b,64c,64d] with acylphosphonates; interestingly phosphorus was not introduced into the final product.



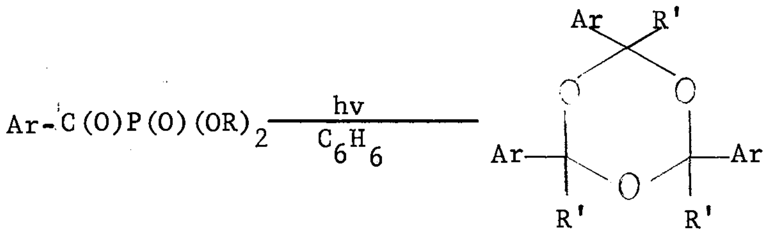
R' = CH_3 or C_6H_5

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

The same reactions occurred when an alkyl phenyl acylphosphinate or methyl phenyl benzoylphosphinate was used but the mechanism is obscure.

The reactions of dimethyl benzoylphosphonate with a series of nucleophiles has been described by Shahak and Peretz[51b]. These reactions fall into two groups: a) those in which dimethyl phosphite is lost and b) those in which a substituted α-hydroxy benzoylphosphonate is formed. Ultraviolet spectra and rates of cleavage by nucleophiles has also recently been reported.[51c]

Photochemical studies on dialkyl aroylphosphonates have been carried out by two groups in Japan. Terauchi and Sakurai[66a,66b] irradiated diethyl benzoylphosphonate (2) with light of wavelength greater than 3200 Å (in cyclohexane) and produced the trimer, a substituted trioxane (4).

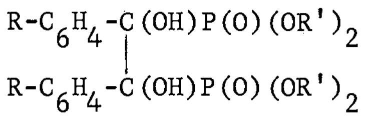


4

$Ar = C_6H_5$

$R' = P(O)(OC_2H_5)_2$

However, irradiation of diisopropyl or di-*n*-butyl benzoylphosphonate under the same conditions gave a substituted pinacol.



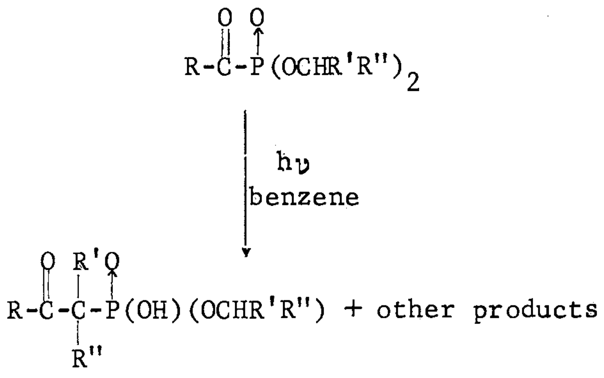
$$\begin{array}{l} R\text{-}C_6H_4\text{-}C(OH)P(O)(OR')_2 \\ \qquad\quad | \\ R\text{-}C_6H_4\text{-}C(OH)P(O)(OR')_2 \end{array}$$

R = H

R' = iso-C_3H_7 or *n*-C_4H_9

The structures of the products were confirmed by IR, elemental analyses and molecular weight determination. The reaction was considered to proceed *via* ketyl radicals. The initially formed lowest excited triplet state of the carbonyl group (of the aroylphosphonates) apparently abstracted hydrogen from solvent.

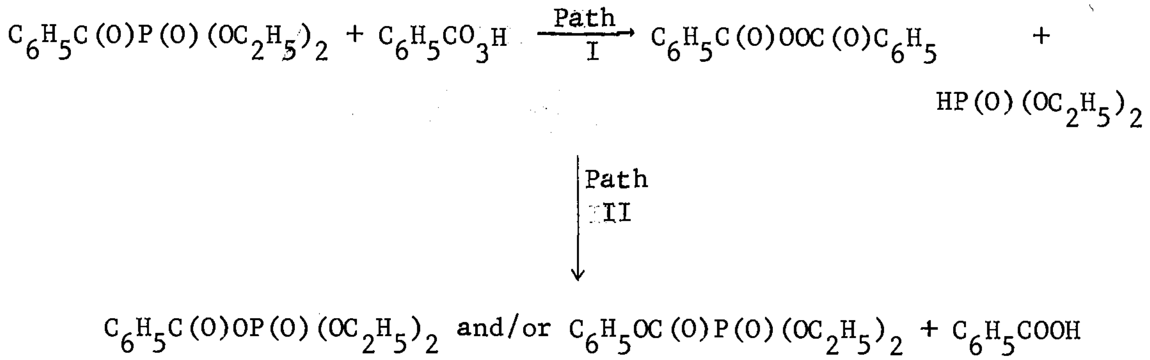
Ogata and Tomioka[51a] showed that irradiation of dialkyl α-oxophosphonates containing tertiary γ-hydrogen atoms gave unusual rearrangement products.



$$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\uparrow}{P}}(OCHR'R'')_2 \xrightarrow[\text{benzene}]{h\nu} R\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{R''}{\overset{R'}{C}}\text{-}\overset{O}{\overset{\uparrow}{P}}(OH)(OCHR'R'') + \text{other products}$$

The reaction was believed to proceed *via* the insertion of a three-carbon fragment into the C-P bond.

Specher and Nativ[63] examined the reaction of diethyl aroylphosphonates with perbenzoic acid.



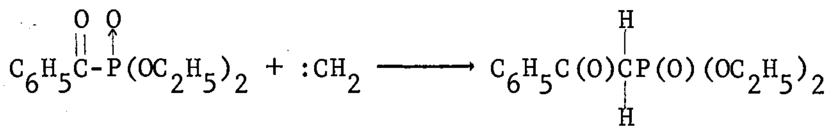
$$C_6H_5C(O)P(O)(OC_2H_5)_2 + C_6H_5CO_3H \xrightarrow[I]{Path} C_6H_5C(O)OOC(O)C_6H_5 + HP(O)(OC_2H_5)_2$$

$$\Big\downarrow \text{Path II}$$

$$C_6H_5C(O)OP(O)(OC_2H_5)_2 \text{ and/or } C_6H_5OC(O)P(O)(OC_2H_5)_2 + C_6H_5COOH$$

Apparently the reaction followed path II almost exclusively to yield diethyl benzoylphosphate. Product analysis and labeling studies support the proposed mechanism.

Methylene[4] was shown to insert into the C-P bond of diethyl benzoylphosphonate (2) when this treated with diazomethane for three days



$$C_6H_5\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2 + :CH_2 \longrightarrow C_6H_5C(O)\underset{H}{\overset{H}{C}}P(O)(OC_2H_5)_2$$

2

Independent synthesis and Raman spectra confirmed the structure of the product.

Polarographic reduction of dialkyl aroylphosphonates has been investigated by two groups. Savicheva and co-workers[56] reported data on several dialkyl benzoyl-, p-methylbenzoyl-, and o-chlorobenzoylphosphonates. They concluded that the phosphono group caused the reduction to occur at more positive potentials than for the nonphosphorylated carbon analogs. This fact was attributed to the negative effect of the phosphoryl group. Results from this Laboratory[10] on reduction of the following dialkyl aroylphosphonates

$R-C_6H_4C(O)P(O)(OR')_2$

R	R'	R	R'
H	C_2H_5	*o*-OCH_3	C_2H_5
p-*t*-C_4H_9	C_2H_5	*p*-CH_3	C_2H_5
o-Cl	C_2H_5	*p*-OCH_3	CH_3
p-Cl	C_2H_5		

provided an approximate ρ value (+ 4.7) indicating that electron-withdrawing substituents facilitated the reductions. The experiments were performed in specially designed cells which permitted gathering of reproducible coulometric data and sufficient conversion of reactants so that product analyses by GLC was also reproducible.

NMR Techniques for the Study of Intramolecular Rate Processes

In this section no attempt will be made to review all of the papers dealing with Dynamic Nuclear Magnetic Resonance (DNMR) analysis published since the critical reviews of Binsch[12] (1968) and Kessler[47] (1970). Instead, a few of the more instructive papers will be discussed and an effort will be made to elucidate the technique, sources of error and error analysis methods.

Unfortunately, there has been little published in the area of DNMR analysis of organophosphorus compounds. Quite recently[28], a few papers have appeared which deal with inversion barriers of cyclic phosphines, but the data are not easily extrapolated for diagnostic purposes to phosphorus esters.

Three recent papers have been chosen to illustrate techniques currently being used in DNMR studies. A very elegant analysis[26] of the spectrum of formamide appeared in early 1970 which demonstrates clearly the use of isotope (^{15}N) substitution to simplify the interpretation. The barrier to internal rotation in amides is of great biological importance. In most cases NMR techniques provide the only simple method available for evaluation of this rotational barrier, since the energy factor is too large to be within the range of microwave spectroscopy and too small to permit application of equilibration techniques.

The NMR analysis of the proton signals is complicated by quadrupole broadening by the ^{14}N signal. Two methods are available to circumvent the difficulty: (1) irradiation of the ^{14}N nucleus; and (2) isotope substitution by ^{15}N. Neither technique is completely problem-free. Irradiation requires special equipment which increases the complexity of the experiment and the cost. Use of isotopically substituted material increases the cost of the experiment and, in this case, the complexity of the resulting spectra. This increase in complexity of the spectra makes the analysis more difficult, but it can sometimes enhance the accuracy of the resulting thermodynamic data since more lines must be simulated.

Drakenberg and Forgen[26] used a density matrix technique based on the equations of Kaplan[45] and Alexander[2] to compute the line shapes for analysis of the formamide spectra. An accurate knowledge of the coupling constants (J), chemical shifts (δ), and the transverse relaxation time (T_2) is required for this method. Transverse relaxation time (T_2) is determined by taking the reciprocal of the line width at half height (W_H) of some line of a proton in the spectrum generated from a proton <u>not participating</u> in the exchange and then multiplying by pi (π). The "best" set of coupling constants and chemical shifts may be obtained by treating the data with a spectral fitting program such as LAOCN 3[16b] or NMRIT 4[16b] (in the formamide study it was necessary to obtain the chemical shifts and coupling constants as a function of temperature; thus spectra were calculated for every temperature). The authors visually fitted the observed spectra to the calculated line shapes, a technique which is quite common in this type of investigation.

From the process of fitting the theoretical spectra to the observed spectra the rate constant k (some authors prefer to use T, which is defined as the mean lifetime of the species and is equal to 1/k) may be determined. Once k is obtained, the activation energy (E_a) for the rotation can be determined from the Arrhenius[11a,22] equation (I).

$$k = A \exp(-E_a/RT) \qquad \text{(I)}$$

where A = Frequency factor
R = Gas constant
T = Temperature

Thermodynamic parameters can be determined from the Eyring[11b,22] equation of transition state theory.

$$k = \varkappa \ (k_\beta T/h) \ \exp(-\Delta G/RT)$$

where $\varkappa$ = Transmission coefficent
k_β = Boltzmann constant
h = Planck's constant
ΔG^* = Free energy of activation
T = Temperature
R = Gas constant

Dahlquist[24] developed an interesting technique for treating special systems in which the equilibrium constant changes with temperature and the independent estimates of its magnitude are difficult or impossible to obtain. Aplinger and co-workers[5] have applied this method to determine the barrier to rotation in N-methylpyrrole-2-carbaldehyde.

The line shape of an NMR signal is a function of the rate constant (k), the population of each of the sites (P), the coupling constants (J), the chemical shift (δ), and the transverse relaxation time (T_2) as indicated. Problems sometimes arise from the fact that there are often several combinations of these parameters which can give rise to similar line shapes. In particular, Dahlquist[24] has given several examples of different combinations of populations and rate constants that resulted in the same general spectra. Obviously, this situation made difficult or impossible an analysis of the data in terms of the thermodynamic parameters. To save the situation, Dahlquist has postulated that the shape of the signal can be characterized by some function of the rate constant and the population which is given the following form.

$$F(1/k,P) = P/\gamma_{max}$$

In this equation P is the population (P = 1 for the coalesced signal and P = P elsewhere). γ_{max} is the maximum height of the coalesced signal and in the slow exchange limit is equal to the height of the peak with population P. However, the function F(1/k,P) could be defined in terms of other spectral parameters (cf. reference 5).

By use of this function, three-dimensional surfaces arising from a series of curves are obtained by plotting ln K ($\ln K = \ln (1-P)/P$) (where K is an equilibrium constant) versus ln k versus F(1/k,P). From these plots, the thermodynamic parameters may be evaluated by constructing a series of curves through points with the same F(1/k,P) values. The curve which corresponds to the coalescence temperature is chosen and a series of tangents to this curve are drawn. From the intersection points of these tangent lines and the other curves (which represent other values of $F(1/k,P)$, values of ln K and ln k are estimated. The values of ln k are plotted against the reciprocals of the temperature. The set which yielded the best straight line was assumed to be the "best" experimental values for ln k. The activation energy is evaluated from the slope of this line.[24]

This method, while showing promise in dealing with difficult cases involving temperature-dependent equilibrium constants, has a major drawback. The amount of computer time required to construct the three-dimensional surfaces is quite large, even for simple systems.

The final work on NMR line shape analysis illustrates the use of digital data in the evaluation of exchanged broadened NMR spectra. In a careful study, Jackman and co-workers[39] investigated a series of substituted N,N-dimethylbenzamides $[X\text{-}C_6H_4C(O)N(CH_3)_2]$ in various solvents and hydrogen ion concentrations. The spectra were manually digitized by reading points from the NMR curve at 0.25 to 0.50 Hz; thirty to sixty points were taken for each trace. Values of an upfield and downfield sweep were then averaged to give the points used in the analysis. The line shape analysis was carried out using the equation of Gutowsky, McCall, and Slichter[12]. Three parameters are required: T, the lifetime for a rotational state (equal to $1/k$); $\Delta\delta$, the chemical shift difference between the two methyl resonances in the low temperature limit; and T_2, the transverse relaxation time.

The program performed the following operations consecutively without any interim manipulations. The parameters mentioned above were used to calculate the theoretical line shape. The program then automatically compared these points to the digital data from the experimental spectrum. In addition, a nonlinear regression analysis was performed via iteration to give the best fit first by adjusting T and, if necessary, adjusting $\Delta\delta$ and T_2. Statistical evaluation of the significance of calculating the values of T_2 by iteration revealed that in all cases, except around the coalescence temperature, T_2 was too strongly correlated to T to be evaluated in this manner.

It is interesting to note that deviations from Lorentzian line shape was a major problem in obtaining a "perfect" fit between calculated and experimental spectra. However, most of the deviation was in the "wings" of the absorption. A better fit could be obtained by using only points on the calculated spectra which had an intensity greater than five per cent of the maximum.

Sources of Error

In this section errors which result from instrumental sources will be discussed. These errors have plagued Dynamic Nuclear Magnetic Resonance studied from the beginning and are responsible, at least in part, for the wide variation in the thermodynamic values reported for compounds which have been studied by several different workers.[13]

Line broadening due to field inhomogenity or saturation is a problem frequently encountered when the temperature within the probe is changed. Careful tuning of the instrument at each temperature using an internal standard such as H_2CCl_2 or $(CH_3)_4Si$ (TMS) is usually sufficient to minimize this problem. However, even tuning at each temperature does not give any indication of instrumental drift during the time necessary to record the spectra. The magnitude of this drift may be obtained by checking the internal standard after each trace and retuning if necessary.

Temperature within the sample must be controlled and monitored accurately. Control of the temperature is generally obtained by a variable-temperature accessory available for most spectrometers. In the case of the Varian A-60, the temperature can be regulated to ± 1.0 degrees over a range of -120 to + 200°C. Monitoring the temperature is usually accomplished by insertion of a capillary tube containing CH_3OH or $HOCH_2CH_2OH$ (depending on the temperature range) and measuring the shift between the OH proton and the CH protons. The temperature can then be interpolated from the plots of chemical shift vs temperature provided by Varian or calculated from equations provided by Van Geet.[68]

Errors introduced through failure to control the temperature accurately are difficult to eliminate completely; however, methods to minimize this error have been discussed by several workers. Calibration of the standards (usually CH_3OH or $HOCH_2CH_2OH$) using a thermocouple over the range of temperatures to be studied permits a more accurate knowledge of the temperatures. Since there is a temperature gradient around the glass insert of the probe, a minimum amount of sample should be used to reduce the effects of nonuniform sample temperature. A steady flow of carrier gas is also essential for maintaining a constant temperature (the use of two regulators in series will help to even the flow).

The following section will deal with errors introduced during the process of analyzing NMR data. Probably one of the most difficult parameters to determine accurately for the exchanging protons is the transverse relaxation time (T_2). There are two principal methods used to determine T_2, other than the use of pulsed NMR. One method[26b] is to measure the line width of an exchanging species in the limit of both fast and slow exchange and them plot these values versus the temperature. The transverse relaxation (T_2) can now be read from the straight line between the two points. However, this requires that T_2 be a linear function of temperature. Another method to obtain an effective value for T_2 is by measuring the linewidth of some non-exchanging line in the spectrum, usually a line from an internal standard, such as TMS (however the use of an external standard has been reported by Arlinger and co-workers[5b]).

The magnitude of the errors arising in the thermodynamic values introduced by an inaccurate knowledge of T_2 has been discussed by Drakenberg and co-workers[26b]. It was estimated to be on the order of ± 0.2 kcal/mole in both E_a and ΔH^*.

The chemical shifts and coupling constants (static parameters) of the exchanging species are also rather difficult to obtain. Unfortunately they can only be determined in the slow exchange limit[13] where instrument stability is often a factor in determining the accuracy of these parameters. In addition, from this data (taken in the slow exchange limit) nothing is known about the temperature dependence of the chemical shifts. To some extent a correction for temperature variation in these parameters may be made by recording the spectrum at several temperatures in the slow exchange limit and plotting the chemical shift versus temperature. Extrapolation to higher temperatures is now possible; however the assumption that the temperature dependence of the chemical shift is linear is inherent in this method.

Drakenberg and co-workers[26b] have attempted to analyze the magnitude of this error in their study of N,N-dimethyltrichloroacetamide. They estimate that an error of ± 0.2 Hz causes an error of ± 0.3 kcal/mole in E_a and ΔH^*.

CHAPTER II

RESULTS AND DISCUSSION

A number of new diisopropyl aroylphosphonates have been synthesized by standard techniques and characterized by NMR, IR, mass spectral and elemental analyses. An interesting temperature-dependent peak-doubling phenomena had been observed in the NMR spectra of these compounds and an attempt has been made to explain this observation in terms of proton nonequivalence and intramolecular rotational processes.

The Michaelis-Arbuzov reaction provides a useful route to an interesting series of diisopropyl aroylphosphonates, several of which have not been reported previously. The structures of these aroylphosphonates are supported by IR (Table II, Plates I-IX), NMR (Table III,

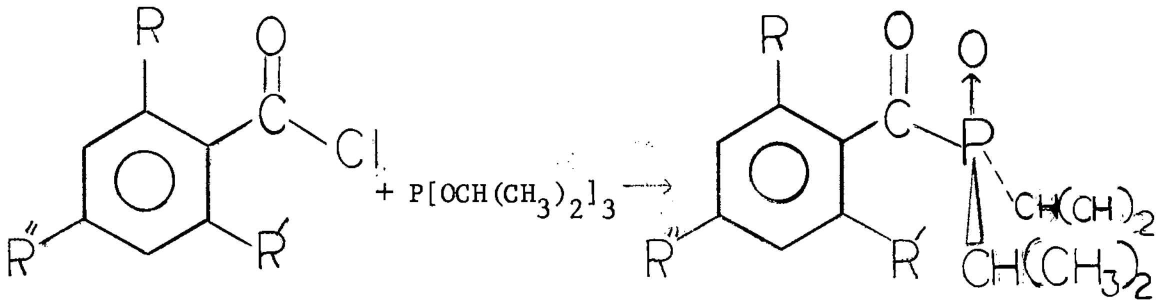


TABLE II

IR SPECTRAL DATA FOR DIISOPROPYL AROYLPHOSPHONATES

Compound	Aryl Group	C=O (cm^{-1}) IR-5A	 IR-7	P→O (cm^{-1}) IR-5A	 IR-7
5	C_6H_5	1658	1657	1255	1255
6	*o*-$CH_3C_6H_4$	1658	1652	1253	1255
7	*p*-$CH_3C_6H_4$	1656	1655	1258	1255
8	2,6-$(CH_3)_2C_6H_3$	1677	1677	1254	1256
9	*o*-$CH_3OC_6H_4$	1658		1260	
10	*p*$CH_3OC_6H_4$	1658		1246	
11	2,6,-$(CH_3O)_2C_6H_3$	1666		1250	
12	*o*-ClC_6H_4	1677		1262	
13	*p*-ClC_6H_4	1658		1256	

TABLE III

NMR DATA FOR DIISOPROPYL AROYLPHOSPHONATES

Compound	R	R′	R″	PLATE	CHEMICAL SHIFTS (Hz)/(ppm)				
					R	R′	R″	a,a′	b,b′
5	H	H	H		---	---	---	278m (4.63)	78d (1.30)
6	H	CH_3	H		---	144s (2.40)	---	276m (4.60)	76d (1.27)
7	H	H	CH_3		---	---	42s (0.70)	275m (4.58)	77d (1.28)
8	CH_3	CH_3	H		134s (2.33)	134s (2.33)	---	280m (4.67)	75qt (1.28)
9	H	OCH_3	H		---	225s (3.75)	---	272m (4.53)	75d (1.25)

Table III (Continued)

Compound	R	R′	R″	PLATE	CHEMICAL SHIFTS (Hz)/(ppm)				
					R	R′	R″	a,a′	b,b′
10	H	H	OCH_3		---	---	228s (3.80)	282m (4.70)	80d (1.33)
11	OCH_3	OCH_3	H		226s (3.77)	226s (3.77)	---	280m (4.67)	75qt (1.25)
12	H	Cl	H		---	---	---	282m (4.70)	82d (1.37)
13	H	H	Cl		---	---	---	283m (4.72)	79d (1.32)

Compound	R	R'	R"
5	H	H	H
6	H	CH_3	H
7	H	H	CH_3
8	CH_3	CH_3	H
9	H	OCH_3	H
10	H	H	OCH_3
11	OCH_3	OCH_3	H
12	H	Cl	H
13	H	H	Cl

Plates XIX-XXVII), mass spectral data (Table IV, Plates X-XVIII) and elemental analyses (Table V). These esters exhibit unusual and previously unreported (for these types of compounds) peak doubling in the methyl signals of the isopropyl function (isopropyl-methyl groups) of the NMR spectra.

Most of the esters studied were yellow or light yellow-green oils except 13 which was a low-melting solid. The phosphoryl group seemingly acts as the chromophoric function, because the benzaldehyde analogs are colorless. However, both compounds 8 and 11 are nearly colorless, which apparently results from loss of conjugation between the Ar and C=O groups.

The nature of the NMR spectra of these aroylphosphonates was found to be dependent upon the substituents R and R'. The spectra of the para-substituted compounds 7, 10, and 13 were similar to that of compound 5 (Plate XXXVI) where R=R'=H. Compounds 5, 7, 10, 12, and 13 exhibited four unresolved peaks (Figure 1) at room temperature for

TABLE IV

MASS SPECTRAL DATA

Diisopropyl benzoylphosphonate (5)

M/e	% RI	M/e	% RI
270	3.59	77	19.10
186	6.03	65	9.23
165	0.50		
106	7.69	43	12.95
105	100.00		

Diisopropyl 2-methylbenzoylphosphonate (6)

M/e	% RI	M/e	% RI
284	0.34	65	7.32
120	9.30	43	11.69
119	100.00	41	5.63
91	19.58		

Diisopropyl 4-methylbenzoylphosphonate (7)

M/e	% RI	M/e	% RI
284	4.77	43	13.74
120	9.63	41	6.54
119	100.00	39	4.21
91	19.07		

Diisopropyl 2,6-dimethylbenzoylphosphonate (8)

M/e	% RI	M/e	% RI
298	2.78	79	5.90
134	10.00	77	6.53
133	100.00	43	7.08
105	17.36		

TABLE IV (Continued)

Diisopropyl 2-methoxybenzoylphosphonate (9)

M/e	% RI	M/e	% RI
300	2.35	119	18.95
136	9.08	77	15.03
135	100.00	43	14.05
124	22.20		

Diisopropyl 4-methoxybenzoylphosphonate (10)

M/e	% RI	M/e	% RI
300	4.56	107	4.41
152	5.00	77	4.84
136	9.19	43	7.28
135	100.00		

Diisopropyl 2,6-dimethoxybenzoylphosphonate (11)

M/e	% RI	M/e	% RI
330	2.06	107	45.00
166	55.00	77	24.38
151	100.00	43	47.50
150	46.88		

Diisopropyl 2-chlorobenzoylphosphonate (12)

M/e	% RI	M/e	% RI
304	1.38	43	22.19
141	33.44	41	26.25
139	100.00	39	22.81
111	13.13		

TABLE IV (Continued)

Diisopropyl 4-chlorobenzoylphosphonate (13)

M/e	% RI	M/e	% RI
304	3.75	139	100.00
165	0.67	111	6.76
141	12.26	75	8.96
140	2.93	43	22.22

TABLE V

ELEMENTAL ANALYSIS, YIELDS AND PHYSICAL PROPERTIES OF DIISOPROPYL AROYLPHOSPHONATES

Compound	Formula	% Calculated			% Found			Boiling Point °C/mm	% Yield
		C	H	P	C	H	P		
5	$C_{13}H_{19}O_4P$			11.48			11.21	100-103/.075^{a}	57.5
6	$C_{14}H_{21}O_4P$	59.15	7.39	10.91	59.08	7.38	10.76	107-110/0.01	54.2
7	$C_{14}H_{21}O_4P$	59.15	7.39	10.91	58.91	7.46	10.86	110-112/0.075	73.1
8	$C_{15}H_{24}O_4P$	60.40	7.71	10.40	60.56	7.84	10.46	93-94/0.05	66.8
9	$C_{14}H_{21}O_5P$	56.02	6.99	10.31	56.30	7.08	10.17	131-133/0.2	72.1
10	$C_{14}H_{21}O_5P$							Decompose^{bc}	71.1
11	$C_{15}H_{23}O_6P$	54.57	6.96	9.38	54.66	7.07	9.20	Decompose^{b}	64.2
12	$C_{13}H_{18}ClO_4P$	51.24	5.95	10.16	51.29	5.92	10.01	114-116.5/0.075	66.1
13	$C_{13}H_{18}ClO_4P$	51.24	5.95	10.16	51.40	5.95	10.04	117-118.5/0.075	62.1

a. This is a known compound; see reference 66a.

b. Analytical sample prepared by a short path distillation technique using an apparatus similar to a Bantam-Ware short/path distillation unit (No. K-284500).

c. This is a known compound; see reference 65.

the isopropyl-methyl protons. The four lines are two sets of doublets (first and third peaks and second and fourth peaks are doublets, respectively), the doubling being a result of coupling of the isopropyl-methyl groups to the methine proton (J≅6.0 Hz for all cases). In contrast, compounds 6 and 9 gave one sharp doublet for the isopropyl-methyl protons due to splitting by the methine proton (Figure 2). Both 8 and 11 gave quartets (Figure 3) in which there were two sets of lines; each set had a J value of about 6 Hz (methine splitting). In all cases the methine proton resonance was a complex multiplet (centered at δ 4.67) which showed little or no detectable temperature dependence.

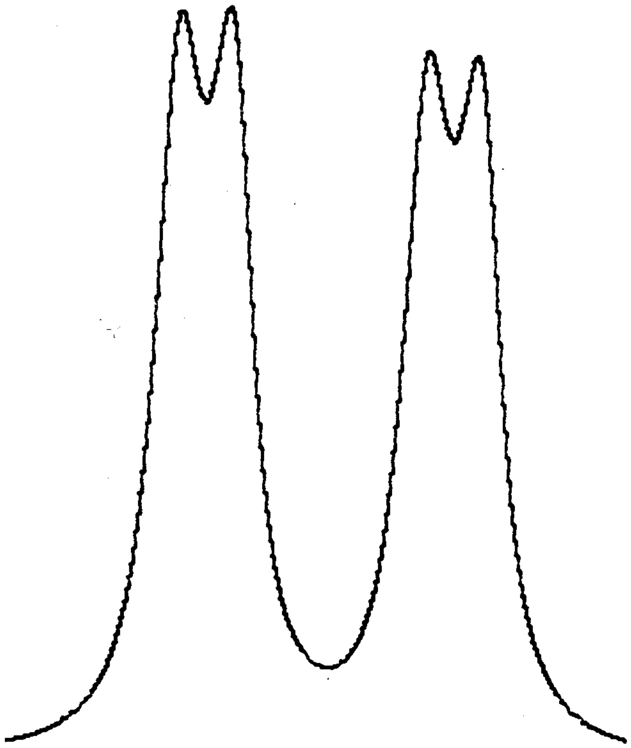


Figure 1. Simulated Spectrum of 5 at Room Temperature

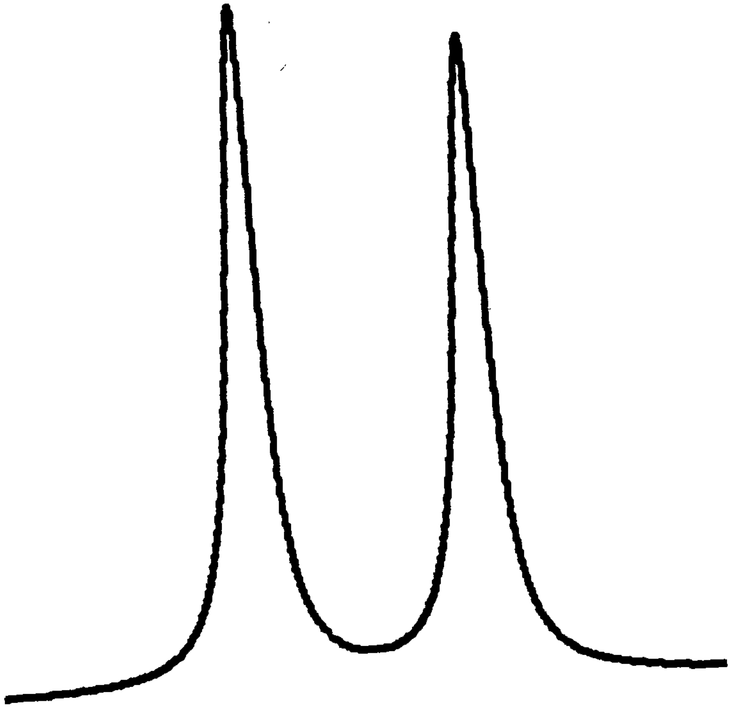


Figure 2.

Simulated Spectrum of 6 at Room Temperature

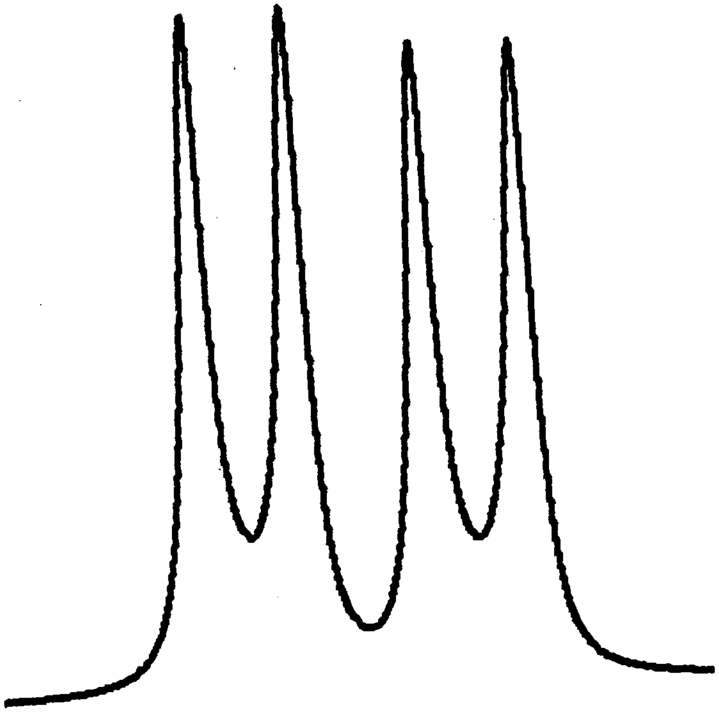


Figure 3.

Simulated Spectrum of 8 at Room Temperature

To determine the origin of the peak doubling, a variable-temperature NMR study was undertaken. Spectra were generally recorded over a range of -50° to +100°C (except where noted). Within this temperature span, the greatest change was noted for all compounds except 6 which displayed a major change from 100-150°C. The isopropyl-methyl region (δ 1.3) of the spectra was found to be temperature-dependent for all of the compounds except 8 and 11. The spectra of both of the latter esters exhibited no change in the quartets over a range of -50° to +150°C. In all other cases, except 12, the trend observed included a quartet, the resolution of which was improved as the temperature was lowered. The exact temperature (Table VI) at which the doublet splits into a quartet was difficult to determine accurately owing to the fact that not much line broadening or change in the peak shape was observed during the onset of the phenomenon.

Doubling of the magnetic resonance of geminal protons or of methyl protons in an isopropyl group adjacent to an asymmetric[1] center is well documented.[33,34,42,46,50,57] Several explanations for this phenomen have been advanced, including partial bond hybridization,[31] hindered rotation[27,36] and stereochemical nonequivalence of protons.[40,70] Of these, partial bond hybridization has been criticized by Waugh and Cotton.[70] There is also the possibility that a temperature-dependent chemical shift is responsible for our observed peak doubling. Of the four considerations, the temperature-dependent chemical shifts may be ruled out by examining a plot (Figure 4) of the peak separation versus temperature (Note the peak separations are obtained from measurements of chemical shift difference between the two sets of exchanging protons--such as on the two isopropyl groups).

TABLE VI

COALESCENCE TEMPERATURES FOR DIISOPROPYL AROYLPHOSPHONATES

Compound	Coalescence Temperature (^{o}K)	
5	314 (Neat)	305 (CS_2)
6	257 (Neat)[a]	
7	331 (Neat)[b]	300 (CS_2)
8	None observed	
9	267 (CS_2)	
10	299 (CS_2)	
11	None observed	
12	321 (C_2Cl_4)	302 (CS_2)
13	317 (C_2Cl_4)	315 (CS_2)

a) See Plate XXXVII

b) See Plate XXXII

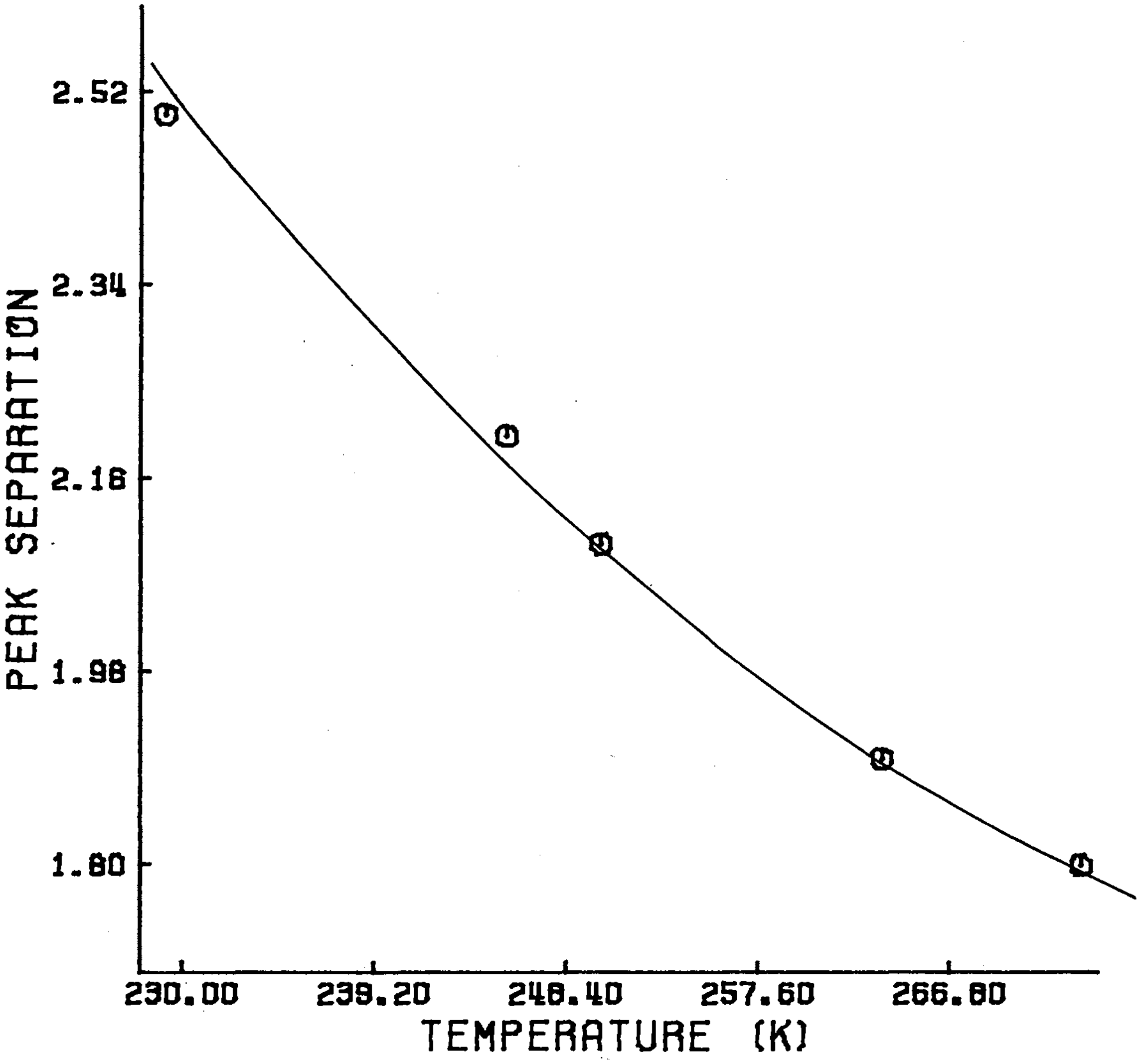


Figure 4. Plot of Peak Separation vs Temperature

The non-linearity suggests some type of *complex* dynamic process as the cause of the nonequivalence rather than a temperature-dependent chemical shift. If 7 were in a rigid conformation, a linear relationship between peak separation and temperature might be expected[30a,48] as, for example, is observed in a rigid system, such as camphor (in the case of camphor a linear change in the chemical shift is noted). Likewise in a mobile system[30b] (N, N-dimethylformamide) one sees a simple rotational process that shows a linear relationship within a temperature range (excluding the high and low temperature limits which, of course, are non-linear). There is, however, a slight linear temperature dependence of the chemical shift observed (Figure 5). This was noted while attempting to fit the experimental and theoretical spectra for compound 7 and was on the order of 0.6 to 0.7 Hz over the temperature range. This is much less than the total change observed in the peak separation (3.0 Hz). Due to the known similarity of the shielding characteristics of the benzene ring and the carbonyl[24] group, a large chemical shift difference between the two conformations would not be expected.[40b]

The possibility that a dynamic process is indeed taking place is supported by the fact that when the ratio of the peak heights to the valley (for 7) between them is plotted (Figure 6) the resulting curve is non-linear. This result is also noted in the case of N,N-dimethyltrifluoroacetamide.[72]

Differentiating between the two other possible causes for the spectra is a more difficult task. A complete analysis of the data does, in fact, indicate that the observed peak doubling is a function of both hindered rotation and stereochemical nonequivalence of protons.

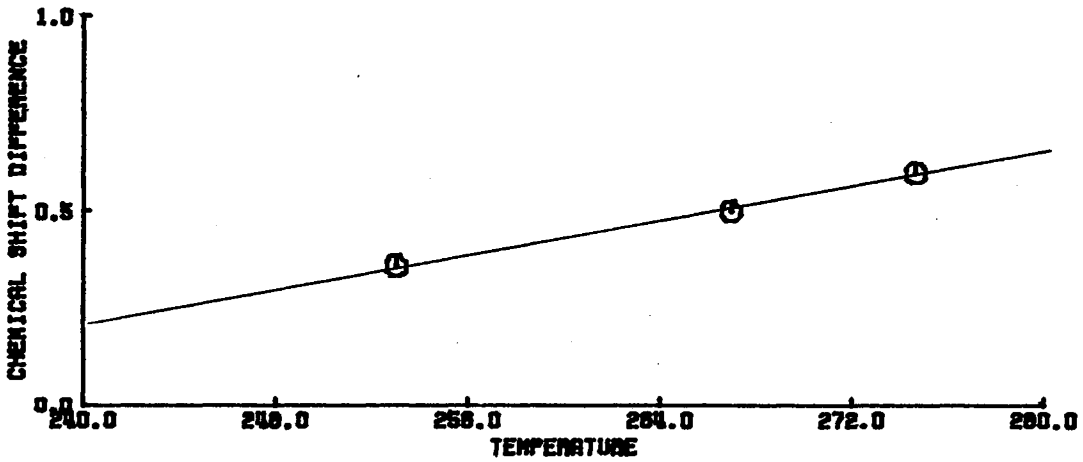


Figure 5. Plot of Chemical Shift Difference Versus Temperature for 7

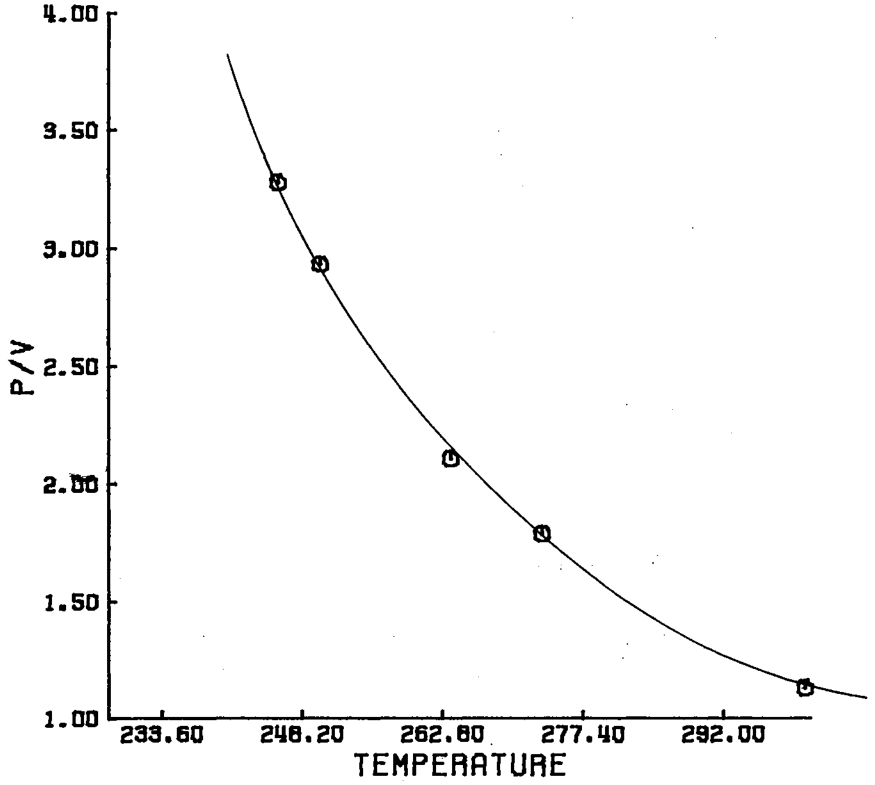
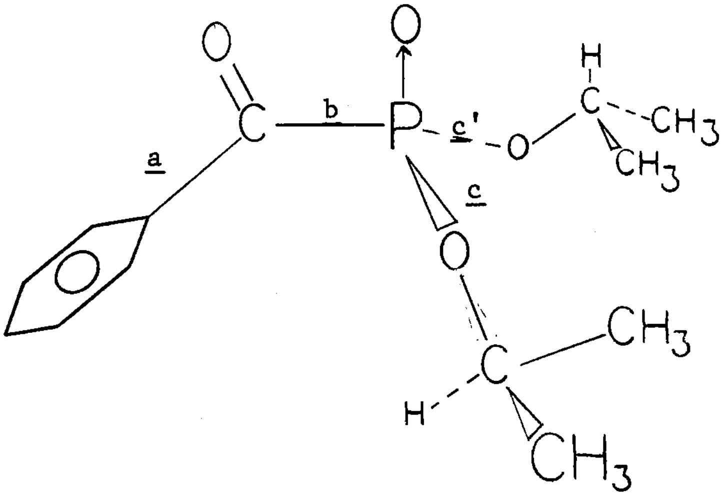


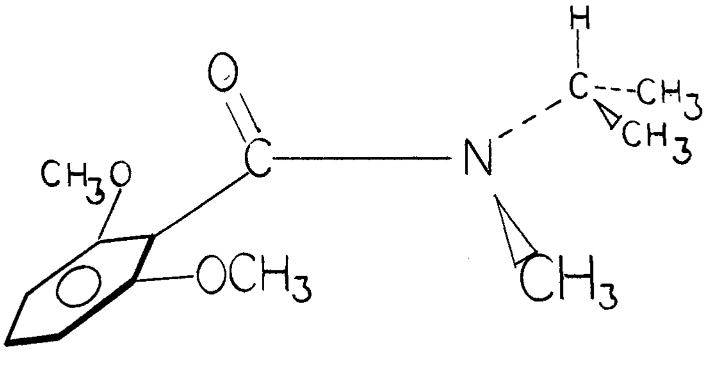
Figure 6. Plot of Peak to Valley Ratio Versus Temperature

There are three generally recognized[58,59] requirements which are necessary before nonequivalence can be observed in the NMR spectrum of a compound: (1) "there must not be any molecular motions which correspond to a symmetry operation for the protons which are completed within a time that is short compared to the NMR signal width," (2) "there must be a field gradient between the protons," and (3) "there must not be any rapid internal molecular motions that produce an approximation of symmetry that is good enough to prevent the observation of nonequivalence." By applying the above conditions to the observed peak doubling, the following considerations can be examined: (1) there exists a configuration (or configurations) in which there is no symmetry element present; (2) there exists some molecular motion (or motions) which, when rapid enough, simulates a symmetry operation; (3) there exists a field gradient between the configurations which is large enough for nonequivalence to be observed; (4) the field gradient is large enough for compounds 8, 11 and 5 (only at elevated temperatures) that the nonequivalence is observable even in the presence of rapid molecular motions which destroy the nonequivalence in all of the other compounds.

There are four bonds (a, b, c and c') about which rotation may be hindered sufficently to cause nonequivalence of the protons in the ester group. Of these bonds, the nature of the rotation about bonds of type a is probably the most well documented. Unlike what was originally thought, the ring was found to rotate slowly about the Ar-C=O bond by Anet and Ahamad[3] in para substituted benzaldehydes. However, one may assume that the ring is in conjugation with the



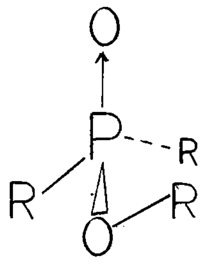
carbonyl carbon much of the time since conjugation energy would favor this configuration at room temperature. The nature of the substituent in the ortho position greatly affects the rate of rotation as noted by Siddall and Garner[60] in certain substituted benzamides. They report[61] the barrier to rotation about the Ar-C=O bond in 14 to be about 20 kcal/mole while the barrier[60] in the mono ortho substituted benzamides is much lower. The authors[61] postulate that the ring is bent out of the plane of the carbonyl group while the lone electron pair on nitrogen remains in conjugation with the carbonyl function



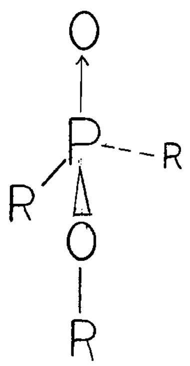
14

In the diisopropyl aroylphosphonates of our study there is no intuitively obvious gain in electronic stabilization by placing the phosphoryl group in any particular configuration with respect to the carbonyl group. This is in contrast to the situation in the amide system. It is reasonable to assume that while slow rotation occurs about the Ar-C bond, the most highly populated conformers must be those in which the ring is in conjugation with the carbonyl group, except in compounds 8 and 11. In these two cases, the most highly populated conformers are those in which the ring is out of the plane of the carbonyl function. Support for this statement is found in the ultraviolet data for 8 (287 mμ, log ϵ_{max} 3.15) and 11 (272 mμ, log ϵ_{max} 3.44). A decrease in the magnitude of ϵ_{max} suggests that conjugation of the phenyl ring and the carbonyl group is greatly reduced as compared to that in 5 (260 mμ, log ϵ_{max} 4.06) or 6 (262 mμ, log ϵ_{max} 4.03). This situation apparently results from steric factors.

The rotational propensities of the remaining bonds (b, c, and c') are not so easily analyzed. The nature of the rotation about the P-OR (c and c') bonds has been discussed by several authors.[17,32,33,42,57a,57b,59,71] The evidence presented by these workers is conflicting and does little to clarify the problem. Jardine and co-workers[42] favor the existence of two conformations with respect to one ester group (shown below), with free rotation beginning at elevated temperatures (+150°C). In contrast Siddall and Prohaska[57a,57b] postulated that there is free rotation about the P-OR bond with the

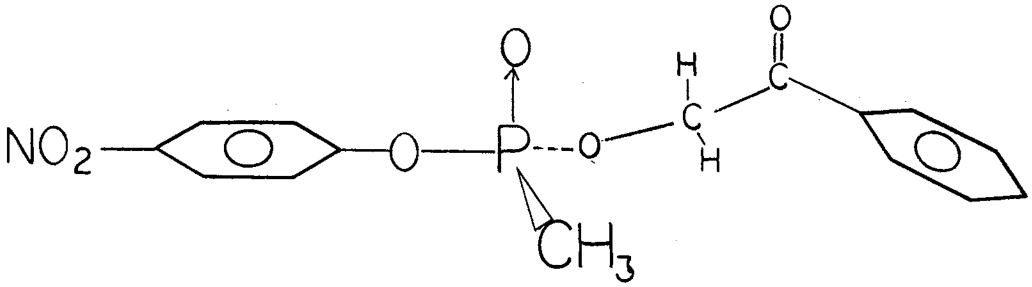


Up



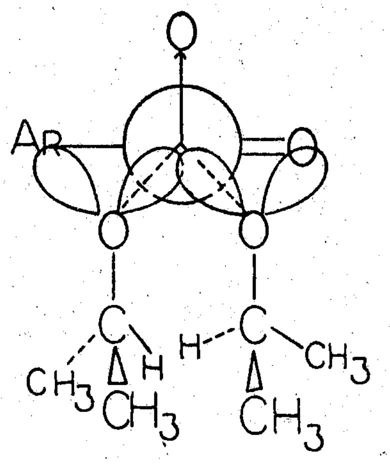
Down

"up" configuration favored. Frankel and co-workers[32] computed the barrier to rotation (from temperature-dependent coupling constants) to be approximately 850 cal/mole for 15 but failed to comment on a preferred conformation.

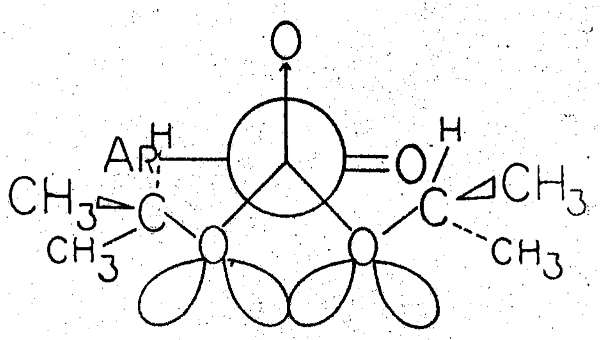


The ^{31}P spectra (Plates XXVIII and XXIX) of 6 and 7 indicate that the ester groups are equivalent at room temperature. If the methine protons were nonequivalent (as would be expected if rotation about the P-OR bond was rapid, excluding accidental equivalence), a doublet or set of doublets would be observed rather than the observed triplet (Plate XXIX). By far the bulk of the data points to free rotation about the P-OR bonds but there is little evidence in the literature to prove the existence of a preferred conformation in any system containing P-OR groups.

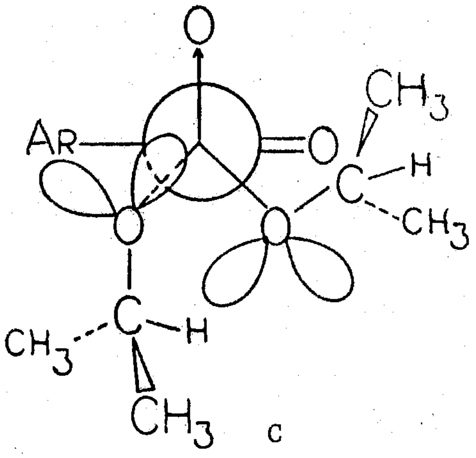
There are several possibilities for conformations in the diisopropyl aroylphosphonates herein reported, some of which may be ruled out on the basis of steric arguments. Note that all of the conformations shown below are interconvertible by rotation about the P-OR bonds (c̲ and c̲').



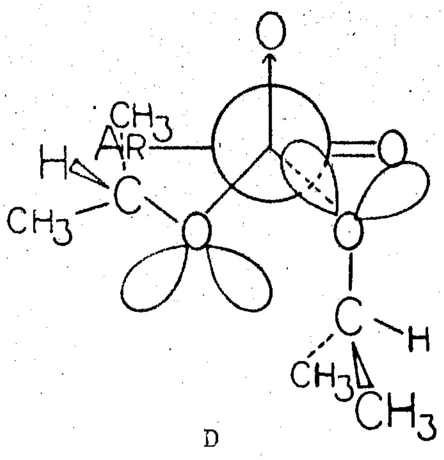
A



B

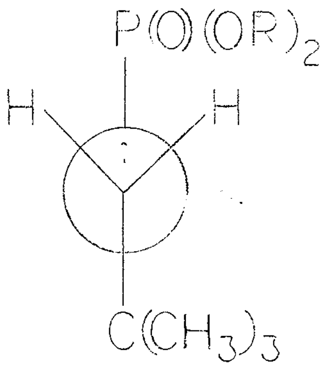


C



D

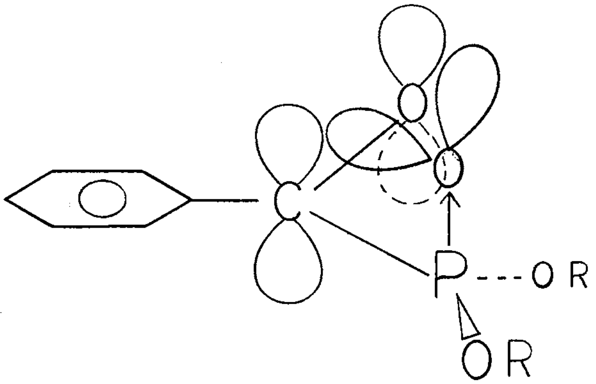
Bothner-By and Trautwine conclude from a study of trineopentyl phosphate that the favored conformation about the C-OP bond is a staggered ethane-like structure[17] (shown below). If this rationale is



applied to the aroylphosphonates, several staggered conformations can be envisioned. Some of these conformers have the isopropyl-methyl groups in close proximity when the arrangement about the P-OC bonds is like those in A or B. Models suggest that the steric crowding in A must limit the contribution of this conformer greatly. It must also be pointed out that both configurations A and B place the orbitals of the non-bonding electrons on oxygen in an arrangement adjacent to each other. This situation, from the standpoint of electronic repulsion, is likely to be unfavorable. In conformations C and D, the interactions between the isopropyl-methyl groups and the interactions between the non-bonding pairs of electrons are minimized. Hence it is not unreasonable that the staggered conformations C and D are probably the favored conformations, although one cannot conclude unequivocally that these are locked conformations and that interconversion between C and D does not occur rather easily.

There has been some speculation[6,8,67a,67b] concerning the configuration around the P-C bond (b) based on an unusually large shift

($10-15\ cm^{-1}$) of the C=O stretching frequency toward longer wavelengths in the dialkyl aroylphosphonates when compared to the benzaldehyde analogs. The shift was tentatively attributed to some type of interaction between the phosphoryl oxygen non-bonding orbitals and the carbonyl carbon p orbital (shown below). A similar shift ($5\ cm^{-1}$),

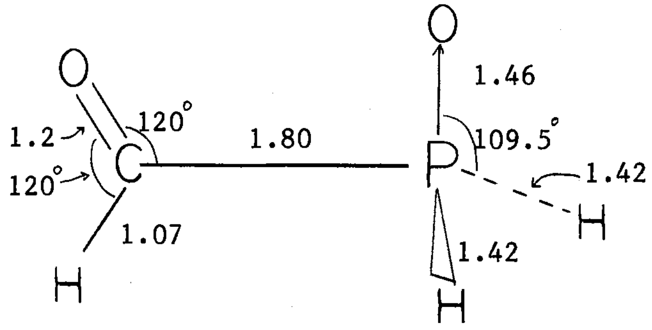


although not as large, is also reported[38a] for the acylphosphines when compared with the amide analogs. The absence of the phosphoryl oxygen in this system indicates that the shift is probably attributable to $2p\pi$-$3d\pi$ type interactions (the dipole moment data of Ishmaeva[38b] indicates that there is a conjugative interaction between the benzoyl and the phosphoryl group in X-$C_6H_4C(O)P(O)(OC_2H_5)_2$, where X = p-Cl, m-Cl, m-Br and p-NO_2).

In an effort to evaluate the possibility of such an interaction between the $p\pi$ orbital of the carbonyl carbon and the P→O group in the acylphosphonates of this study, an Extended Hueckel calculation using a program developed by Hoffmann[37] was carried out. This program approximates the off-diagonal Hamiltonian matrix elements by

$H_{ij} = S_{ij} \cdot (H_{ii} + H_{jj})$, where H_{ii} and H_{jj} are the valence-state ionization potentials and S_{ij} is evaluated by a recurrence technique developed by Ruedenberg and co-workers.[55] All of the empirical parameters were taken from those used in previous work[19,37] on other phosphorus-containing systems.

The model chosen to represent the system was restricted to 24 orbitals by core space limitations in the computer memory. The ester groups bonded to the phosphorus atom were replaced by hydrogen atoms as was the phenyl ring. No attempt was made to optimize bond angles



or bond lengths shown. All angles and bond lengths were taken from X-ray data published on other phosphorus compounds.[19,37] The calculations were performed both with and without consideration of the d orbitals on phosphorus and the results are shown in Table VII.

TABLE VII

EXTENDED HUECKEL DATA

Angle in Degrees	E_T (without d orbitals)	E_T (with d orbitals)
0.0	-501.30	-508.25
45.0	-501.24	-508.21
90.0	-501.20	-508.28
135.0	-501.26	-508.24
180.0	-501.30	-508.20

It must be recognized that steric interactions are not considered important in this calculation because of the small size of the hydrogen substituents compared to the actual substituents. Therefore any difference in the energy of a conformation compared to the other conformations must be almost entirely electronic in origin. As can be seen from the plot of the total energy versus dihedral angle ϕ, the conformation with $\phi = 90$ degrees does not appear to be favored energetically for the computation in which d orbitals were not included (Figure 7). However, when d orbitals are included, the conformation at $\phi = 90$ appears to be favored by a few hundredths of an e.v. (Figure 8).

Perhaps of equal importance are the values of the overlap integrals for the $2p_z$ ($2p\pi$) orbital on carbon and the 2p orbitals on the phosphoryl oxygen (Table VIII). These values are not large enough to bring about any significant interaction between the two atoms, a fact which might have been anticipated from the calculated distance (2.66 Å) between them.

TABLE VIII

OVERLAP INTEGRAL VALUES

Angle in Degrees	$2p_z$-$2p_z$	$2p_z$-$2p_x$	$2p_z$-$2p_y$
0.0	0.0070	0.0000	0.0000
45.0	0.0005	-0.0152	0.0065
90.0	-0.0060	-0.0215	0.0000
135.0	0.0005	-0.1520	-0.0065
180.0	0.0070	0.0000	0.0000

Again it must be emphasized that these calculations do not preclude a favored conformation arising from steric factors due to internal non-bonded interactions.

Another piece of evidence bearing on this point arose while trying to explain the unusual NMR spectrum observed at high temperature for **6**. A temperature study using a laser Raman spectrometer showed that there was a significant and reproducible shift of 3 cm^{-1} to higher frequency for the C=O group around 150° C. This shift was not noted in compound **7** at that temperature. The shift is believed to be due to a breaking of conjugation between the aryl ring and the carbonyl group in **6**. If

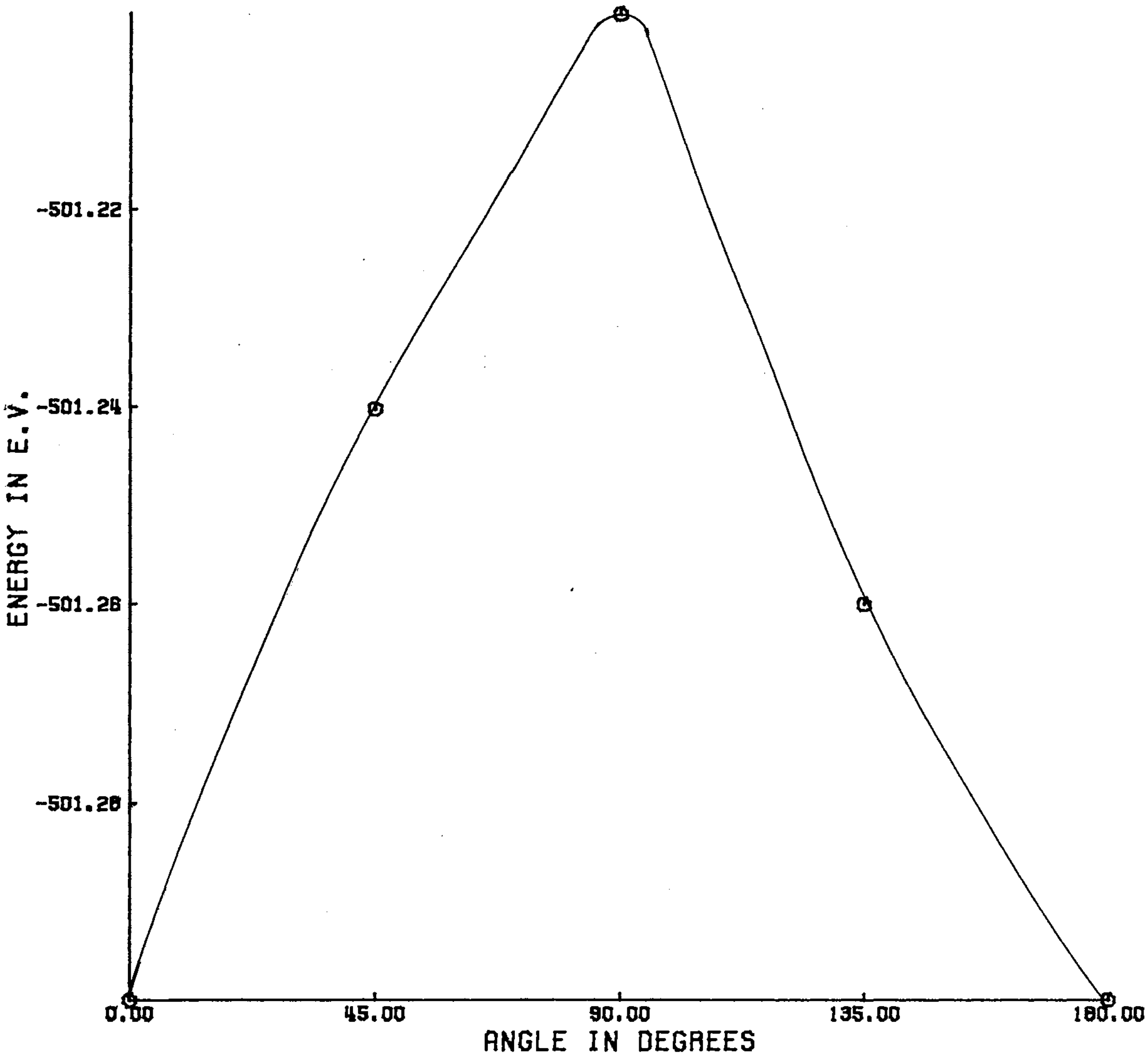


Figure 7. Plot of Energy versus Angle for the Calculation Which Did Not Include d Orbitals

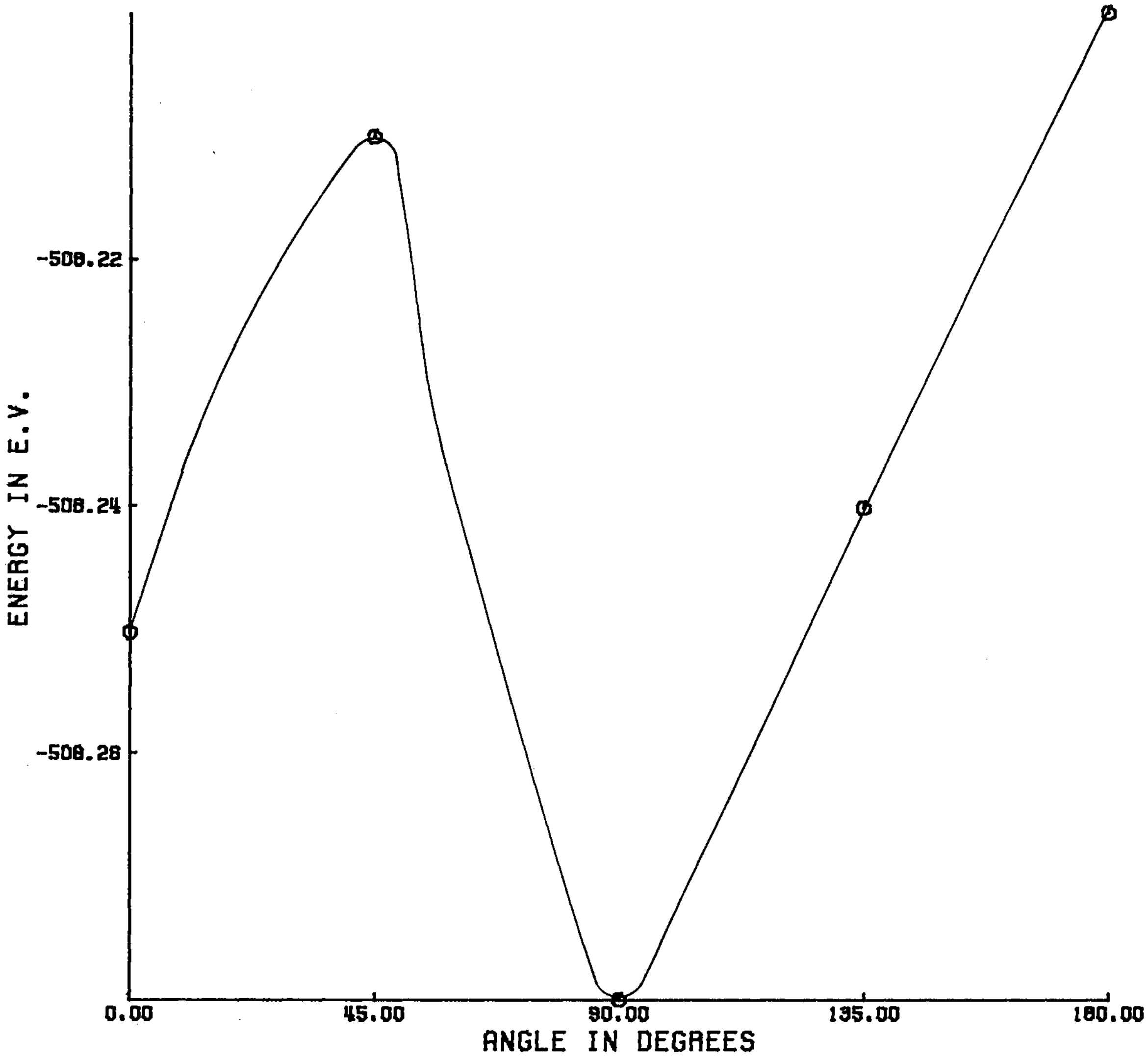


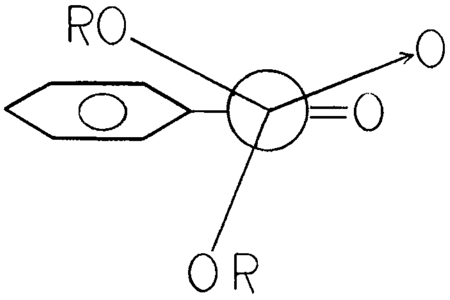
Figure 8. Plot of Energy versus Angle for the Calculation Which Included d Orbitals

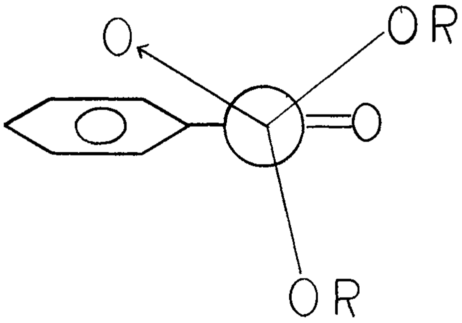
the 10-15 cm^{-1} shift for $\nu_{C=O}$ in simple aroylphosphonates[6,8] (compared to the corresponding benzaldehyde analogs) was caused by interaction of the carbonyl carbon with the phosphoryl oxygen, this interaction would be destroyed by free rotation about the C-P bond (*b*) at this temperature. If the shift was due to the 2*p*π-3*d*π interactions, little change would be expected even with free rotation about the C-P bond, if one accepts the argument that there is little angular dependence for interaction with *d* orbitals.[41] Unfortunately, the P→O bond was inactive or very weak in the Raman spectrum and no conclusions could be made concerning the influence of the C=O on the P→O absorption.

There is, however, other data which can only be reasonably explained by a favored conformation about the P-C bond (*b*) with a OPCO dihedral angle (ϕ) of approximately 90 degrees. The experimental dipole moments of **5** (2.53 D) and **6** (2.69 D) taken in carbon tetrachloride at 25° C are somewhat lower than the previously reported[6] values for dimethyl benzoylphosphonate (2.93 D), dimethyl 4-methoxybenzoylphosphonate (3.20 D) and dimethyl 4-chlorobenzoylphosphonate (2.64 D). The difference in the experimental moment of **5** and that of the dimethyl benzoylphosphonate could be the result of the larger size of the isopropyl group (as compared to the methyl group in the ester functions) which *could impose a slight conformational change on the system*. Calculations indicate that the magnitude of the moments of **5** and **6** is lower than expected for a conformation where the dihedral angle (ϕ) between the carbonyl oxygen atom and the phosphoryl oxygen is 0.0 and higher than for a dihedral angle of 180 degrees.

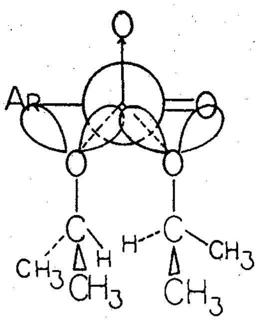
the 10-15 cm^{-1} shift for $\nu_{C=O}$ in simple aroylphosphonates[6,8] (compared to the corresponding benzaldehyde analogs) was caused by interaction of the carbonyl carbon with the phosphoryl oxygen, this interaction would be destroyed by free rotation about the C-P bond (b) at this temperature. If the shift was due to the $2p\pi$-$3d\pi$ interactions, little change would be expected even with free rotation about the C-P bond, if one accepts the argument that there is little angular dependence for interaction with d orbitals.[41] Unfortunately, the $P\rightarrow O$ bond was inactive or very weak in the Raman spectrum and no conclusions could be made concerning the influence of the C=O on the $P\rightarrow O$ absorption.

There is, however, other data which can only be reasonably explained by a favored conformation about the P-C bond (b) with a OPCO dihedral angle (ϕ) of approximately 90 degrees. The experimental dipole moments of 5 (2.53 D) and 6 (2.69 D) taken in carbon tetrachloride at 25° C are somewhat lower than the previously reported[6] values for dimethyl benzoylphosphonate (2.93 D), dimethyl 4-methoxybenzoylphosphonate (3.20 D) and dimethyl 4-chlorobenzoylphosphonate (2.64 D). The difference in the experimental moment of 5 and that of the dimethyl benzoylphosphonate could be the result of the larger size of the isopropyl group (as compared to the methyl group in the ester functions) which could impose a slight change on the system. Calculations indicate that the magnitude of the moments of 5 and 6 is lower than expected for a conformation where the dihedral angle (ϕ) between the carbonyl oxygen atom and the phosphoryl oxygen is 0.0 and higher than for a dihedral angle of 180 degrees.

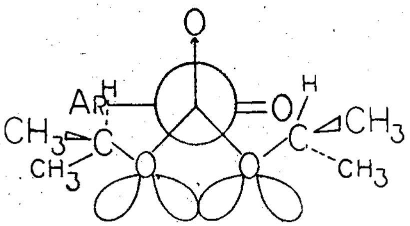




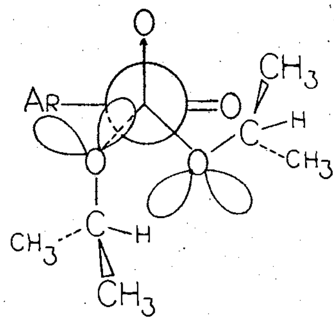
Empirical dipole moments were calculated using a computer program based on equations of Smyth.[62] The coordinates of all of the atoms were first calculated using a computer program obtained from the Quantum Chemistry Program Exchange.[25] The bond moments were then summed to produce the molecular dipole moment (see Table X, see Experimental for a detailed description of the calculation). Moments were calculated for four different models (below) in each case varying the OPCO dihedral angles (ϕ) of 0.0, 45.0, 90.0, 135.0 and 180.0 degrees. The models were set up to explore both the dihedral angles (ϕ) and the different orientations of the ester groups with respect to the phosphoryl oxygen atom.



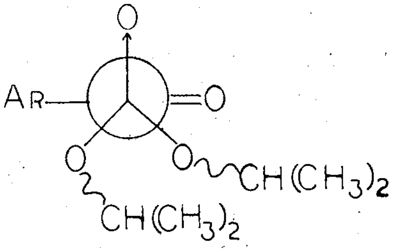
Model I



Model II



Model III



Model IV (Free rotation)

Upon examination of the calculated data (Table IX and Table X) for models I through III, it becomes apparent that there are different combinations of ∅ and ester group conformations which give values which are within 0.5 D of the measured values for 5. What is immediately obvious is that the molecular dipole moment does not depend so much on the configuration of the ester groups as it does on the dihedral angle (∅), as evidenced by the free rotation model (IV). In the free rotation model, there is no weighting of any of the configurations of the ester groups. The obvious conclusion is that the experimental data is best matched in those cases where the dihedral angle is approximately 90 degrees. Although it is difficult to draw any definite conclusions from this data because of the mobility of the system, it can be surmised that the preferred dihedral angle may be about 90 degrees. An examination of Courtauld models also indicates that there is a great deal of interaction between the substituent at the <u>ortho</u> position and the oxygens on the phosphorus atom. This interaction appears to be large enough to hinder rotation about the C-P bond (<u>b</u>).

TABLE IX

CALCULATED DIPOLE MOMENTS (DEBYE UNITS)

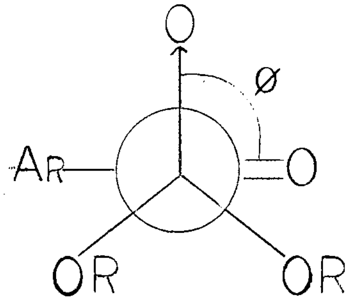
Dihedral Angle (ϕ)	Model I	Model II	Model III	Model IV[a]
0.0	3.56	5.15	6.78	5.08
45.0	3.37	4.47	6.31	4.70
90.0	2.88	3.15	5.02	3.64
135.0	2.29	1.50	3.24	2.09
180.0	1.99	1.19	2.10	0.82

a. Free rotation model

Assuming that hindered rotation is probable and that there is a preferred conformation about the C-P bond (<u>b</u>), it is necessary to examine the observed nonequivalence in terms of the three requirements for nonequivalence discussed previously. The stereochemical nonequivalence of the isopropyl-methyl protons when adjacent to an asymmetric[1] center has been well established by several workers.[33,34,42,46,50,57]

TABLE X

CALCULATED DIPOLE MOMENTS (DEBYE UNITS) FOR DIISOPROPYL BENZOYLPHOSPHONATE

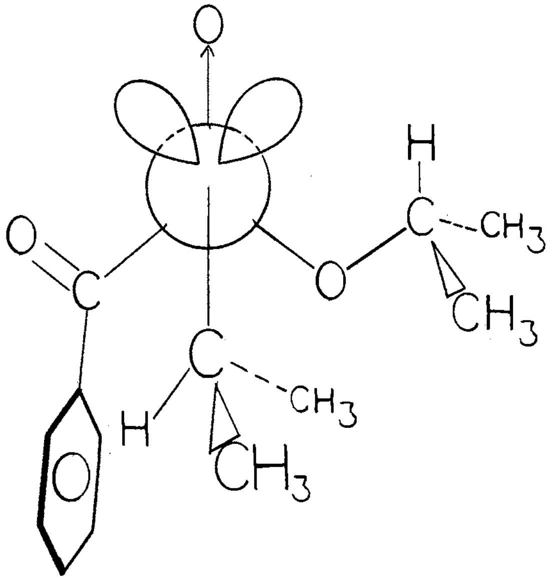


Model[a]	$C_6H_5{\rightarrow}C(O)$[b]			$C_6H_5{\leftarrow}C(O)$			$C_6H_5{\rightarrow}C(O)$	$C_6H_5{\leftarrow}C(O)$
ϕ	I	II	III	I	II	III	IV	IV
0.0	3.56	5.15	6.78	3.14	4.56	6.10	5.08	4.48
45.0	3.37	4.47	6.31	3.0	4.03	5.74	4.70	4.18
90.0	2.88	3.15	5.02	2.61	3.02	4.76	3.64	3.35
135.0	2.29	1.50	3.24	2.16	1.92	3.51	2.09	2.23
180.0	1.99	1.19	2.10	1.95	1.77	2.83	0.82	1.55

a. ϕ is the OPCO dihedral angle.

b. Arrow indicates the direction of the assumed bond moment (0.4 D).

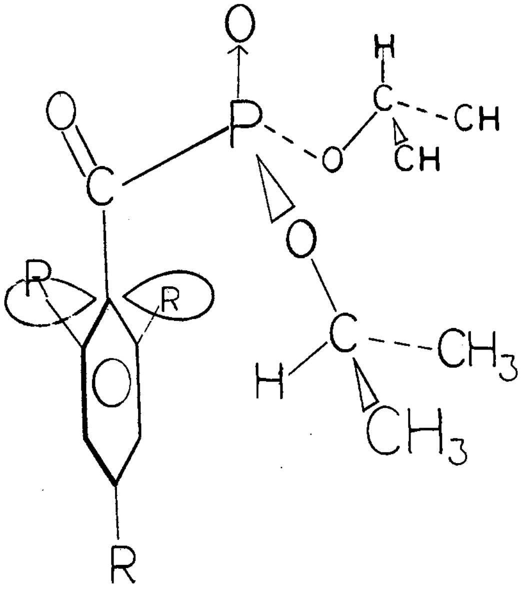
Also known is the tendency for these protons to be nonequivalent in systems where there is no formal center of asymmetry but where there is a pseudo center of asymmetry "from the viewpoint of the isopropylmethyl protons." It is not necessary for this pseudo center of asymmetry to be immediately adjacent to the isopropyl group. The same effect is still possible when there is an intervening oxygen. This situation has also been observed in diisopropylphenylphosphine but <u>not</u> in



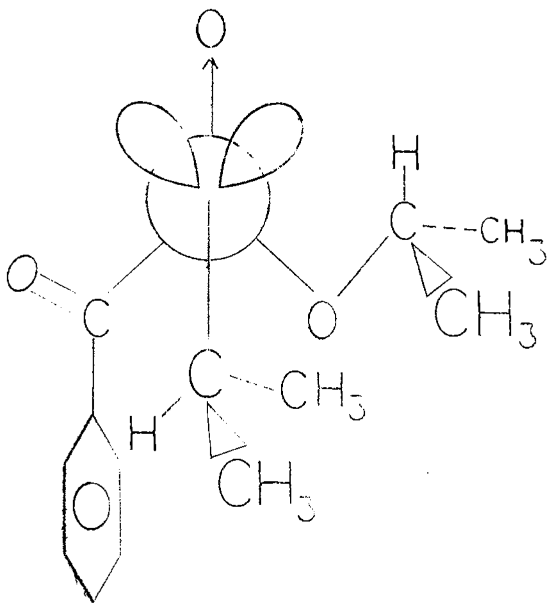
isopropyldiphenylphosphine.[50] The necessity of having an anisotropic group, such as the phenyl ring, for nonequivalence to be observable, has been suggested by Siddall and Prohaska.[57a] Jardine and co-workers[42] questioned this requirement but neglected to indicate that in their study a true center of asymmetry was present and one of the substituents contained a benzene ring. In the diisopropyl aroylphosphonates under consideration, the phenyl ring is present and the conformation of this ring with respect to the carbonyl group appears to play an important role in determining the nature of the observed spectra for the various aroylphosphonates, as evidenced by the spectra of **8**

(Plate XXII) and 11 (Plate XXV) when compared with the spectra of 5 (Plate XIX) or 6 (Plate XX).

As has been previously mentioned, UV data suggests that in compounds 8 and 11 the extent of conjugation between the aryl ring and the carbonyl group is not as great as in the other esters. This implies that there is a highly populated configuration in which the ring is bent out of the plane of the carbonyl group as shown below.



In this case the isopropyl groups fall directly within the shielding cone of the aryl ring, but it may <u>not</u> be true that the <u>sets</u> of isopropyl-methyl protons will be affected equally. The presence of a field gradient (provided by the aryl ring) and the inherent stereochemical nonequivalence of isopropyl-methyl protons could serve to explain the quartet observed for compounds 8 and 11 at all temperatures. As pointed out by Pople[52] in situations such as shown, the methyl groups in the isopropyl function may never be equivalent (although accidental equivalence may be possible) no matter what the rate of

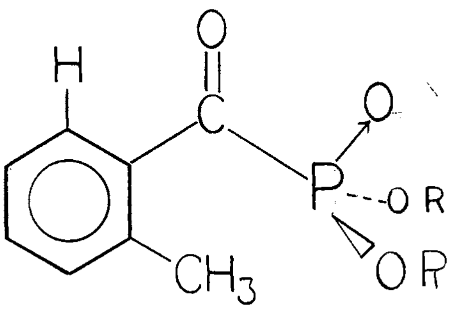


rotation. It should be noted that it is often difficult to predict nonequivalence on topological grounds but once observed the nonequivalence may be explained on this basis.

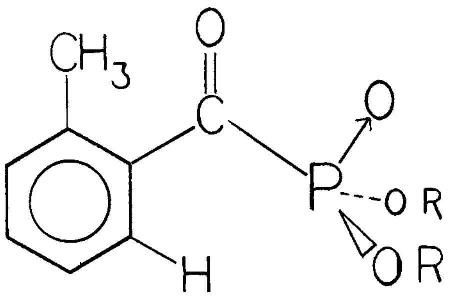
A similar explanation will serve to account for the unusual behavior of compounds 6 (Plate XXXIV) and 12 (Plate XXXVIII). The NMR spectra of these esters exhibit an inverse temperature dependence. The doublet which is present at room temperature splits into a quartet as the temperature is raised. The larger number of peaks present in the 100 MHz spectrum of 6 (Plate XXXIV) at 150° C (as compared to 5 Plate XXXV) may be due to several configurations which contribute significantly to the total spectrum. The nature of the temperature dependence indicates that above a certain temperature the population of the configuration in which the ring is out of the plane of the carbonyl group must be quite large and so produce the same effect that is seen in the spectra of 8 (Plate XXII) and 11 (Plate XXV).

The difference in the temperature above which this phenomenon is observed can be explained by the difference in the inductive effect of a methyl group as compared to a chloro group coupled with the difference in the steric requirements between the two groups. In compound 6 the electron-donating ability of the methyl group may make the configuration in which the ring is in conjugation with the carbonyl group much more favorable than it is in compound 12. In the chloro compound 12 the electron-withdrawing property of the chlorine atom may destabilize this configuration. Consequently, the conformations in which the ring is out of conjugation with the carbonyl could be more highly populated in the *ortho* chloro compound than in the *ortho* methyl compound 6.

Courtauld models suggest that in 6 the conformation with the methyl substituent on the phenyl ring near the phosphoryl function 6a is



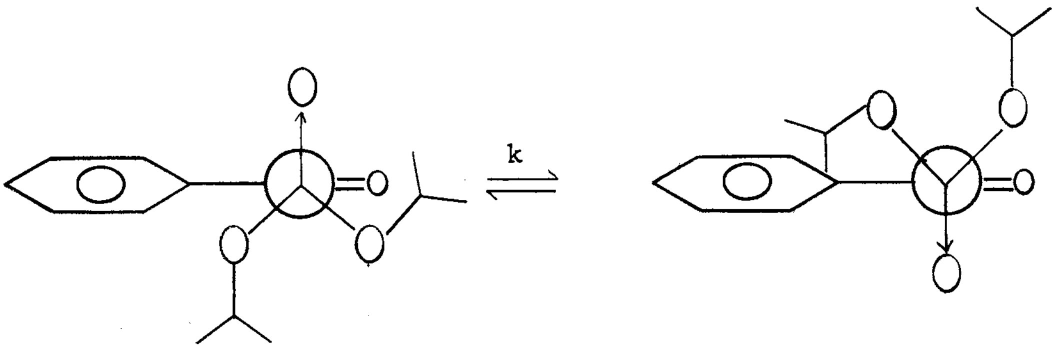
6a



6b

sterically unfavorable. However, NMR analysis implies that there is possibly a significant contribution made by the conformer 6a. Neither the ring methyl (Plate XXXIII) nor the ^{31}P absorption lines are sharp (Plate XXVIII). The broad triplet observed for the ^{31}P signal (produced by coupling to the methine protons) appears to be two triplets of almost equal intensity. The broadening of the resonance lines of the ^{31}P spectra cannot be due to nonequivalent methine protons. If this were the case, the peaks would appear as two sets of doublets, not two sets of triplets. The above argument may also be used to explain the broadening of the ring methyl resonance. Thus, the ^{31}P data suggests that there are two almost equally favored conformations (6a and 6b) of the methyl group on the ring with respect to the phosphorus atom.

Having determined the configuration about the Ar-C=O bond (a), having showed that stereochemical nonequivalence of the isopropylmethyl groups is possible in these compounds, and having explained the rotational properties of the ester groups in terms of previous work, we should now examine the C-P bond (b) in terms of its rotational properties. A dihedral angle between the carbonyl oxygen and the phosphoryl oxygen, as mentioned previously, of about 90 degrees seems best to explain the dipole moments. To rotate the phosphoryl group 180 degrees to achieve an interchange of the ester groups requires that at least one of the oxygens on the phosphorus eclipse the ortho



substituent on the ring.

If the field gradient is not too great, i.e. the ring is not bent out of conjugation with the carbonyl (so that the shielding of the isopropyl-methyl protons by Ar is greatly altered) this type of rotation, if sufficiently rapid, could simulate a symmetry operation closely enough to cause equivalence. On the assumption that this situation occurs, the above mechanism was used as a model for calculation of the theoretical NMR line shapes using DNMR2[14] and DNMR3[15]. Since neither program is set up to treat a system with fourteen protons the individual methyl groups were treated as a single spin. This is a reasonable assumption in view of the fact that the methyl groups are not coupled to each other, nor are they coupled to the phosphorus atom, and there is little or no temperature dependence in the absorptions of the methine protons. Therefore little information is to be gained by including them in the analysis. The theoretical line shapes are seen to fit the experimental curves quite well (Table IX, Plates XXXI and XXX).

Even though a good fit was obtained, when an Arrhenius plot (ln k vs 1/T, Figure 9) of the data (Table XI) was constructed, an activation energy of approximately 5 kcal/mole was obtained. With such a low value of E_a one would not expect the observed phenomena to occur around room temperature. The value calculated for ΔS^* (-50 cal/deg mole) from the Eyring equation is also unreasonable for a process of this type where ΔS^* is expected to be near zero.[12]

Since this simple mechanism fails to give defensible values for the thermodynamic parameters, a more complex process is likely responsible for the experimental observations. Critical examination of the system reveals that a combination of rotations is conceivable about

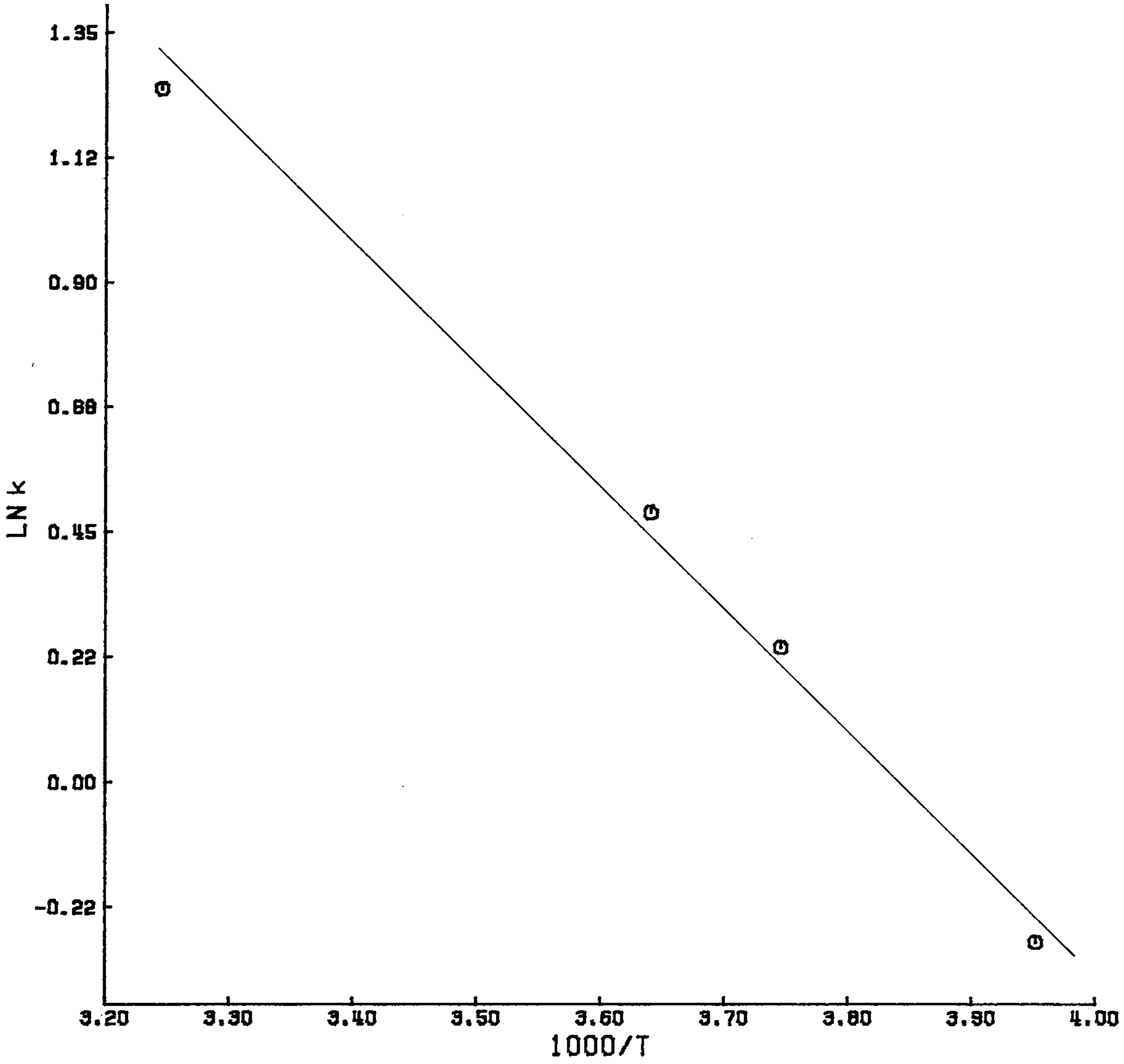
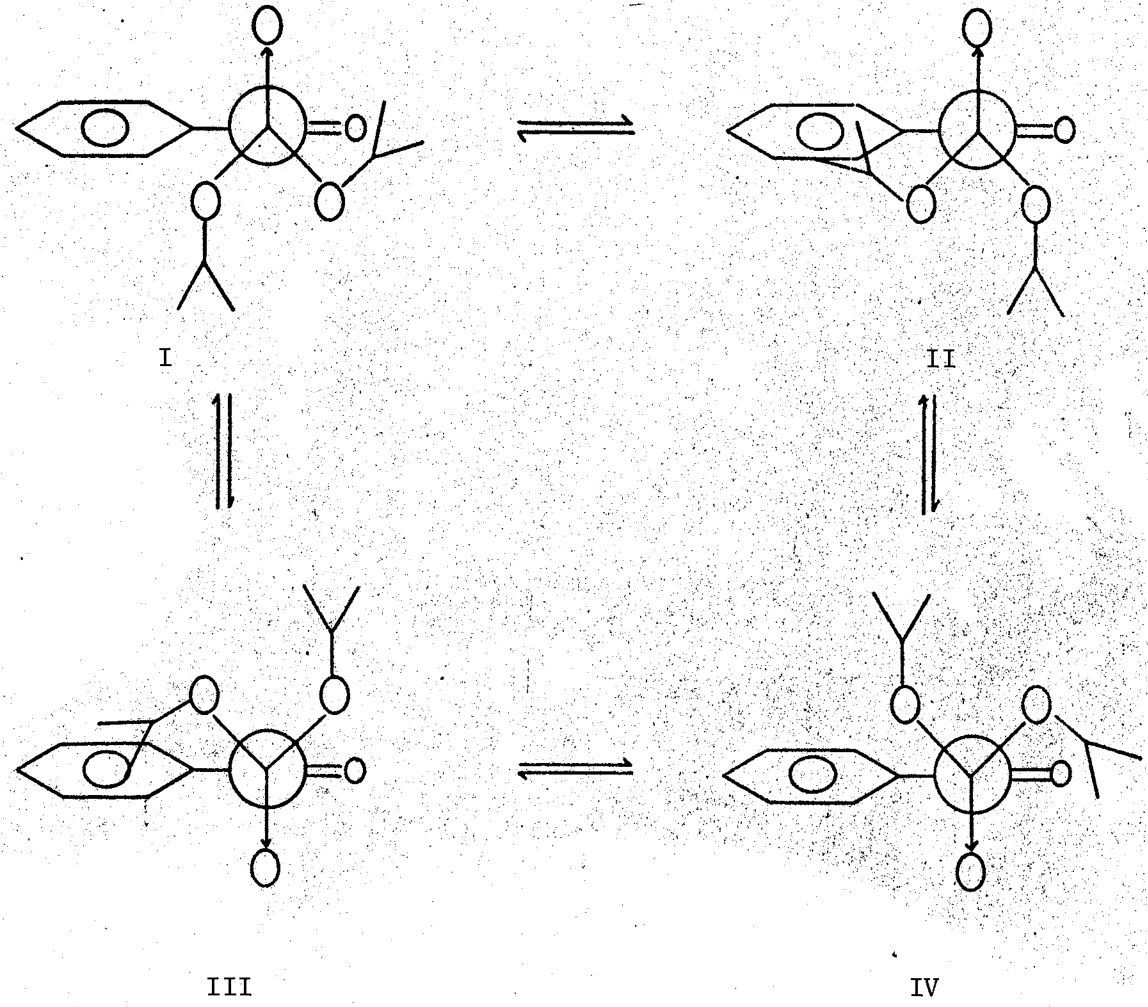


Figure 9. Plot of Ln k versus 1000/Temperature

TABLE XI

PARAMETERS USED TO FIT CALCULATED TO EXPERIMENTAL SPECTRA WITH DNMR3

Rate Constant (k)	Temperature (^{o} K)	T_2	Chemical Shifts (Isopropyl-Methyl Protons) in Hz 1	2	3	4
0.750	250.2	0.424	79.45	79.45	81.58	81.93
1.275	263.6	0.531	79.45	79.45	81.48	81.83
1.625	273.2	0.548	79.45	79.45	81.33	81.73
3.49	308.16	0.795	76.0	76.0	78.17	78.47



the C-P bond (b) and the two P-OC (c and c') bonds as shown. It should be noted that conformers I and IV are magnetically equivalent as are II and III. In order to demonstrate that the experimental line shapes might be reproduced theoretically using this model, a calculation was undertaken using the same assumptions regarding the methyl groups as were used in the previous calculation. In this instance, however, no rigorous attempt was made to match the experimental lines exactly, because in most of the cases only one coalescence point was noted.

Therefore no unique determination of the separate rate constants is possible. Several combinations of the rate constants and populations were found to give curves which match the general shapes of the experimental spectra. It must be pointed out that there is also no obvious way to determine experimentally the populations of I, II, III or IV and they can only be treated as experimental parameters.

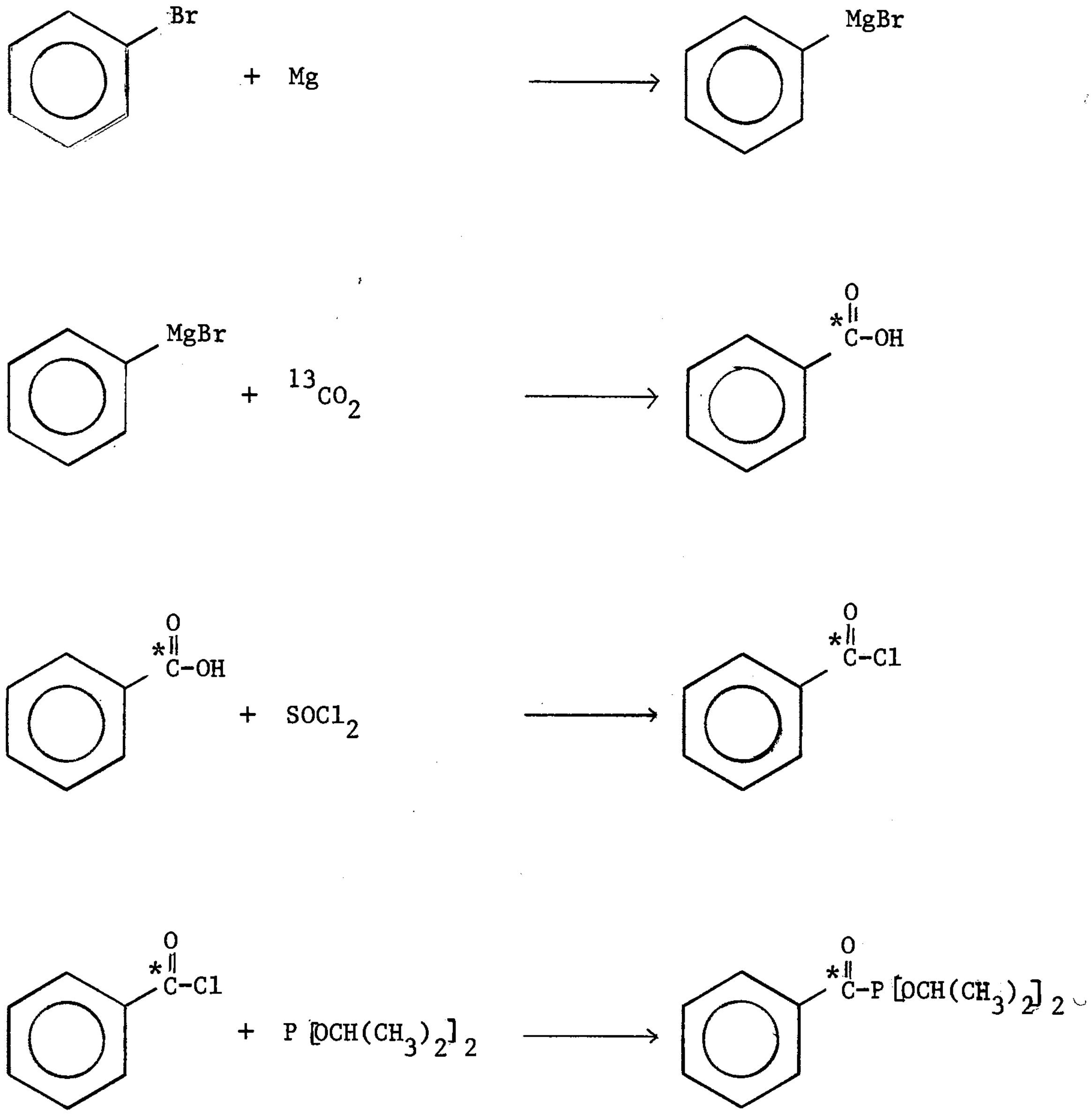
Unfortunately no unique set of thermodynamic information can be extracted from the present data. However, it can be concluded from the information available that rotation about the P-C bond is hindered and the effect of this rotational process on the general NMR line shape is perturbed by rotation about the P-OR bonds causing erroneous calculated values for ΔE_a and ΔS^*. It may also be deduced that rotation about the P-OR bond is probably not greatly hindered. However, the dipole moment data strongly suggests a preferred conformation about the P-C bond with the OPCP dihedral angle of approximately 90 degrees. The unusual temperature dependence of the isopropyl-methyl region of the NMR spectra has been explained in terms of stereochemical nonequivalence of the isopropyl-methyl groups and molecular motions which can simulate a symmetry operation.

Suggestions For Further Work

The diisopropyl aroylphosphonate system provides several ways in which the problem of determining rotational barriers may be approached. In our study we utilized only one of them extensively, Proton Magnetic Resonance. The other possibilities include variable temperature NMR studies over a range of temperatures, variable temperature studies employing UV and IR and selective deuteration or ^{13}C enrichment coupled with variable temperature studies of ^{1}H, ^{31}P and ^{13}C. The methods of approach and expected results will be discussed below.

Nuclear Magnetic Resonance studies with temperature variation using nuclei other than ^{1}H are not common. To examine the usefulness of this type of study, it is necessary to consider the magnetic environments in which the various nuclei reside and how a change in temperature might affect this environment. Looking first at the phosphorus atom, it can easily be seen that it is coupled only to the methine proton on the isopropyl group. The magnitude of this coupling is known to be a function of the POCH dihedral angle.[17] Since the methine proton signal is a complex multiplet, observing the change in POCH coupling constant can most easily be accomplished by observing the ^{31}P resonance. When the ^{1}H resonance of the isopropyl-methyl protons is observed down to -100°C, only one coalescence point is detected for most of the aroylphosphonates studied. If the coalescence point observed is for slowing of rotation about the C-P bond, then the only simple way to obtain information about the rotation of the P-OC bond is to observe the change in the POCH coupling constant as the temperature is lowered.

It is well known[40b] that ^{13}C chemical shifts are quite sensitive to the type of bonding of the particular carbon nucleus. If this is true, using $^{13}C{=}O$ (introduced by the following method) a variable temperature NMR study could be instructive. Changes in the chemical shift of ^{13}C might provide some insight into the nature of the rotational processes occurring at both the C_6H_5-C(O) bond and the C-P bond.



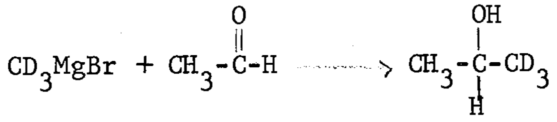
Dipole moment measurements have been used for a number of years in conformational analysis but there has not been much work done using a *variable-temperature dipole moment apparatus*. One would expect that a great deal of information concerning the rotation about the C-P bond would be accessible. As mentioned previously, dipole moment calculations indicate that the relative position of the phosphoryl oxygen and carbonyl oxygen is the primary determinant of the dipole moment of the molecule.

Since the UV spectra of aroylphosphonates show an interesting shift when compared to those of the benzaldehyde analogs, it might be possible to ascertain whether or not the shift was due to interaction of the phosphoryl group with the carbonyl carbon atom by observing the change in the spectra as a function of temperature. One would expect that if there was a great deal of interaction between the P→O and the C=O there would be a shift to shorter wave lengths for $\nu_{C=O}$ as the temperature was raised (increasing the rate of rotation of the b bond).

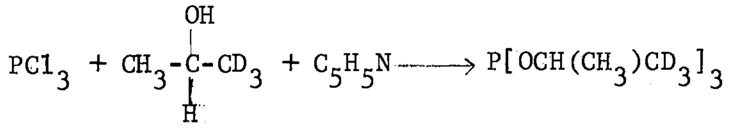
A variable-temperature IR study might provide some further information but the data would be somewhat more difficult to interpret. If IR was used rather than Raman, as in this study, observation of both the P→O and the C=O stretching band would be permitted. At room temperature there is no appreciable shift in the P→O stretch and any variation of this absorption band with temperature could help to determine the extent of the C-P rotation.

Selective deuteration has been used in other variable-temperature studies[18] to simplify the spectrum. In our work, the unsymmetrically deuterated isopropyl group coupled with a variable-temperature study could help to unravel the exact nature of the observed nonequivalence of the isopropyl-methyl groups. The preparation of the compounds could be carried out as follows.

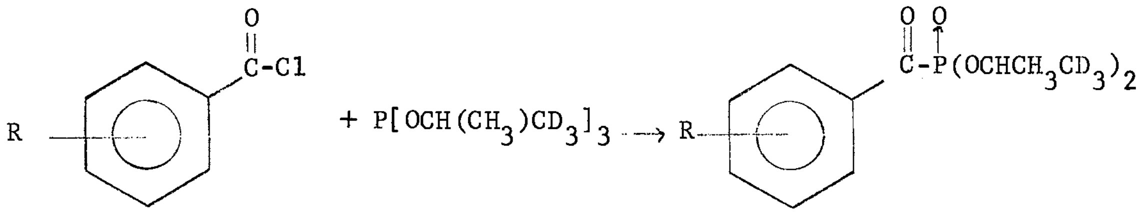
$$CD_3I + Mg \longrightarrow CD_3MgBr$$



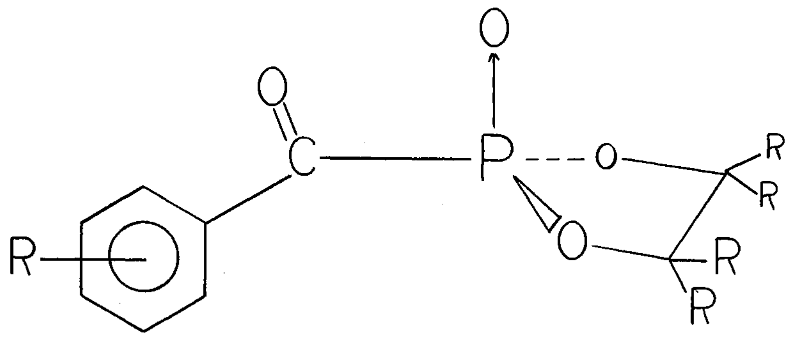
$$CD_3MgBr + CH_3-\overset{O}{\overset{\|}{C}}-H \longrightarrow CH_3-\underset{H}{\overset{OH}{C}}-CD_3$$



$$PCl_3 + CH_3-\underset{H}{\overset{OH}{C}}-CD_3 + C_5H_5N \longrightarrow P[OCH(CH_3)CD_3]_3$$



One technique which might be used to freeze the rotation about the P-OC bond is to prepare the ester with a diol to produce a cyclic compound of the type shown below. By freezing the rotation one may be able to ascertain whether or not nonequivalence is due to rotation about the C-P bond.



Of the above methods of attack, some require special equipment, some of which is only just now becoming available (i.e. variable-temperature dipole moment and high-temperature UV equipment); others require only the application of well known experimental techniques to the aroylphosphonate system. I feel that the suggestion with the most potential for determining the exact nature of the system is the use of variable-temperature NMR with nuclei other than ^1H. There has been little done in this area and yet the potential for simplifying the analysis is great.

CHAPTER III

EXPERIMENTAL[1-7]

Preparation of Diisopropyl Benzoylphosphonate (5). Triisopropyl phosphite (15.28 g., 0.074 mole; Mobil Chemical Company) was added dropwise to benzoyl chloride (10.0 g., 0.074 mole; Eastman reagent grade) without solvent. The resulting mixture was stirred at room temperature (under anhydrous N_2) for 12 hr. after which time excess

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[1] The PMR spectra were recorded on a Varian Model A-60, Analytical NMR spectrometer equipped with a V-4341/V-6057 variable-temperature accessory. The ^{31}P spectra were obtained on a Varian XL-100 spectrometer. Tetramethylsilane (TMS) was used as a low-temperature internal reference standard and tetramethylurea was used as a high-temperature internal reference standard.

[2] The temperature was monitored using CH_3OH (low temperature) or $HOCH_2CH_2OH$ (high temperature) as external references. Shift differences were converted into temperature readings by interpolation of the plots of chemical shift vs. temperature provided by Varian Associates.

[3] The infrared spectra were obtained on a Beckman IR-5A recording spectrometer (or, where noted on a Beckman IR-7 recording spectrometer) as films on sodium chloride cells for liquid samples or in potassium bromide pellets for solids.

[4] The ultraviolet spectra were recorded on a Model 14 Cary recording spectrophotometer.

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

[6] The mass spectra were obtained on a LKB-9000 prototype, magnetic sector, GLC-mass spectrometer, Biochemistry Department, Oklahoma State University.

[7] The 100 MHz spectra were recorded on a Varian HA-100 NMR spectrometer, at Continental Oil Company, Ponca City, Oklahoma.

starting materials were removed by distillation. The crude mixture was then distilled in a short-path distilling apparatus and the fraction boiling at 105-110°/0.15 mm. was refractionated using a vacuum-jacketed distillation column (15 cm.). Pure 5 (b.p. 91-92°/0.02 mm.) [11.5 g., 57.5%] was obtained as a yellow-green, viscous liquid and sealed[8] in vacuum.

Anal. Calcd. for $C_{13}H_{19}O_4P$: P, 11.48.

Found: P, 11.21.

Preparation of Diisopropyl 2-Methylbenzoylphosphonate (6).

Triisopropyl phosphite (20.0 g., 0.13 mole) and 2-methylbenzoyl chloride (27.1 g., 0.13 mole; Aldrich Chemical Company) were combined and the mixture was treated as for 5, except that the reaction time was only 4 hr. The ester 6 was obtained, a yellow-green, viscous liquid (b.p. 107-110°/0.01 mm.; 24.1 g. (54.2%).

Anal. Calcd. for $C_{14}H_{21}O_4P$: C, 59.15; H, 7.39; P, 10.91.

Found: C, 59.08; H, 7.38; P, 10.76.

Preparation of Diisopropyl 2,6-Dimethylbenzoylphosphonate (8).

Triisopropyl phosphite (4.40 g., 0.021 mole) was added slowly to 2,6-dimethylbenzoyl chloride (3.56 g., 0.021 mole)[all acid chlorides were prepared from commercially available acid and $SOCl_2$ by standard techniques, Columbia Chemical Company (acid source)] and the mixture was stirred for 13 hr. at 60° C (under anhydrous N_2). Distillation as for 5 gave 8 (4.2 g., 66.8%) as a clear, brown-tinted oil (b.p. 93-94°/0.05 mm.).

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[8] All samples were sealed in glass ampoules to prevent exposure to air or moisture.

Anal. Calcd. for $C_{15}H_{23}O_4P$: C, 60.40; H, 7.71; P, 10.40.

Found: C, 60.56; H, 7.84; P, 10.46.

Preparation of Diisopropyl 2-Methoxybenzoylphosphonate (9). Triisopropyl phosphite (25.6 g., 0.125 mole) and 2-methoxybenzoyl chloride (20.0 g., 0.125 mole) were combined by the same procedure as used for 5 to yield 9 (26.9, 72.1%) as a yellow-green oil (b.p. 131-132°/0.2 mm.).

Anal. Calcd. for $C_{14}H_{21}O_5P$: C, 56.02; H, 6.98; P, 10.31.

Found: C, 56.30; H, 7.08; P, 10.17.

Preparation of Diisopropyl 4-Methoxybenzoylphosphonate (10). Triisopropyl phosphite (24.4 g., 0.1175 mole) and 4-methoxybenzoyl chloride (20.0 g., 0.1175 mole) were combined, and the crude product was obtained by stripping excess starting materials in a short-path still. Attempts to fractionate the liquid resulted in decomposition, so partial purification was accomplished by shaking a $HCCl_3$ solution of 10 with a saturated sodium bicarbonate solution. After drying ($MgSO_4$), a chloroform solution of 10 was obtained as a viscous, yellow liquid (25 g., 71.1%). This is a known compound.[6,65]

Preparation of Diisopropyl 2,6-Dimethoxybenzoylphosphonate (11). Triisopropyl phosphite (5.2 g., 0.025 mole) and 2,6-dimethoxybenzoyl chloride [(4.0 g., 0.02 mole; Koppers Chemical Company (acid supplier)] were combined as before and starting materials were removed by short-path distillation. Attempts to distill under normal high vacuum conditions led to decomposition, thus a Bantam-wave short-path distillation apparatus (K-284500) was employed (evaporation point 70° C/0.01 mm.). The ester (4.22 g., 64.2%) was obtained as a yellow-tinted, viscous oil.

Anal. Calcd. for $C_{15}H_{23}O_6P$: C, 54.57; H, 6.96; P, 9.83.
Found: C, 54.66; H, 7.07; P, 9.20.

*Preparation of Diisopropyl 2-Chlorobenzoylphosphonate (**12**).* Reaction of triisopropyl phosphite (23.6 g., 0.0114 mole) and 2-chlorobenzoyl chloride (15.3 g., 0.0114 mole) and distillation as usual produced **11** (20.2 g., 66.1%) as a yellow-green, viscous liquid (b.p. 114.5-116.5°/0.075 mm.).

Anal. Calcd. for $C_{13}H_{18}ClO_4P$: C, 51.24; H, 5.95; P, 10.16.
Found: C, 51.29; H, 5.92; P, 10.01.

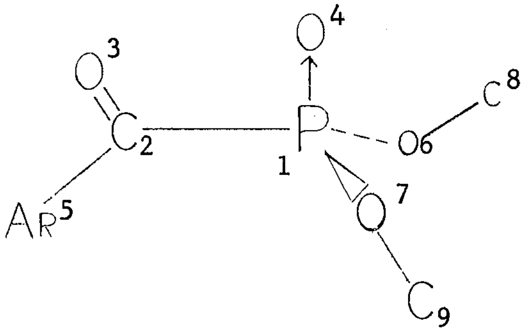
*Preparation of Diisopropyl 4-Chlorobenzoylphosphonate (**13**).* Triisopropyl phosphite (24.0 g., 0.15 mole) and 4-chlorobenzoyl chloride (20.0 g., 0.15 mole; Aldrich Chemical Company) were combined as before to yield 22.1 g. (62.1%) of a pale-green, waxy solid **13** (b.p. 117.0-118.5°/0.075 mm.).

Anal. Calcd. for $C_{13}H_{18}ClO_4P$: C, 51.24; H, 5.95; P, 10.16.
Found: C, 51.40; H, 5.95; P, 10.04.

Method For Calculating Dipole Moments. To calculate the dipole moments of the esters under consideration, a simple program was written to compute the molecular moment from the Cartesian coordinates and the empirical bond moments. The Cartesian coordinates were first calculated by a subprogram[25] obtained from the Quantum Chemical Program Exchange. The program then yielded the moments along each of the principal coordinate axes. The component of the moment along each axis was calculated and the resultant moment was obtained from the square root of the sum of the squares of each of the component moments.

$$\mu = (m_x^2 + m_y^2 + m_z^2)^{\frac{1}{2}}$$

A simple example is shown below with a sample output from the program.



Note in this calculation the C-H moments are assumed to cancel out and are not taken into account and the ring is taken as a composite moment.

Bond Lengths		Bond Angles		Bond Dipole[a,b]	
Atoms		Atoms		Atoms	
1-2	1.80 Å	1-2-3	120.0°	1→2	0.8
2-3	1.20 Å			2→3	2.3
2-5	1.57 Å	1-2-5	120.0°	5→2	0.4[c]
1-4	1.46 Å	2-1-4	101.5°	1→4	3.5
1-6	1.63 Å	2-1-6	101.5°	1→6	1.2
6-8	1.43 Å	1-6-8	113.0°	8→6	1.12
1-7	1.63 Å	2-1-7	101.5°	1→7	1.20
7-9	1.43 Å	1-7-9	113.0°	9→7	1.12

a. Bond moments are taken from Smyth.[24]

b. Arrows indicate the direction of the dipole.

c. Bond moment taken from Exner and Jehlicka.[29]

The calculation is based on the following equations.

$$\overset{+\!\!\!\longrightarrow}{\mathrm{C{=}O}}$$

$$r = [(x_c - x_o)^2 + (y_c - y_o)^2 + (z_c - z_c)^2]^{\frac{1}{2}}$$

$$x = [(x_c - {}_x o) / r][2.3]$$

$$y = [(y_c - y_o) / r][2.3]$$

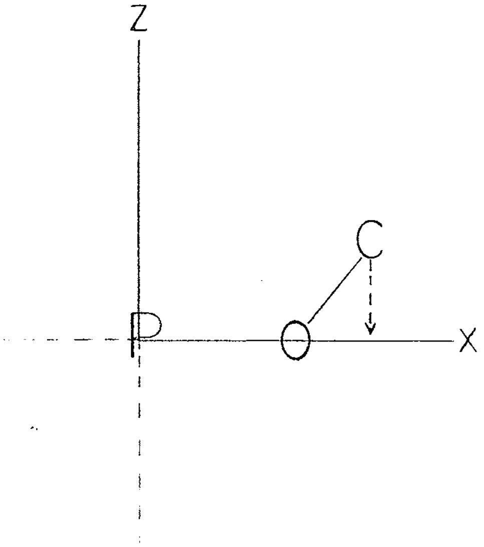
$$z = [(z_c - z_o) / r][2.3]$$

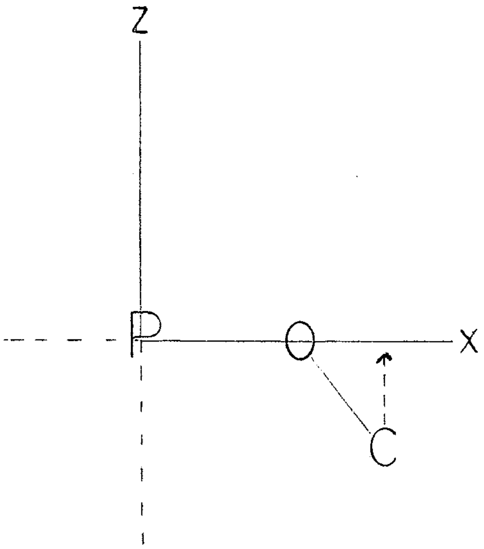
After this process has been performed for each atom pair of importance, the following procedure is used to produce the molecular moment.

$$\mu_{\text{calcd.}} = [(\Sigma x)^2 + (\Sigma y)^2 + (\Sigma z)^2]^{\frac{1}{2}}$$

To produce the effect of free rotation about a given bond the following method is used.

In the free rotation case all of the resultant moments cancel except the component of the moment along the axis of rotation. This component is added to the bond moment of the axis of rotation and the molecular moment is computed using this value.





$\sin 67^\circ = z / 1.12$

$z = [\sin 67^\circ][1.12]$

$\cos 67^\circ = x / 1.12$

$x = [\cos 67^\circ][1.12]$

$\sin 67^\circ = z / 1.12$

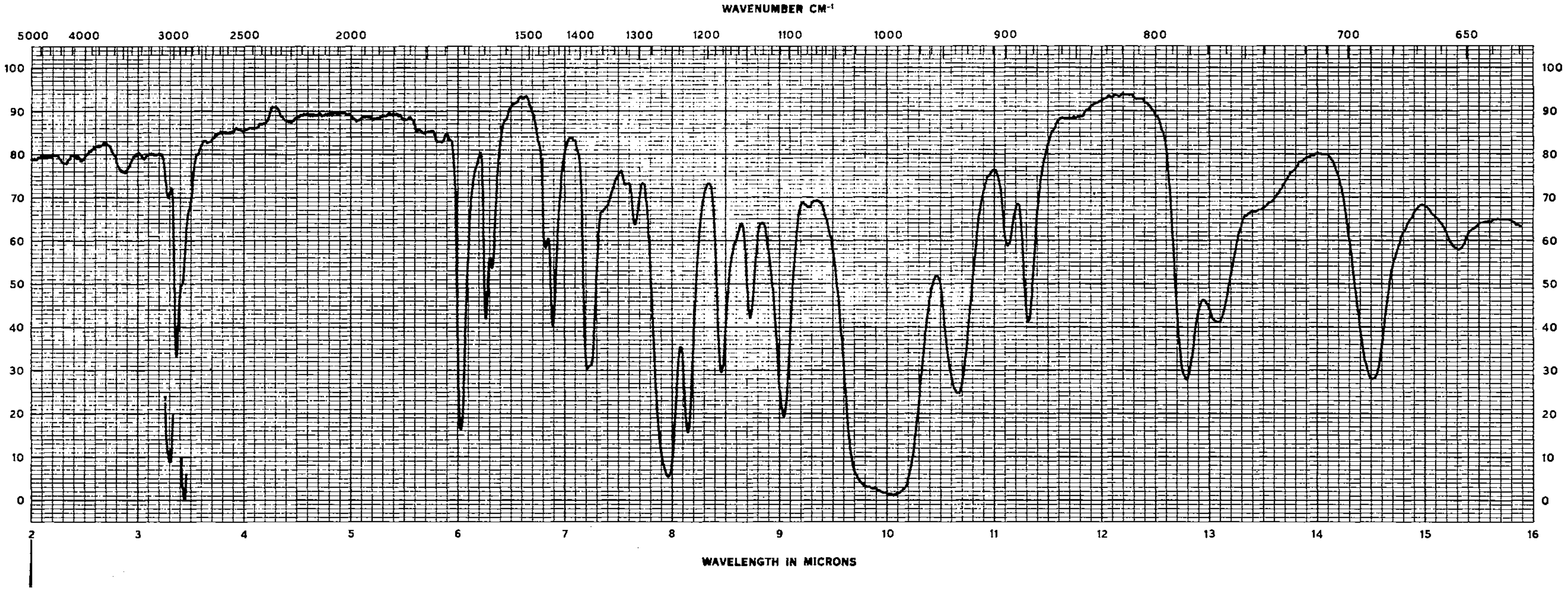
$z = [\sin 67^\circ][1.12]$

$\cos 67^\circ = x / 1.12$

$x = [\cos 67^\circ][1.12]$

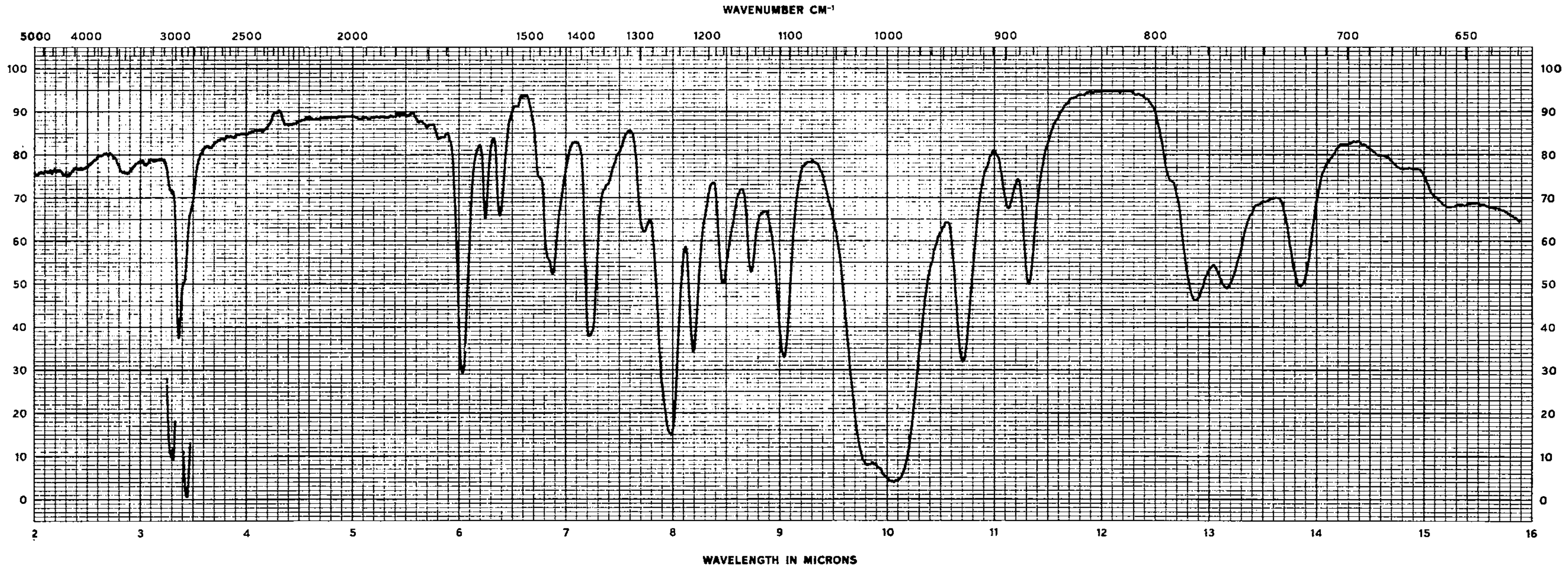
As can be easily seen, the z components are equal in magnitude but opposite in direction and therefore they cancel each other. The same argument holds for the y components.

Plate I



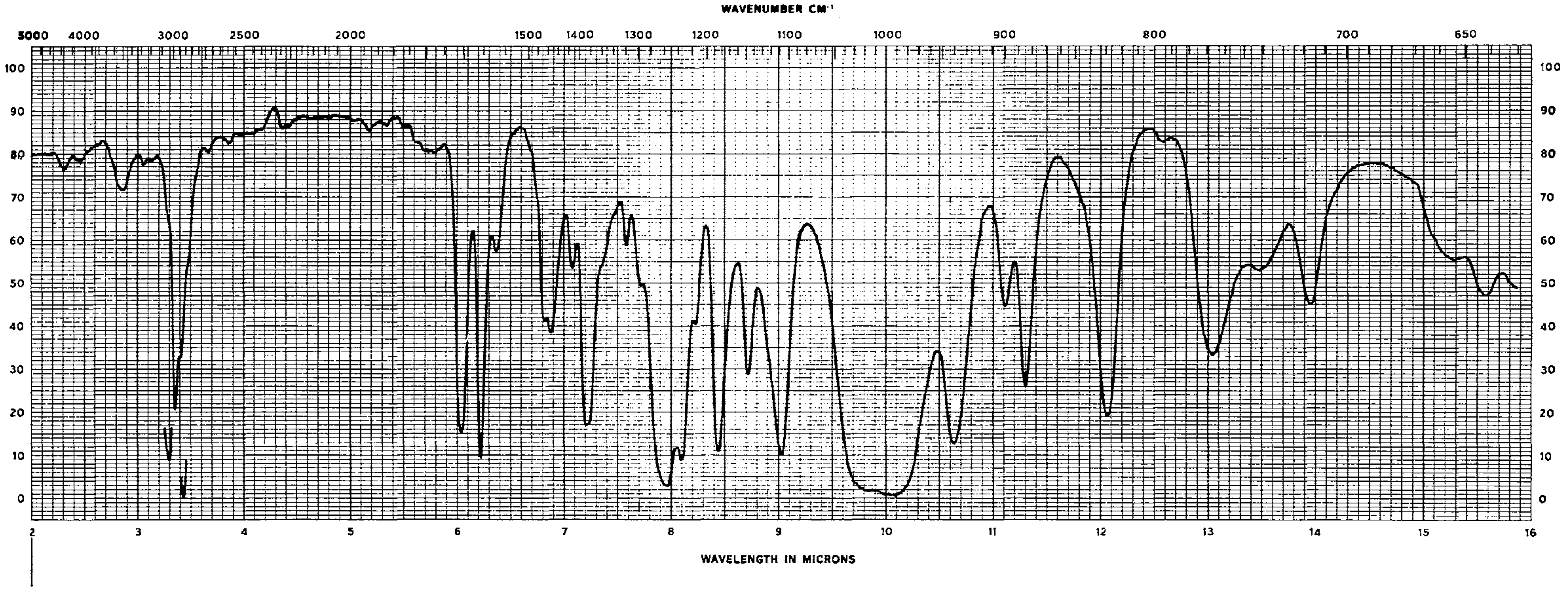
Diisopropyl Benzoylphosphonate (5), Film on NaCl Plates

Plate II



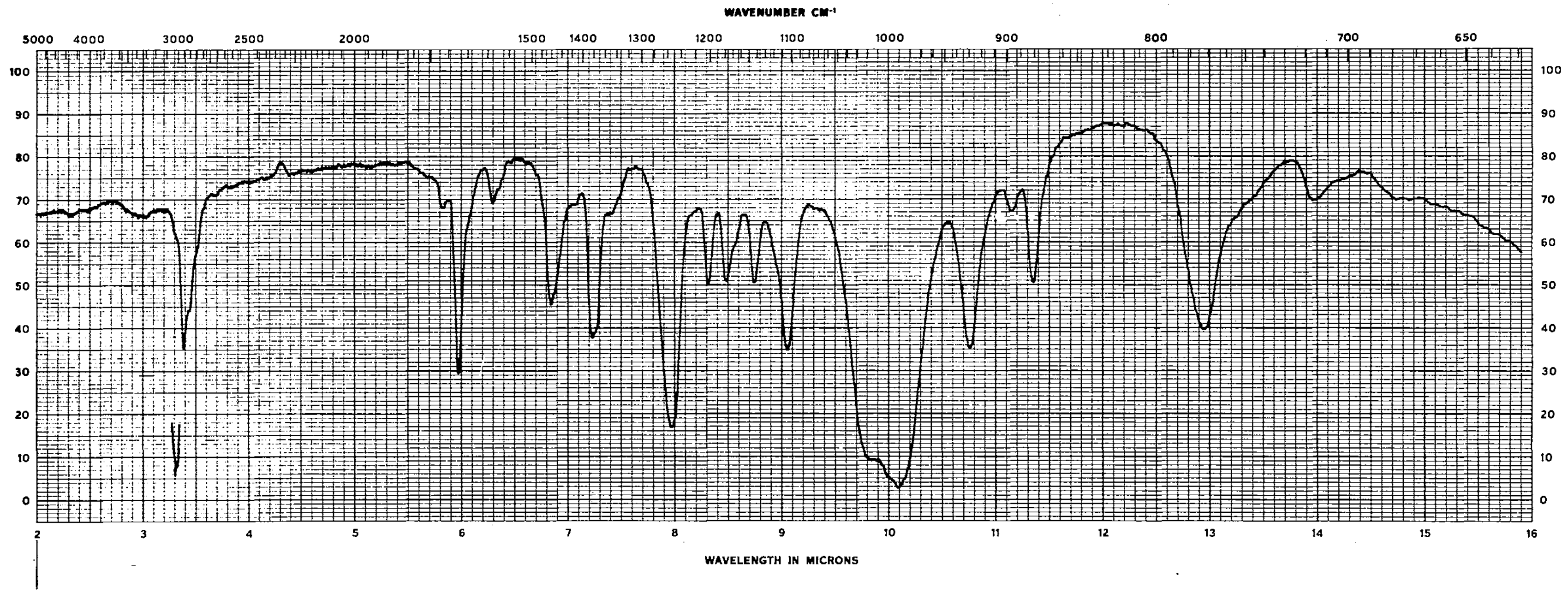
Diisopropyl 2-Methylbenzoylphosphonate (6), Film on NaCl Plates

Plate III



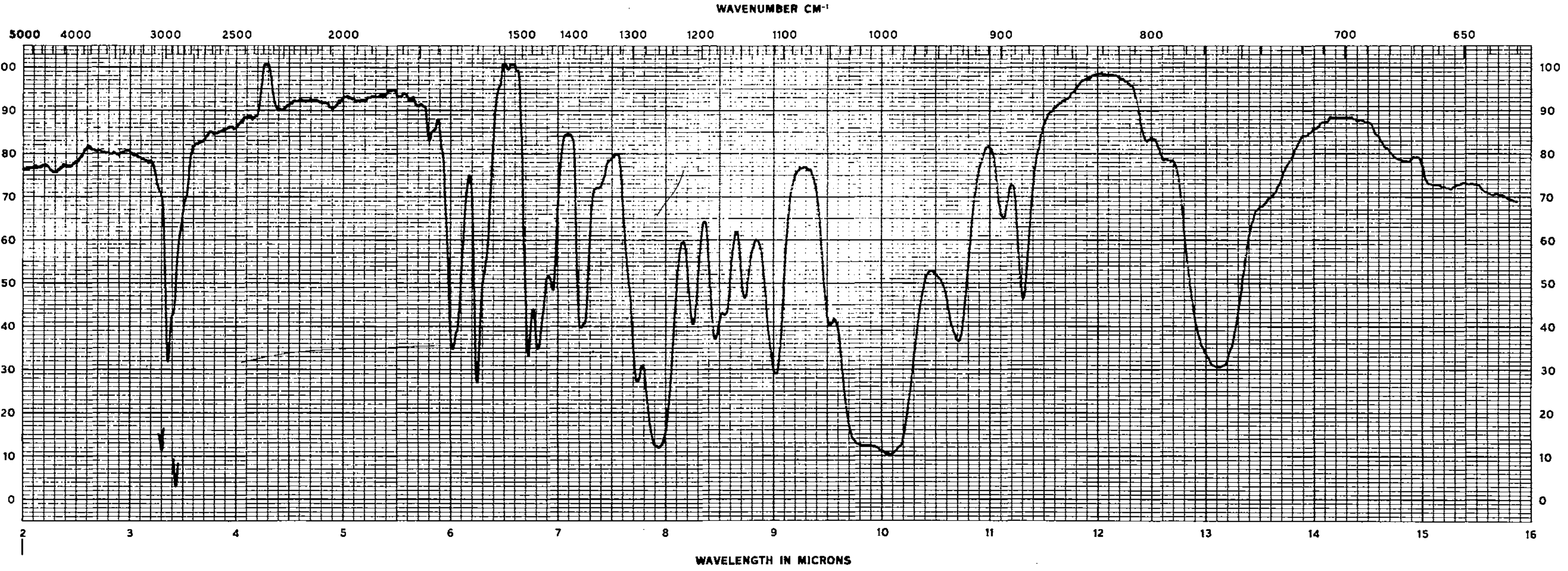
Diisopropyl 4-Methylbenzoylphosphonate (7), Film on NaCl Plates

Plate IV



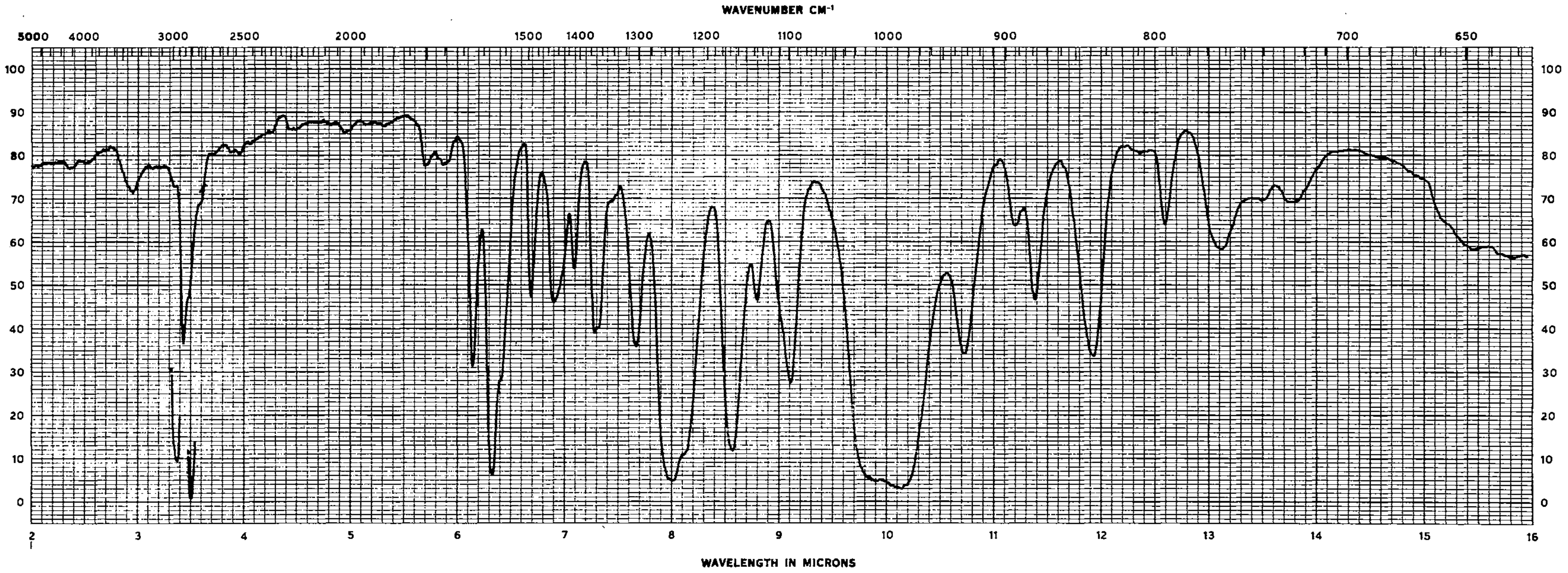
Diisopropyl 2,6-Dimethylbenzoylphosphonate (8), Film on NaCl Plates

Plate V



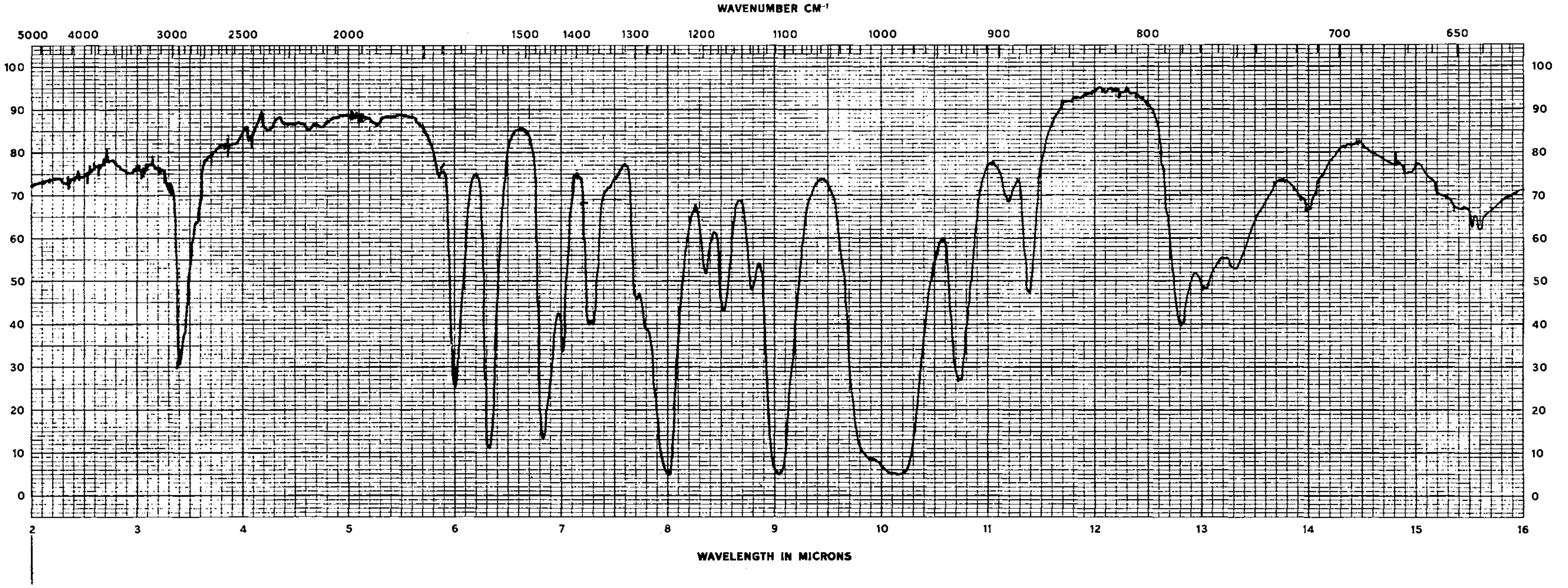
Diisopropyl 2-Methoxybenzoylphosphonate (9), Film on NaCl Plates

Plate VI



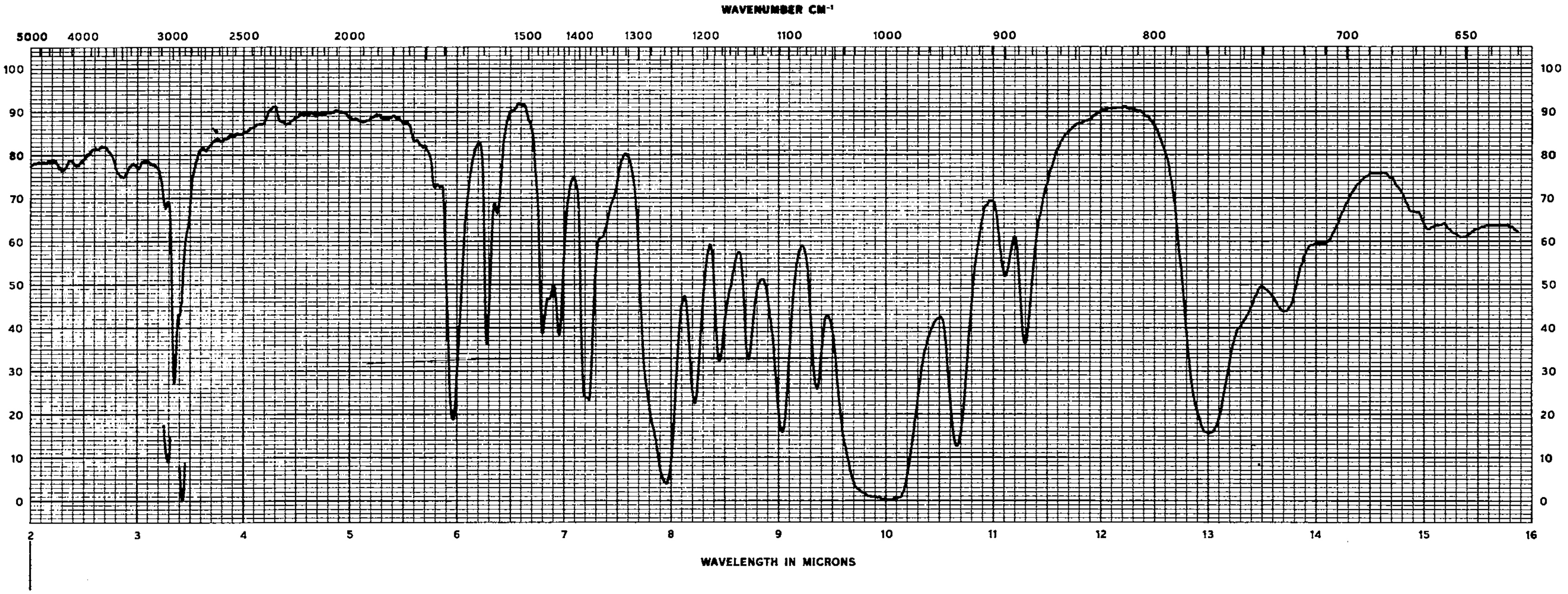
Diisopropyl 4-Methoxybenzoylphosphonate (10), Film on NaCl Plates

Plate VII



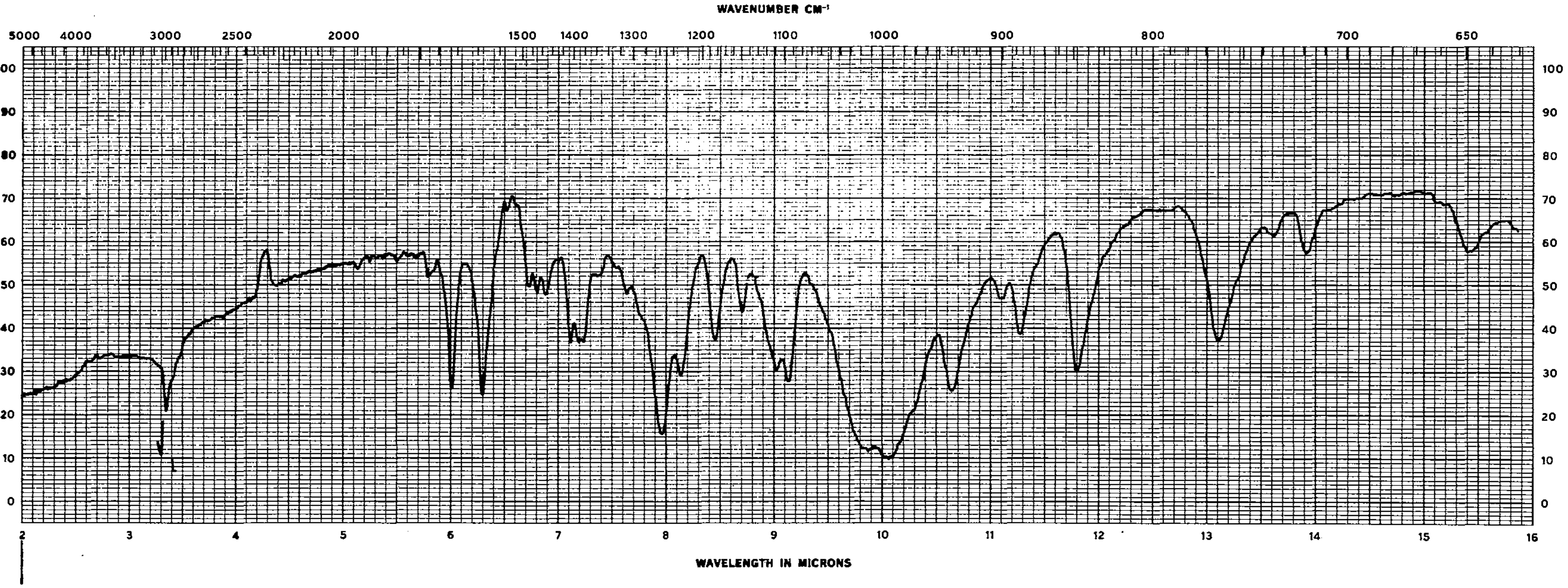
Diisopropyl 2,6-Dimethoxybenzoylphosphonate (11), Film on NaCl Plates

Plate VIII



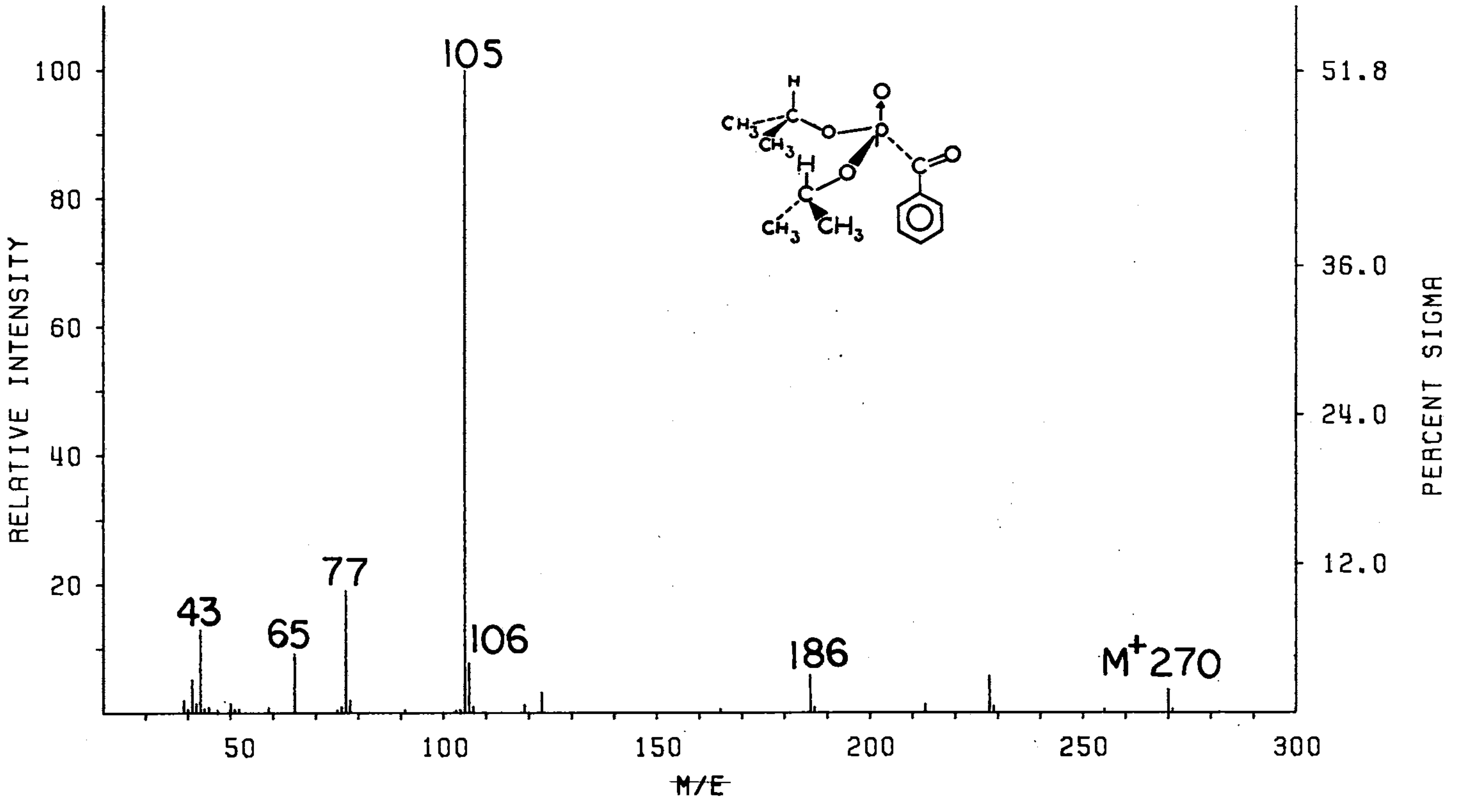
Diisopropyl 2-Chlorobenzoylphosphonate (12), Film on NaCl Plates

Plate IX



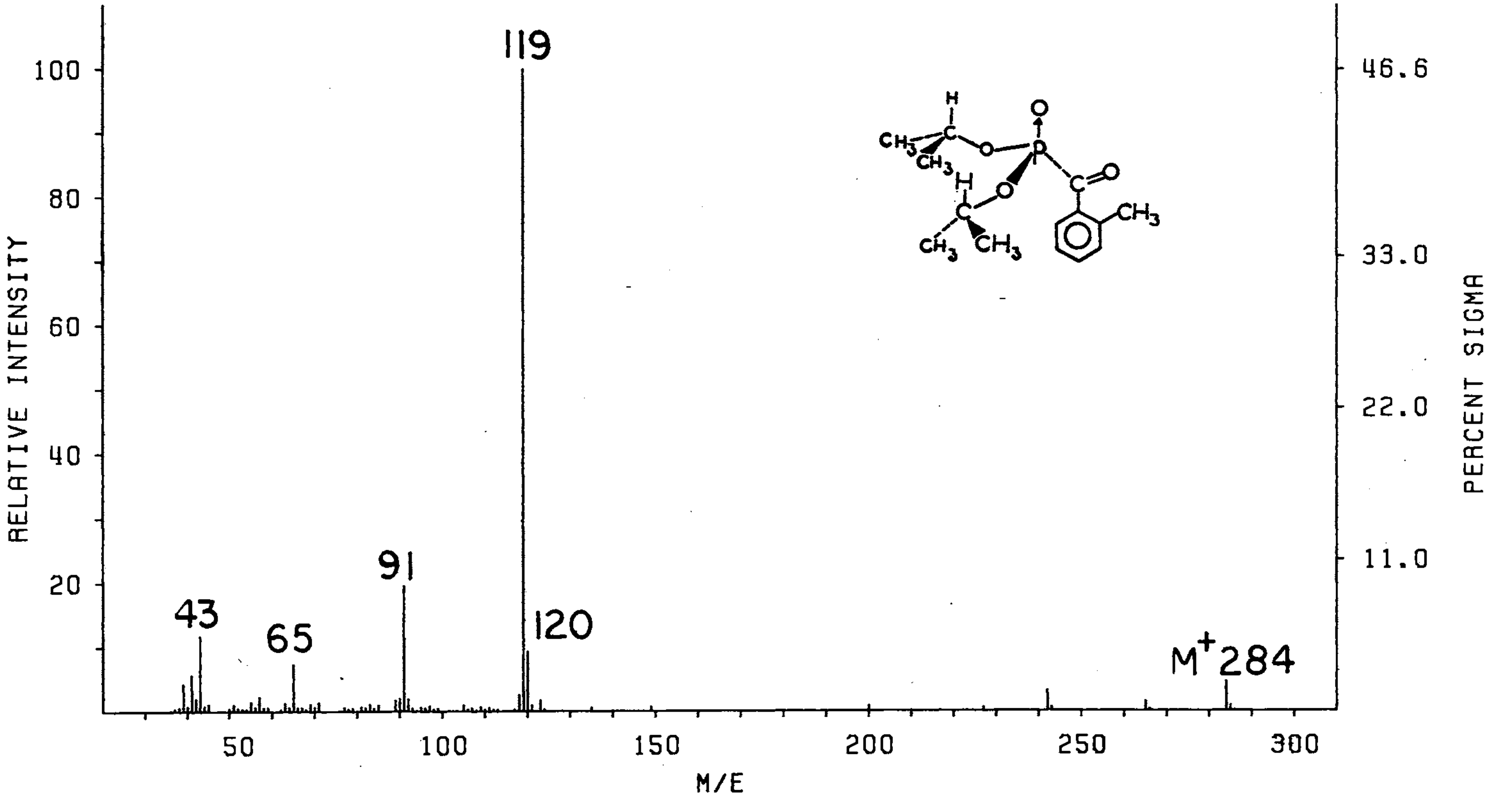
Diisopropyl 4-Chlorobenzoylphosphonate (13), KBr Pellet

Plate X



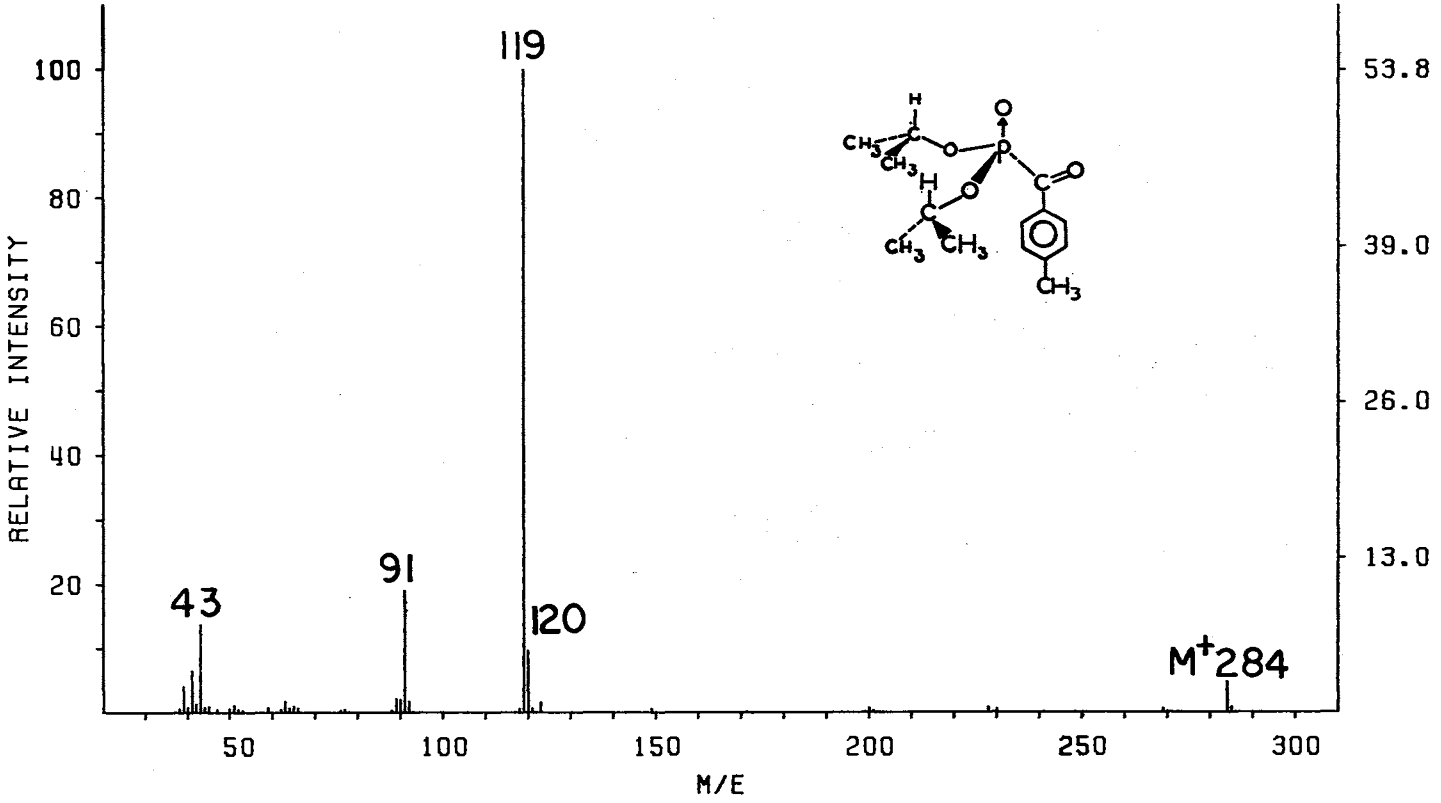
Diisopropyl Benzoylphosphonate (5)

Plate XI



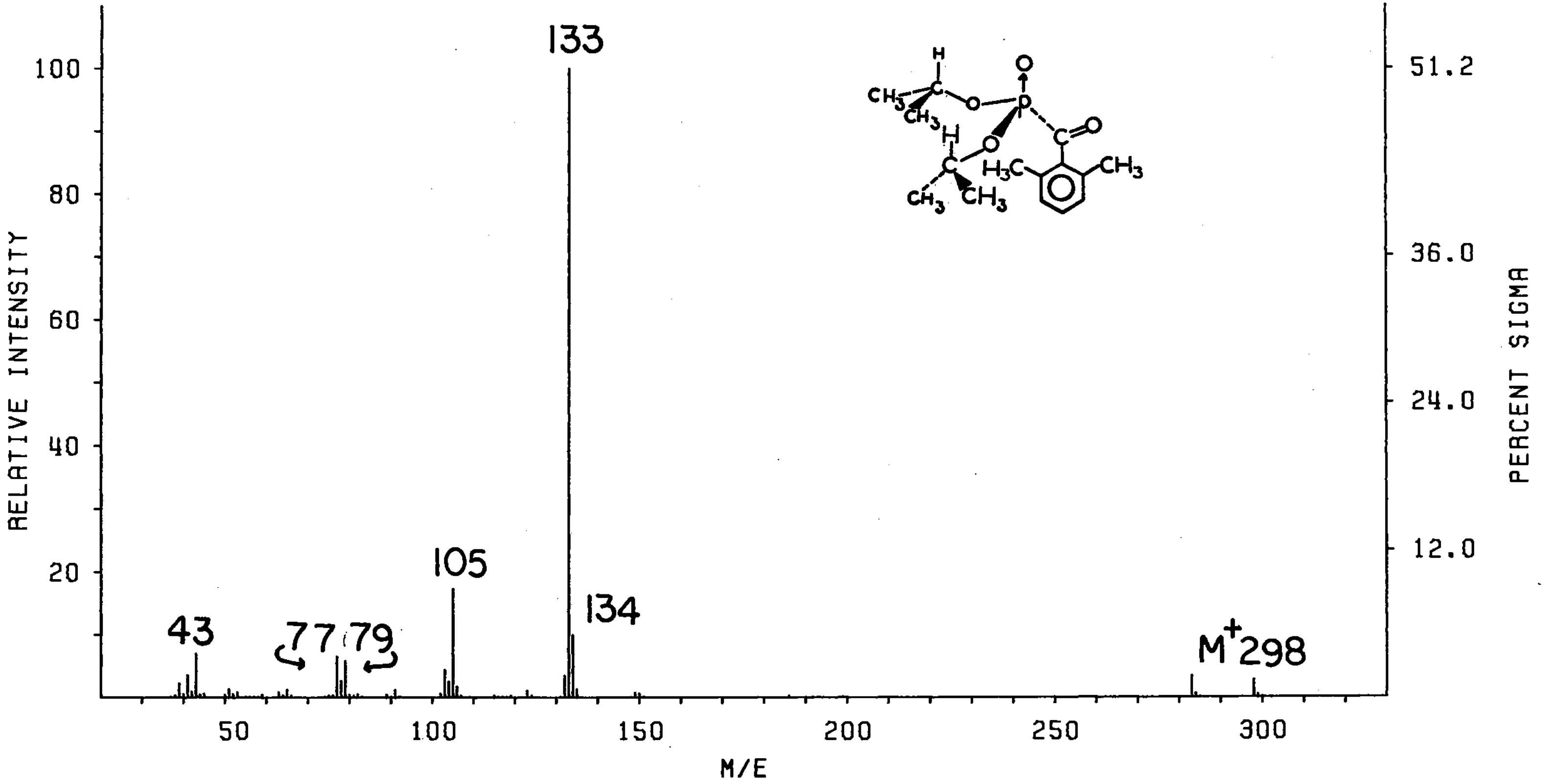
Diisopropyl 2-Methylbenzoylphosphonate (6)

Plate XII



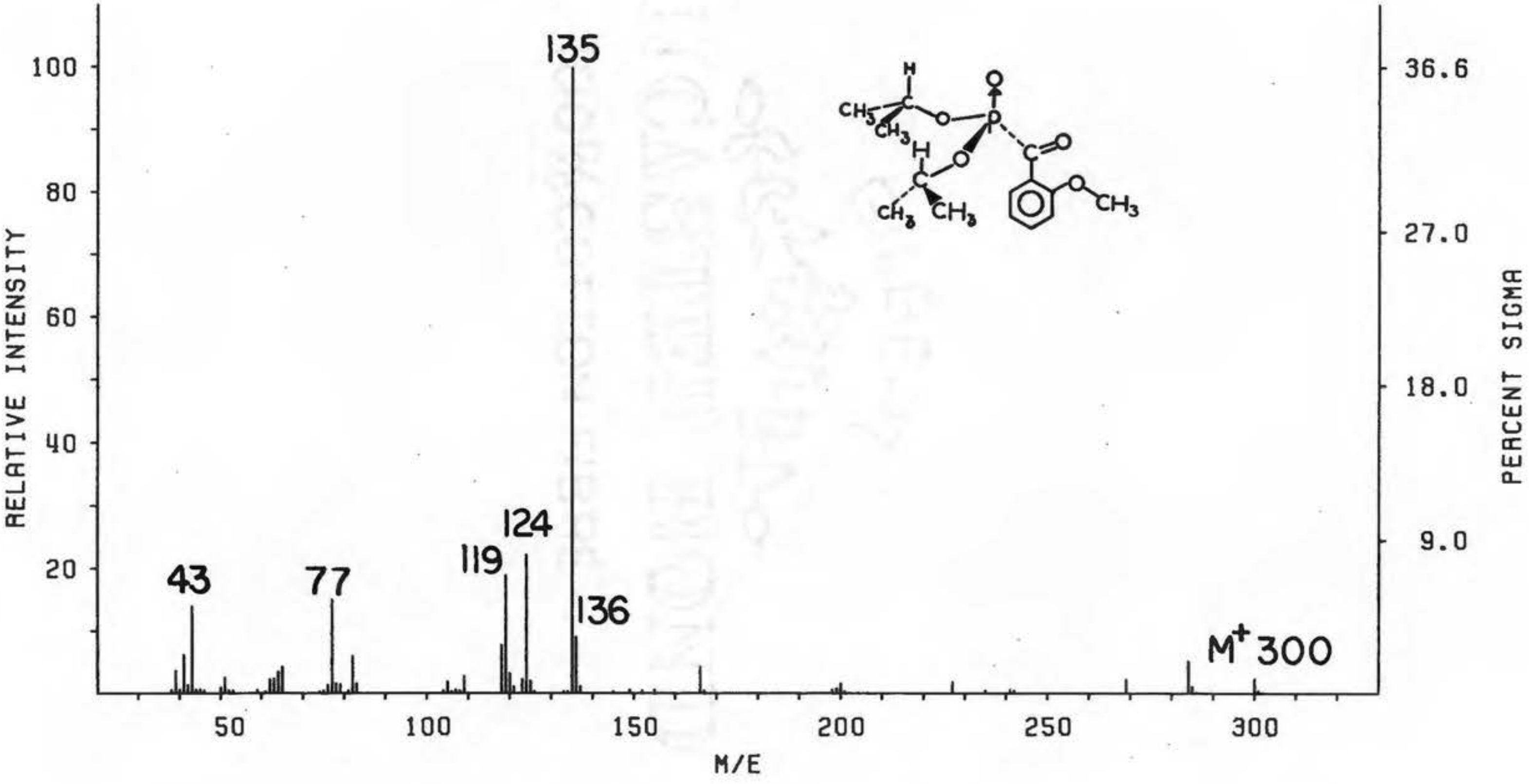
Diisopropyl 4-Methylbenzoylphosphonate (7)

Plate XIII



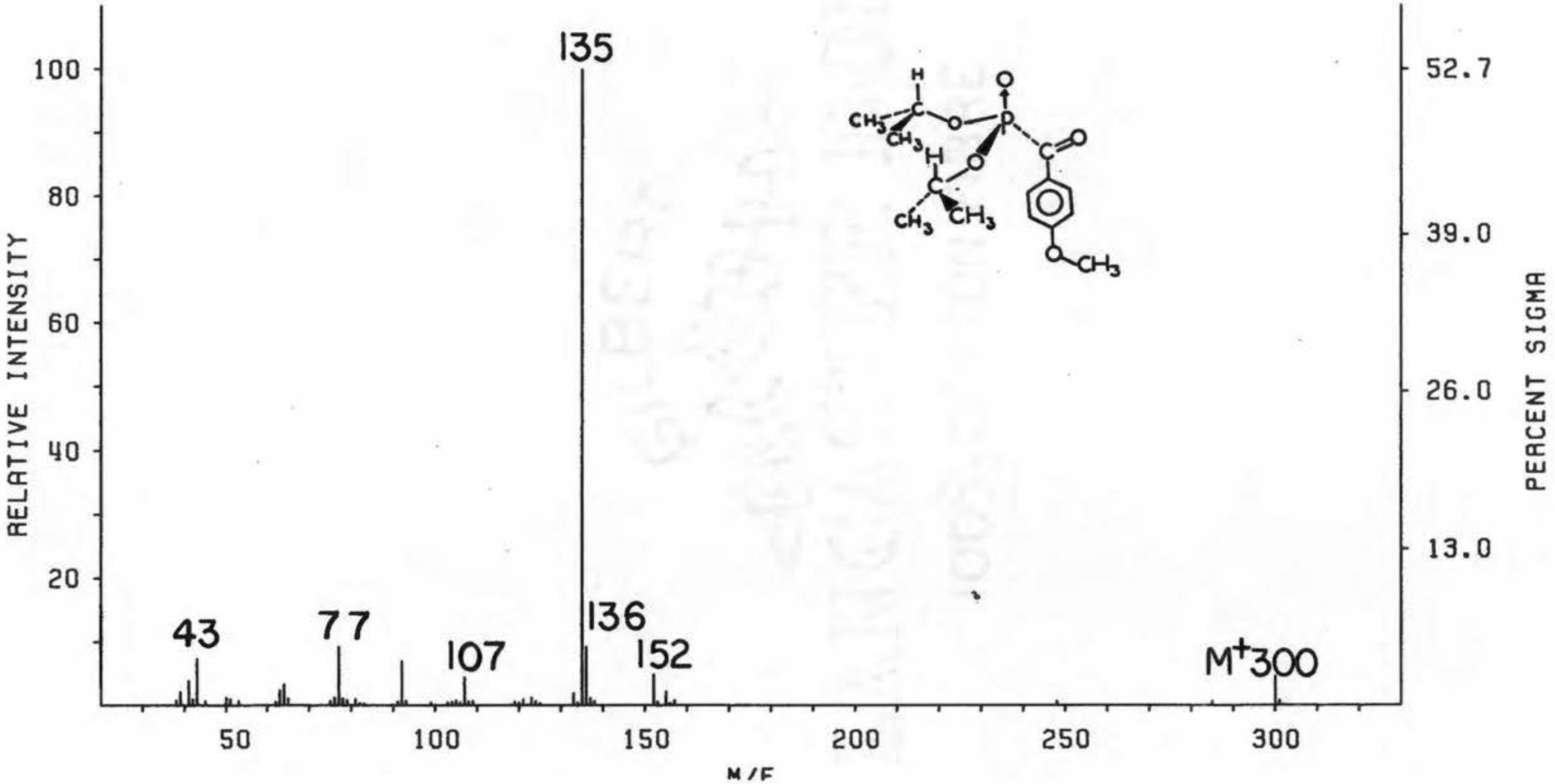
Diisopropyl 2,6-Dimethylbenzoylphosphonate (8)

Plate XIV



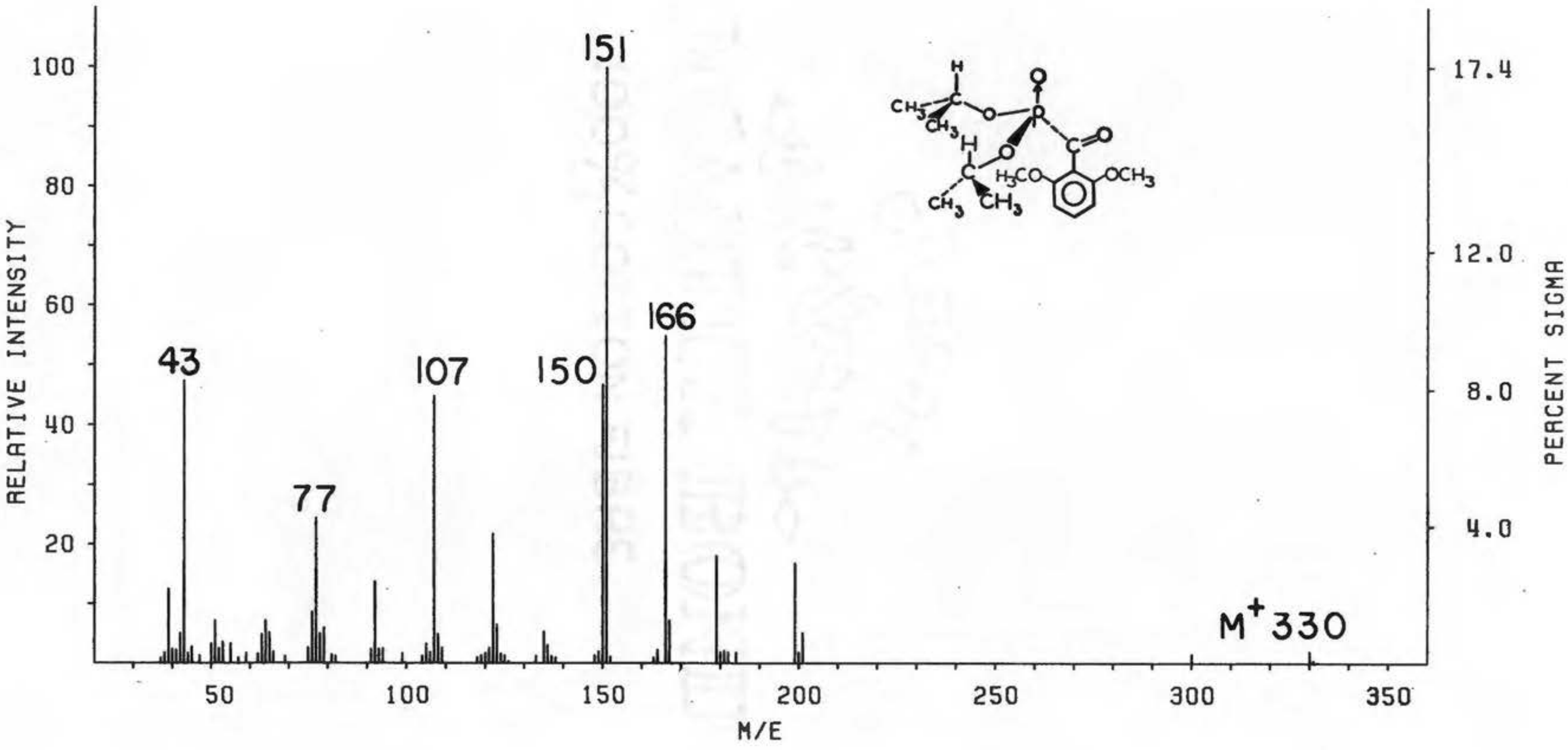
Diisopropyl 2-Methoxybenzoylphosphonate (9)

Plate XV



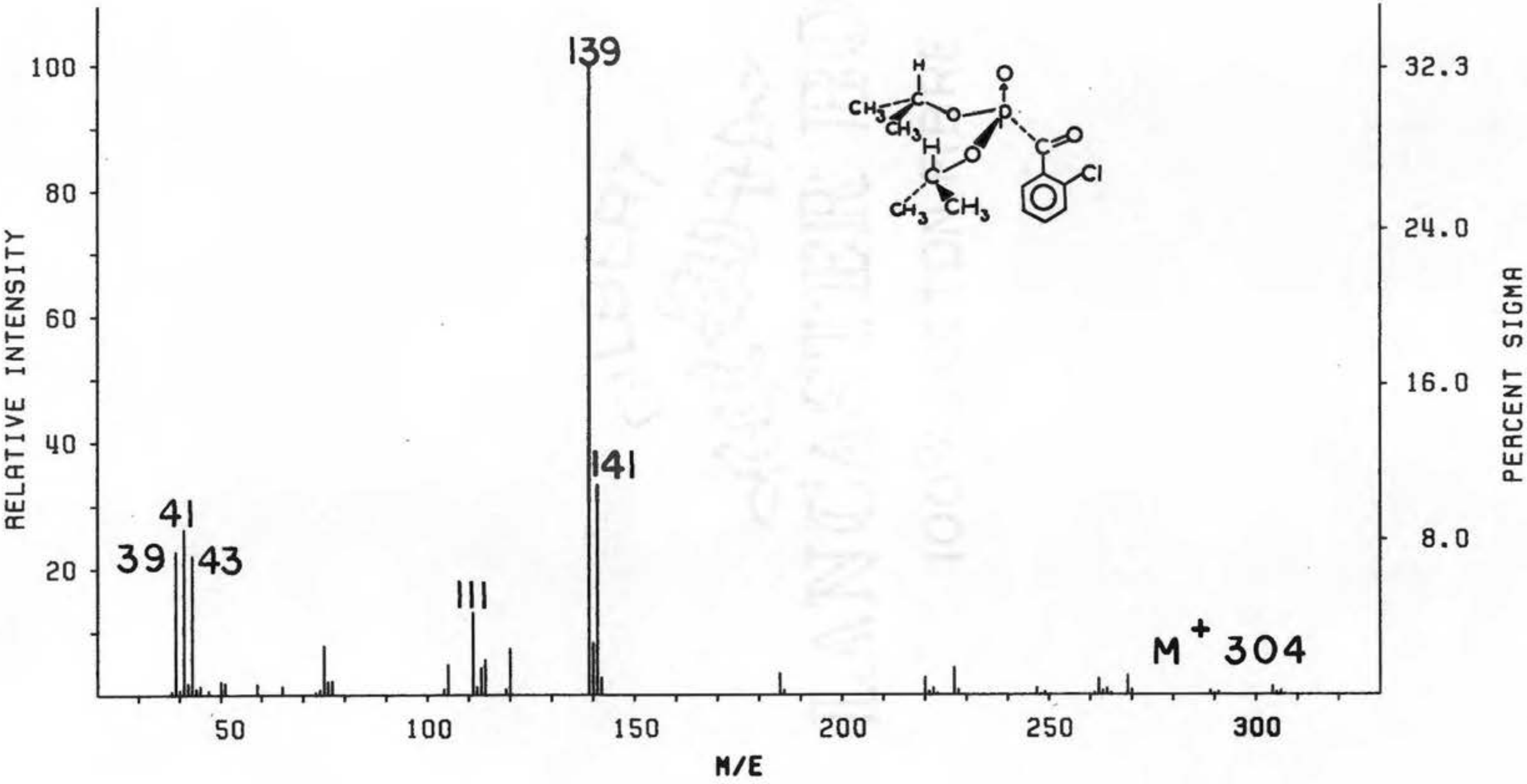
Diisopropyl 4-Methoxybenzoylphosphonate (10)

Plate XVI



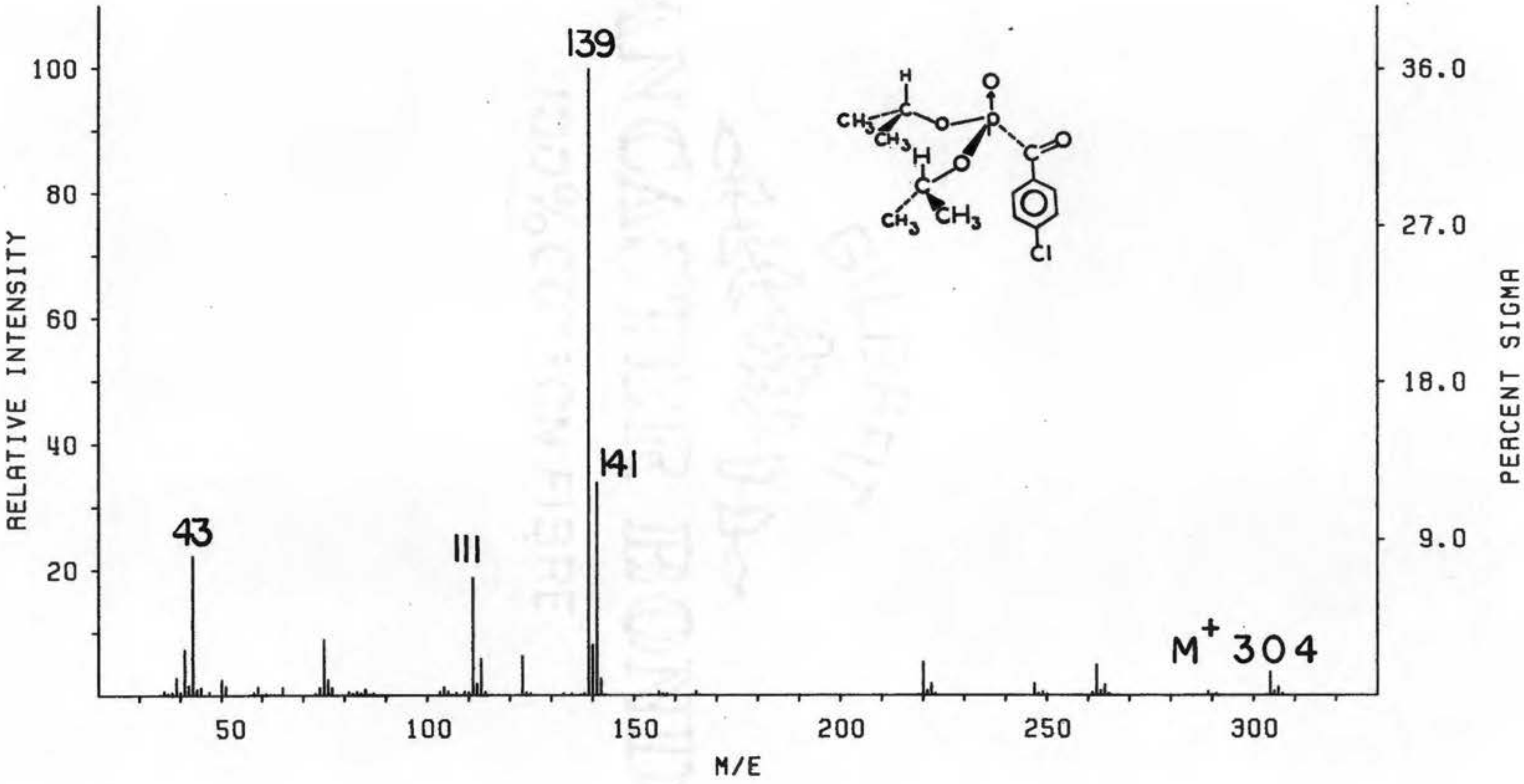
Diisopropyl 2,6-Dimethoxybenzoylphosphonate (11)

Plate XVII



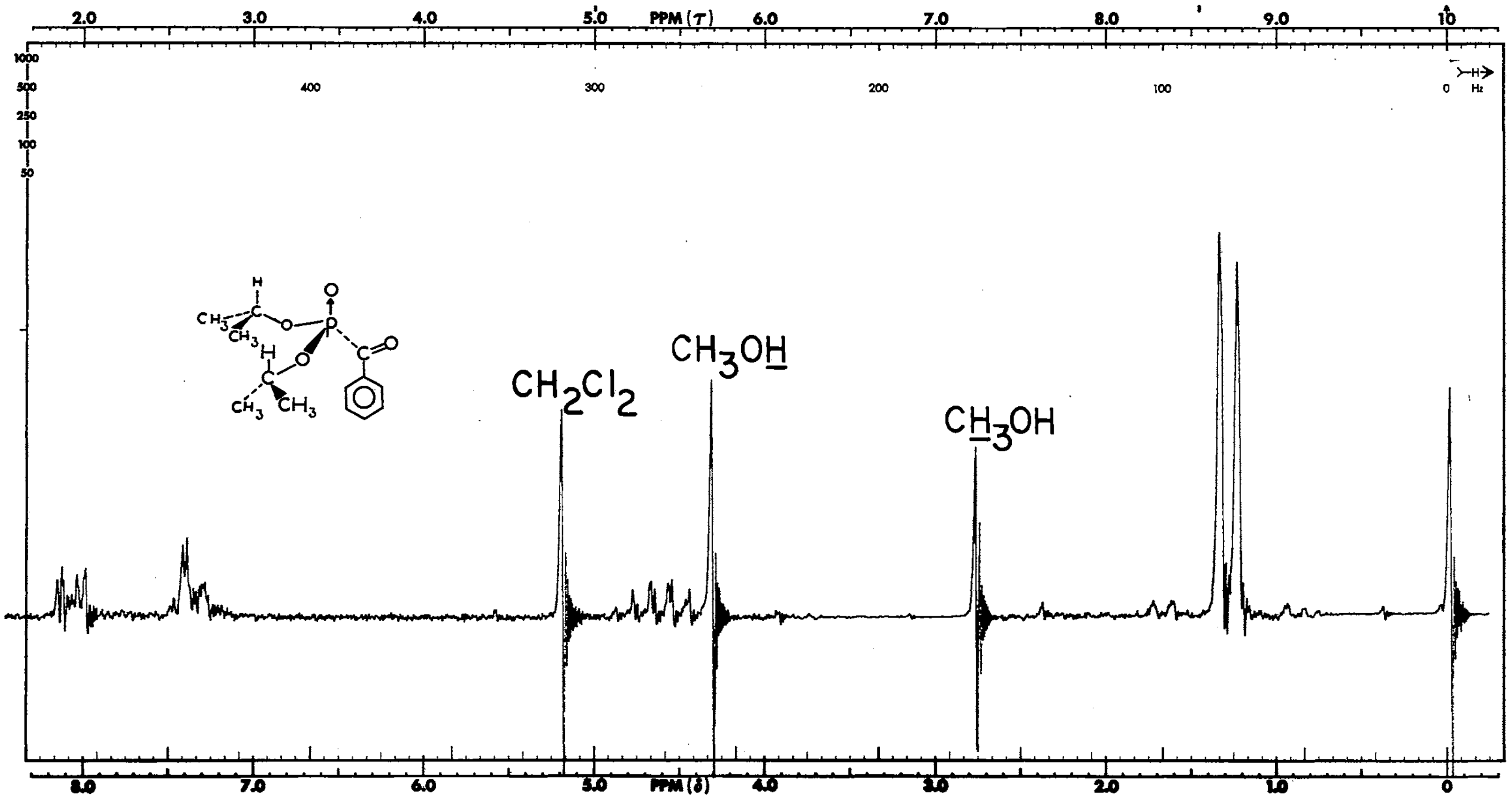
Diisopropyl 2-Chlorobenzoylphosphonate (12)

Plate XVIII



Diisopropyl 4-Chlorobenzoylphosphonate (13)

Plate XIX



Diisopropyl Benzoylphosphonate (5)

Solvent. . . . . . CS_2

R.F. . . . . . . .0.03 mG

S.W. . . . . . . 500 Hz

S.A. 4.0

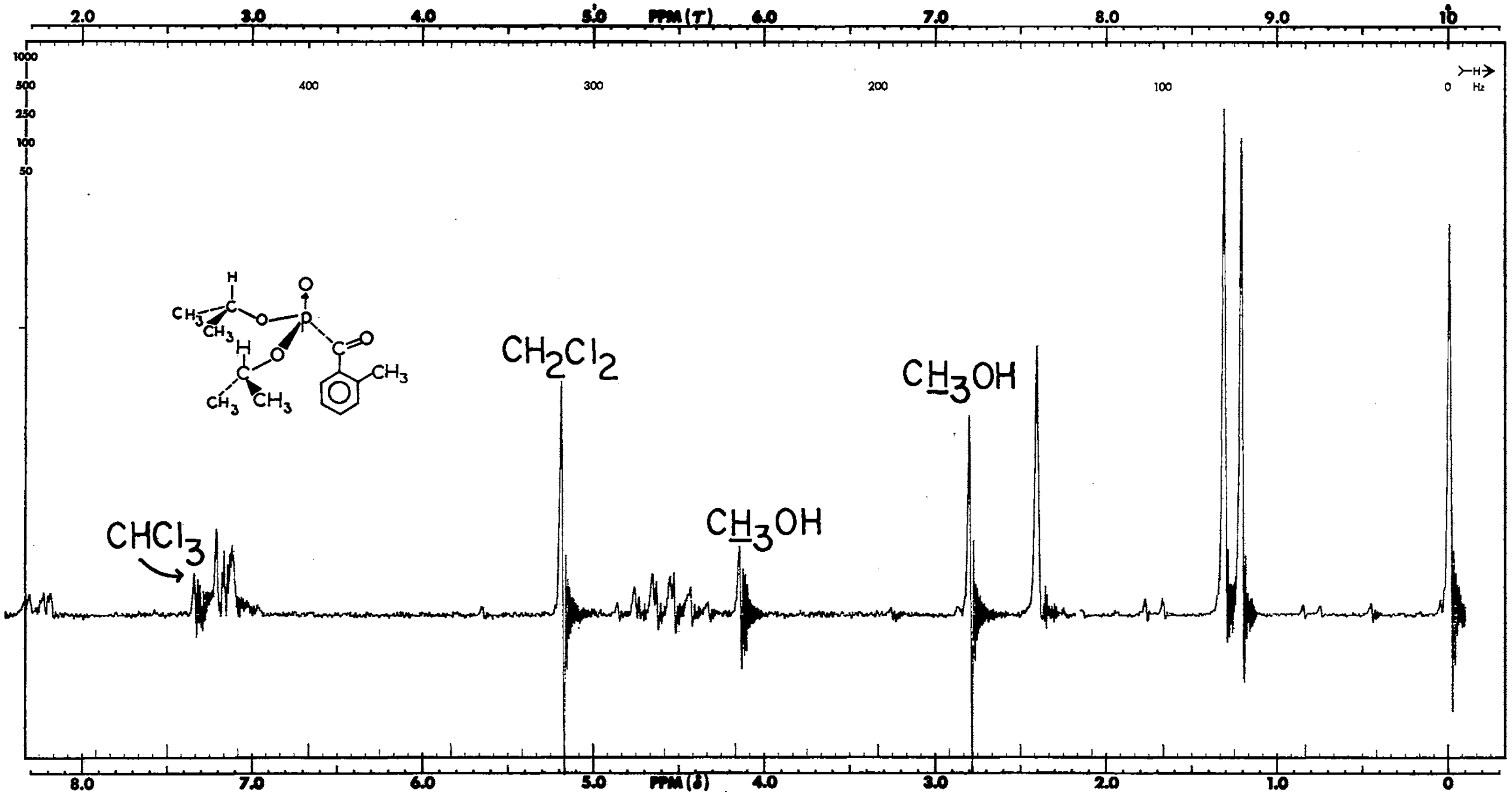
F.B. . . . . . 4.0 Hz

S.T. . . . . . . .250 sec

S.O. . . . . . . 0.0 Hz

I.A. . . . . . . off

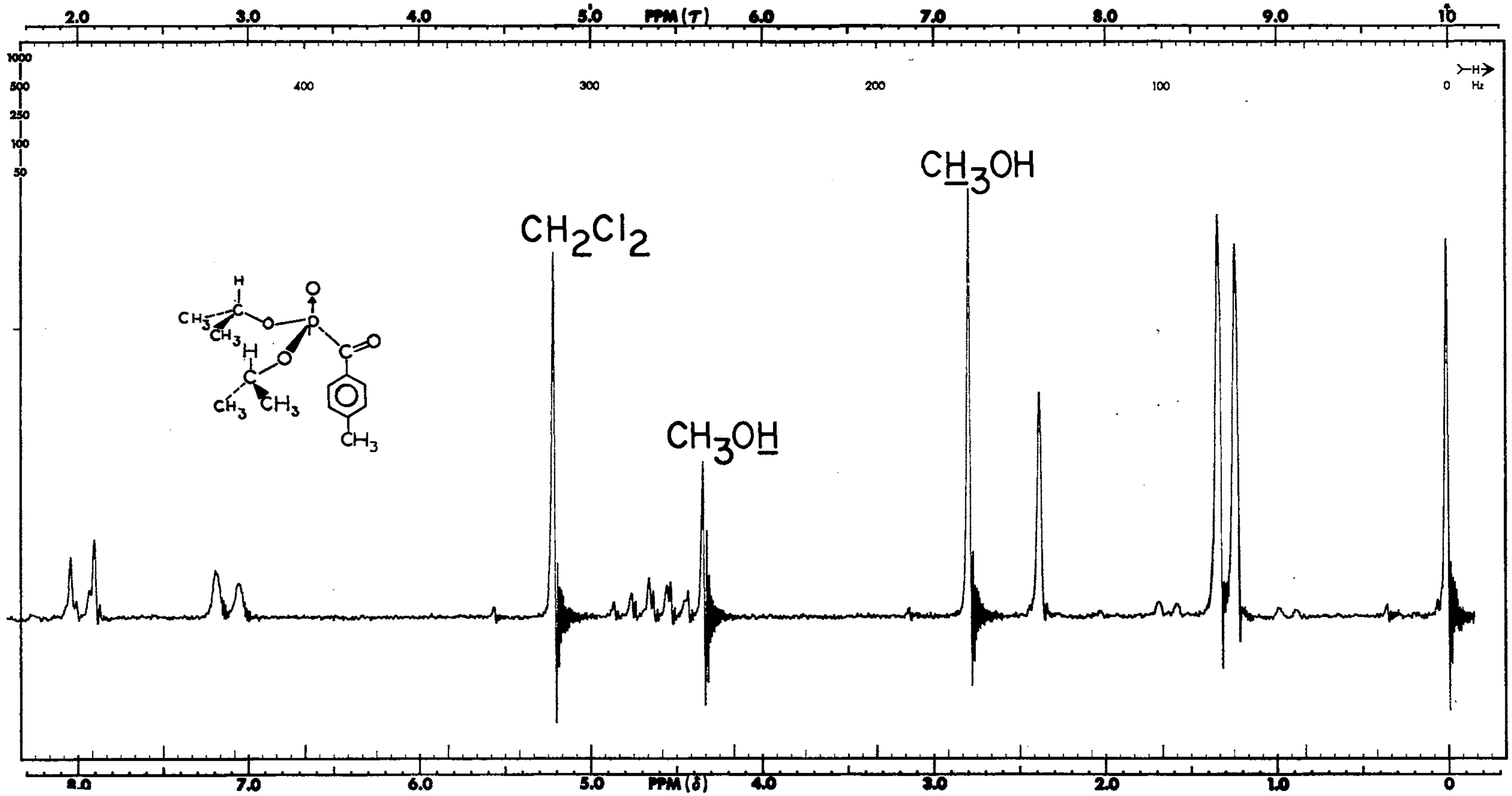
Plate XX



Diisopropyl 2-Methylbenzoylphosphonate (6)

Solvent.	CS$_2$	R.F.	0.03 mG	S.W.	500 Hz	S.A.	3.2
F.B.	4.0 Hz	S.T.	250 sec	S.O.	0.0 Hz	I.A.	off

Plate XXI

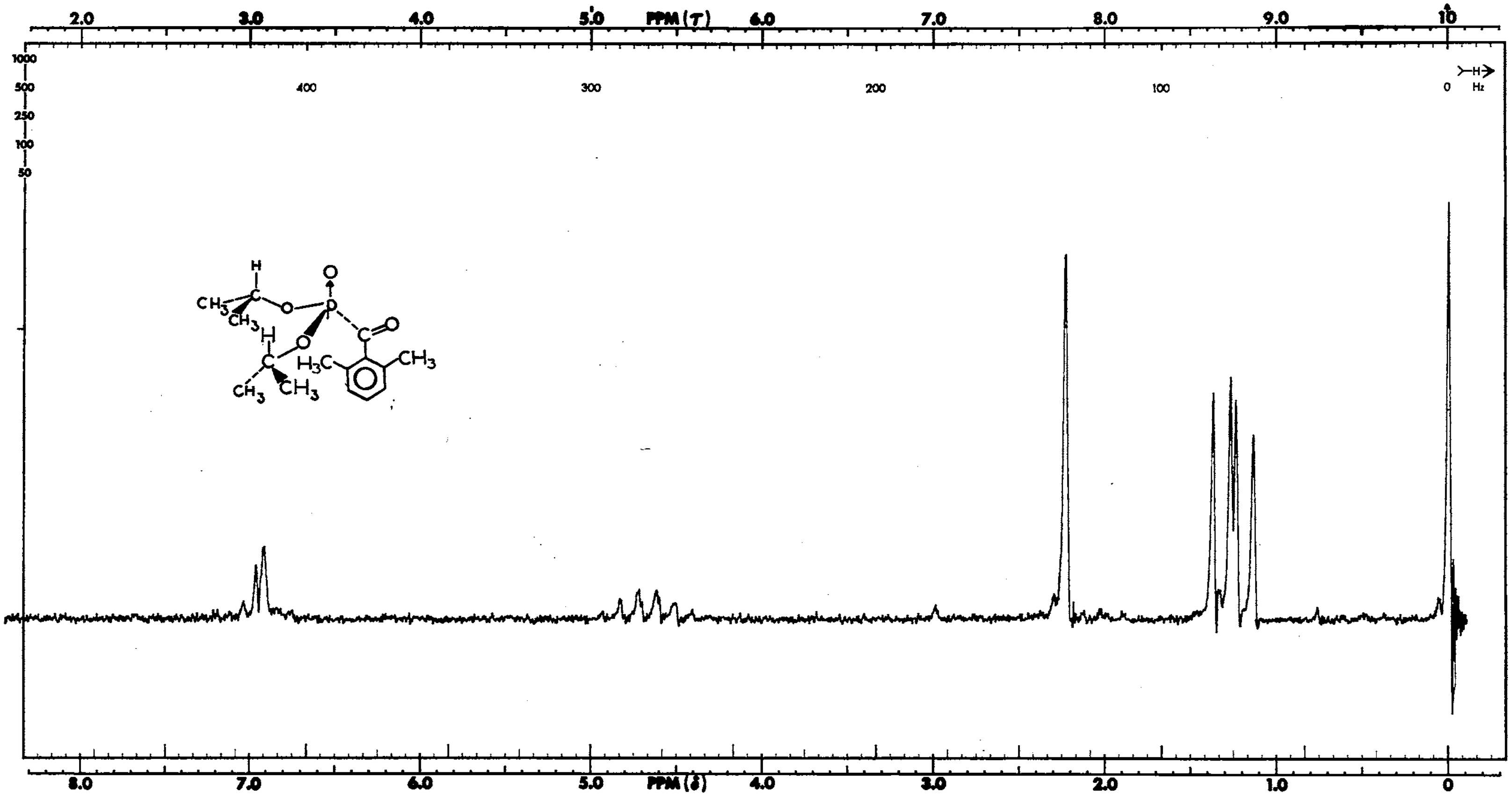


Diisopropyl 4-Methylbenzoylphosphonate (7)

Solvent. . . . . . CS_2 R.F. . . . . . 0.03 mG S.W. . . . . . 500 Hz S.A. 3.2

F.B. . . . . . 4.0 Hz S.T. . . . . . 250 sec S.O. . . . . . 0.0 Hz I.A. . . . . . off

Plate XXII

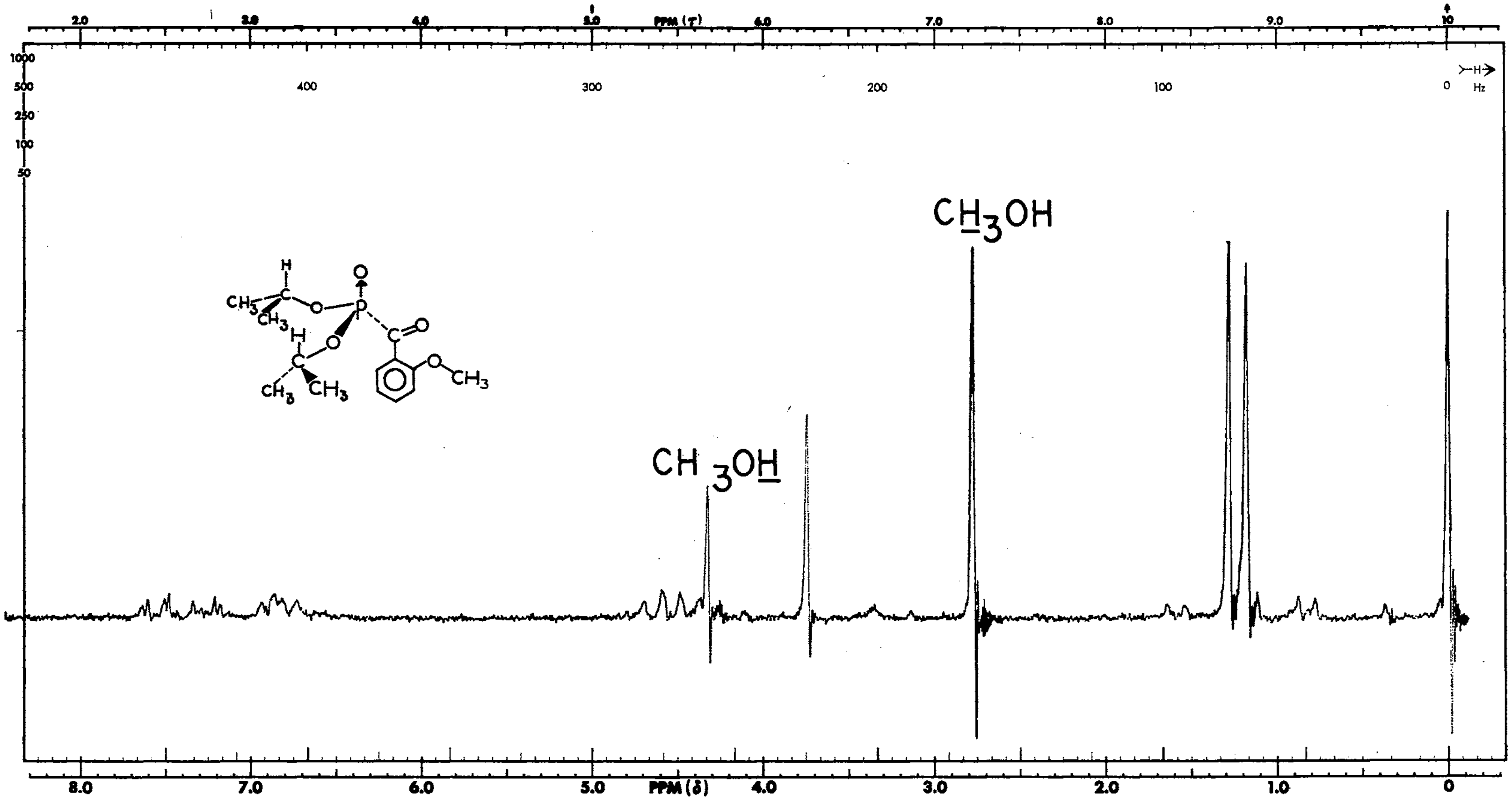


Diisopropyl 2,6-Dimethylbenzoylphosphonate (8)

Solvent. . . . . . CCl_4 R.F. . . . . . . 0.03 mG S.W. . . . . . . 500 Hz S.A. 5.0

F.B. . . . . 4.0 Hz S.T. . . . . . . 250 sec S.O. . . . . . . 0.0 Hz I.A. . . . . . . off

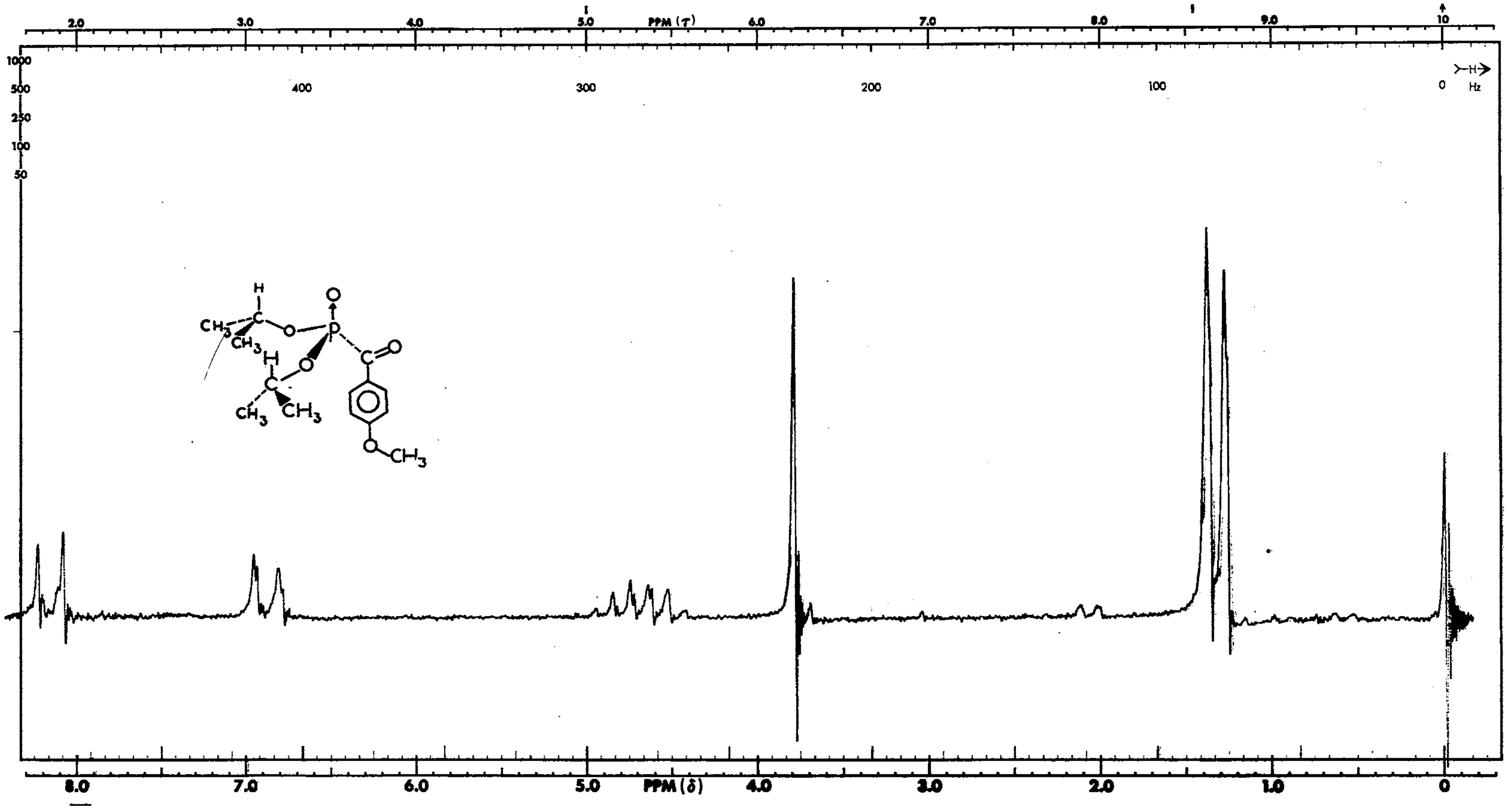
Plate XXIII



Diisopropyl 2-Methoxybenzoylphosphonate (9)

Solvent. . . . . . CS_2 R.F. . . . . . 0.02 mG S.W. . . . . . 500 Hz S.A. 2.5
F.B. . . . . . 4.0 Hz S.T. . . . . . 250 sec S.O. . . . . . 0.0 Hz I.A. . . . . . . off

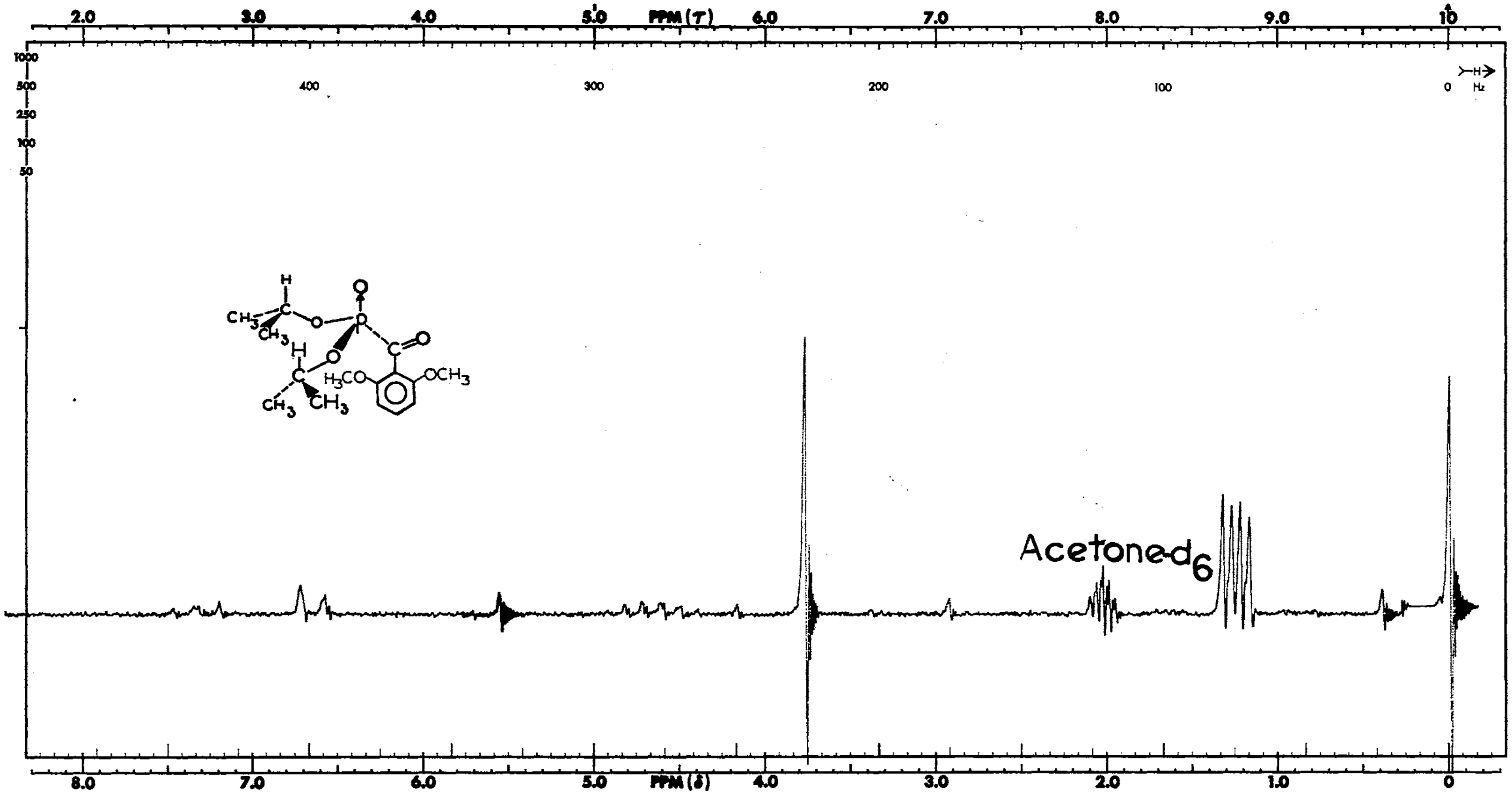
Plate XXIV



Diisopropyl 4-Methoxybenzoylphosphonate (10)

Solvent.	CCl_4	R.F.	0.075 mG	S.W.	500 Hz	S.A.	0.8
F.B.	4.0 Hz	S.T.	250 sec	S.O.	0.0 Hz	I.A.	off

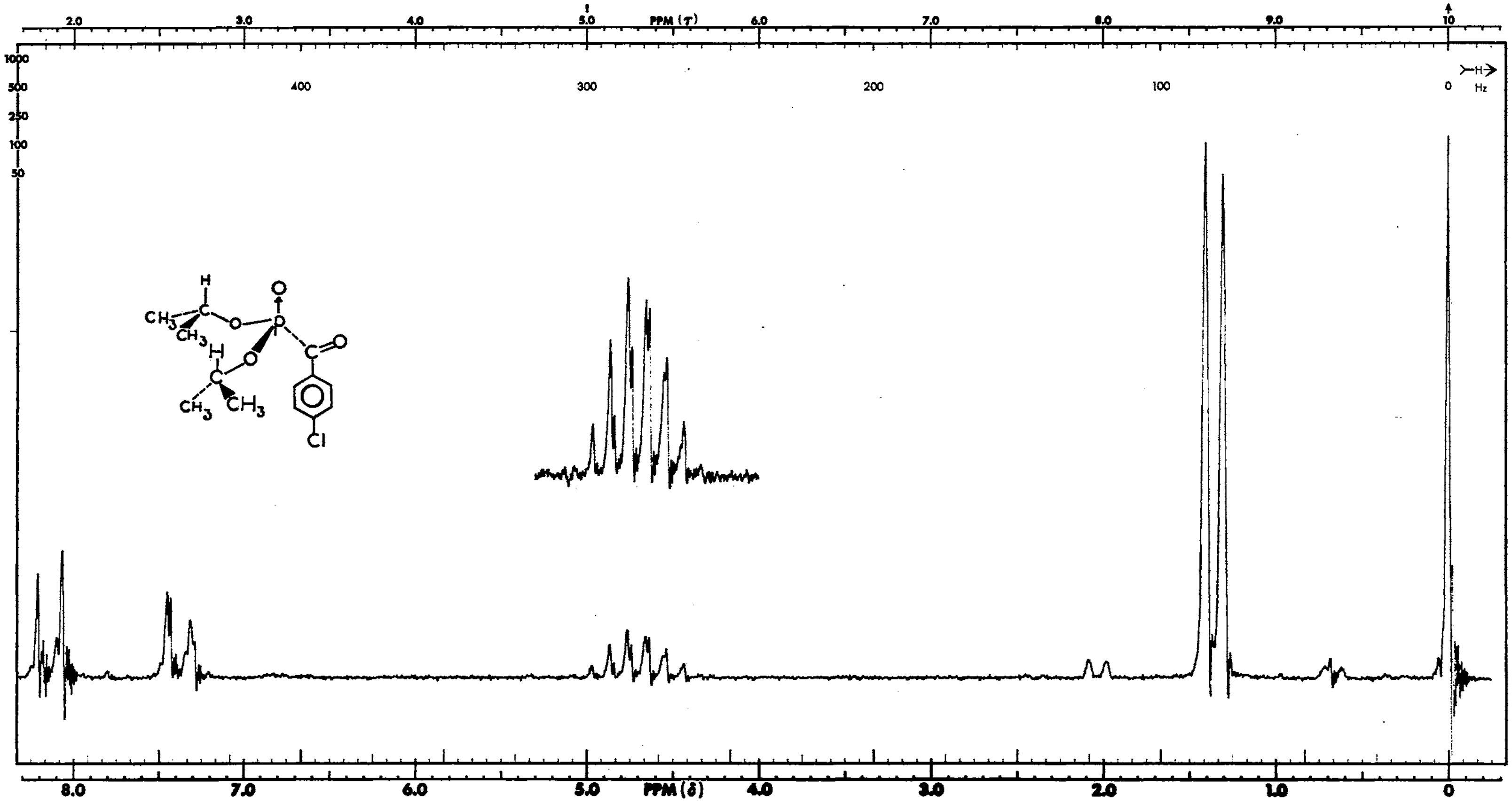
Plate XXV



Diisopropyl 2,6-Dimethoxybenzoylphosphonate (11)

Solvent.	Acetone-d$_6$	R.F.	0.04 mG	S.W.	500 Hz	S.A.	3.2
F.B.	4.0 Hz	S.T.	250 sec	S.O.	0.0 Hz	I.A.	off

Plate XXVI

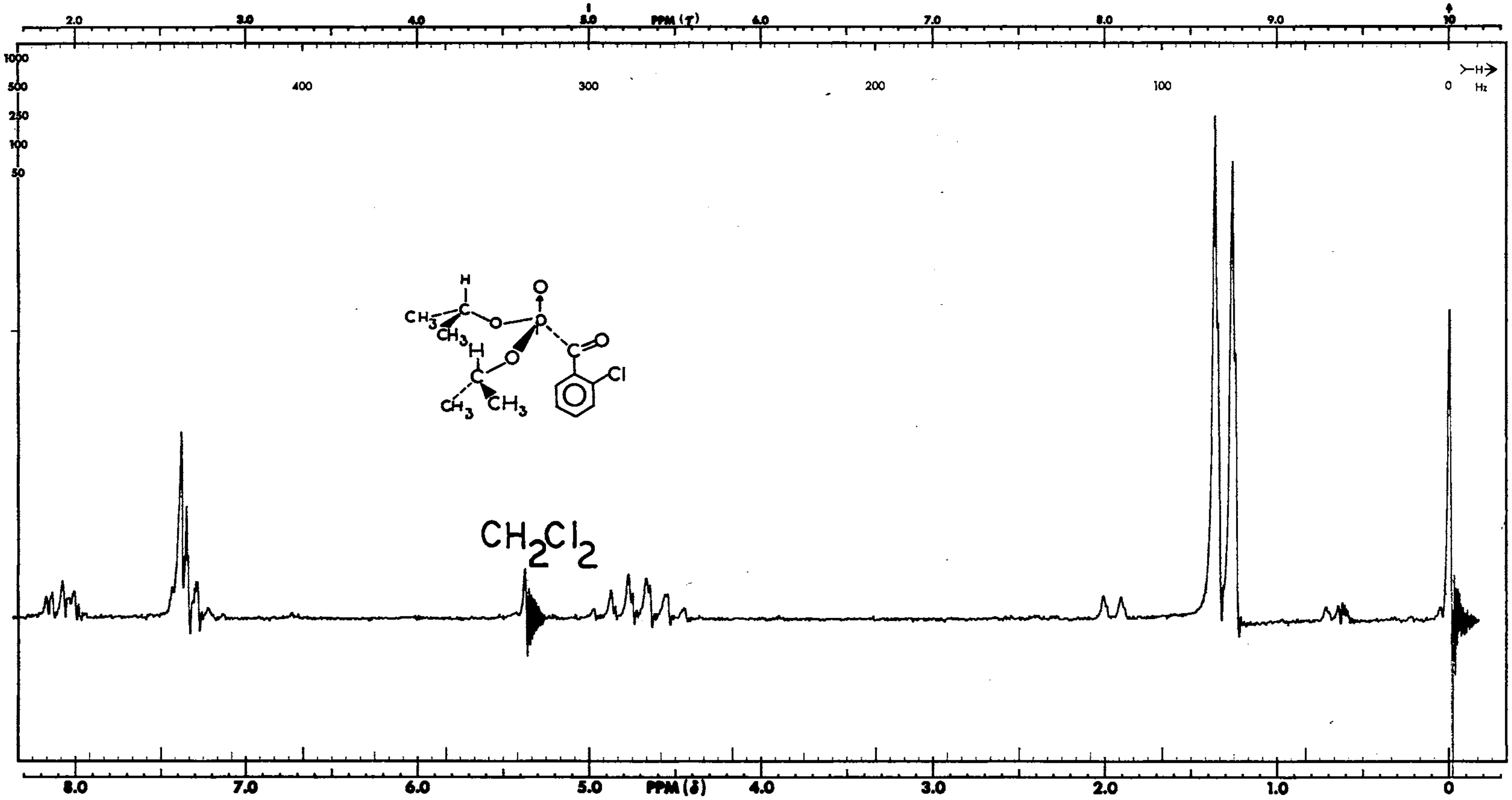


Diisopropyl 4-Chlorobenzoylphosphonate (13)

Solvent. . . . . . CCl_4 R.F. . . . . . . 0.01 mG S.W. . . . . . . 500 Hz S.A. 0.8

F.B. . . . . 4.0 Hz S.T. . . . . . . 250 sec S.O. . . . . . . 0.0 Hz I.A. . . . . . . off

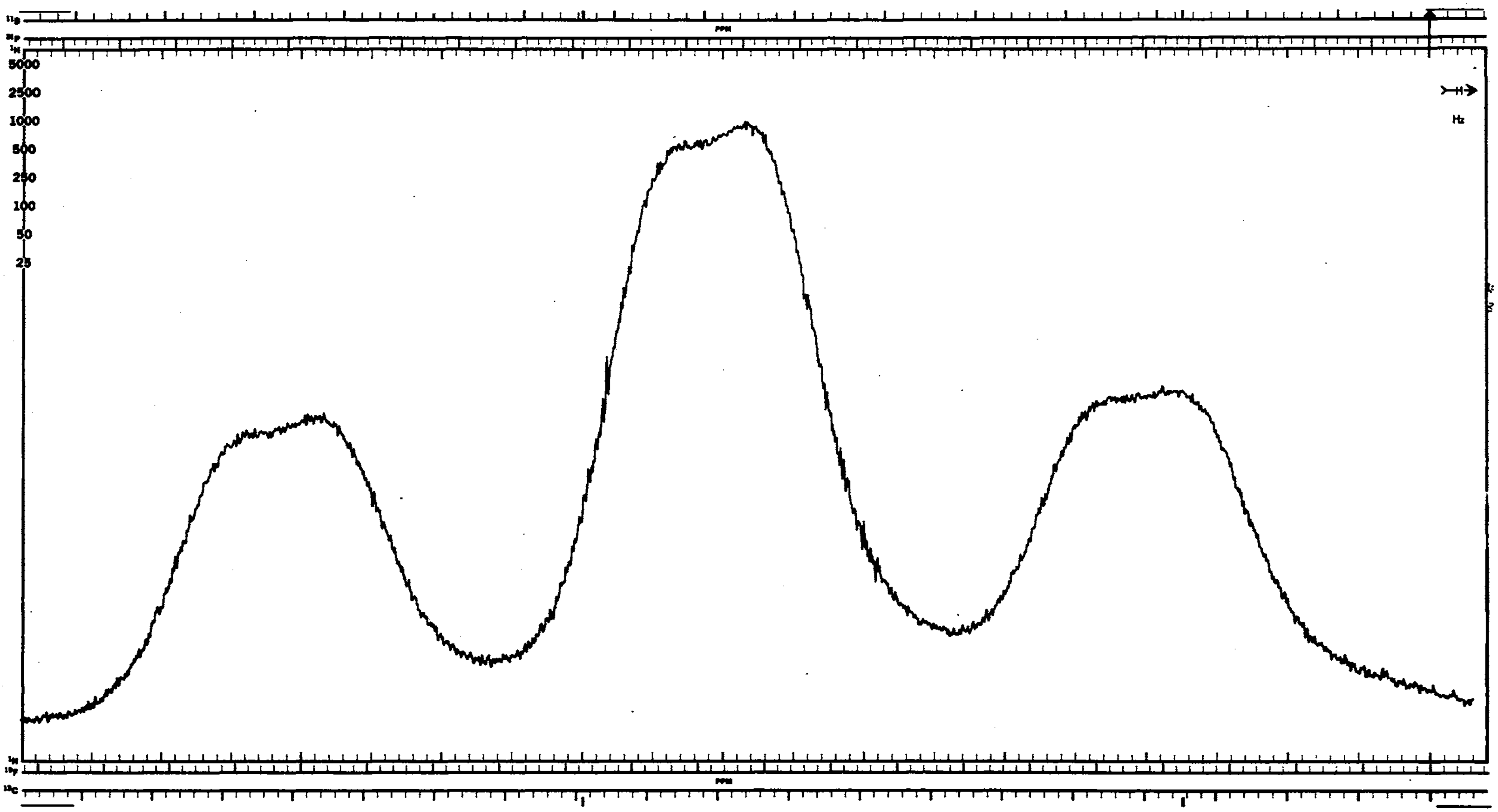
Plate XXVII



Diisopropyl 2-Chlorobenzoylphosphonate (12)

Solvent. . . . . . CCl_4	R.F. . . . . . . 0.04 mG	S.W. . . . . . . 500 Hz	S.A. 3.2, 16.0
F.B. . . . . 4.0 Hz	S.T. . . . . . . 250 sec	S.O. . . . . . . 0.0 Hz	I.A. . . . . off

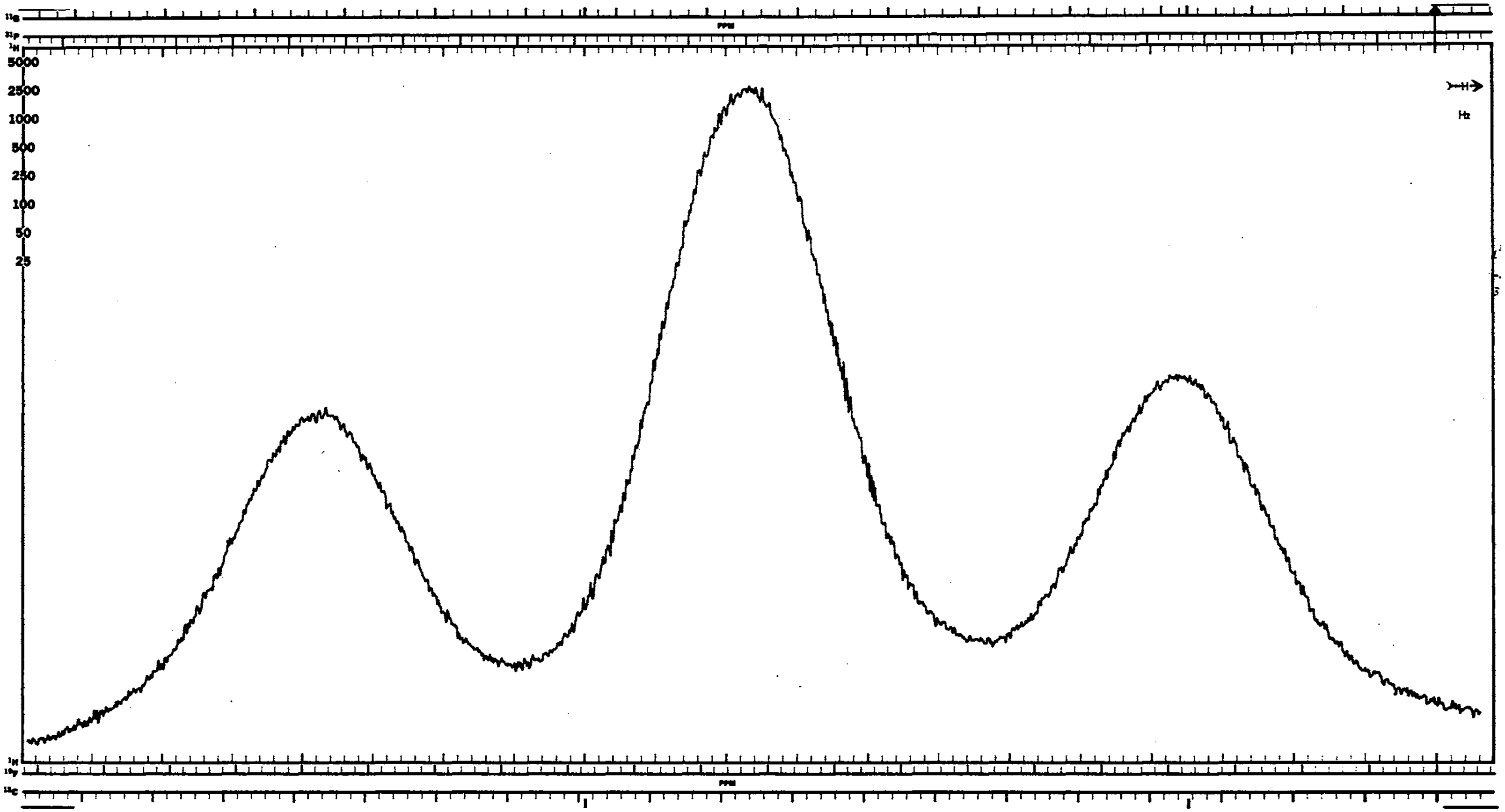
Plate XXVIII



^{31}P Spectrum of 2-Methylbenzoylphosphonate (6)

Solvent. . . . . . Neat	R.F. . . . . . 76 dB	S.W. . . . . . 25 Hz	S.A. 16
F.B. . . . . . . 2.0 Hz	S.T. . . . . 250 sec	S.O. . . . 88,909 Hz	O.F. . . 40.5 MHz

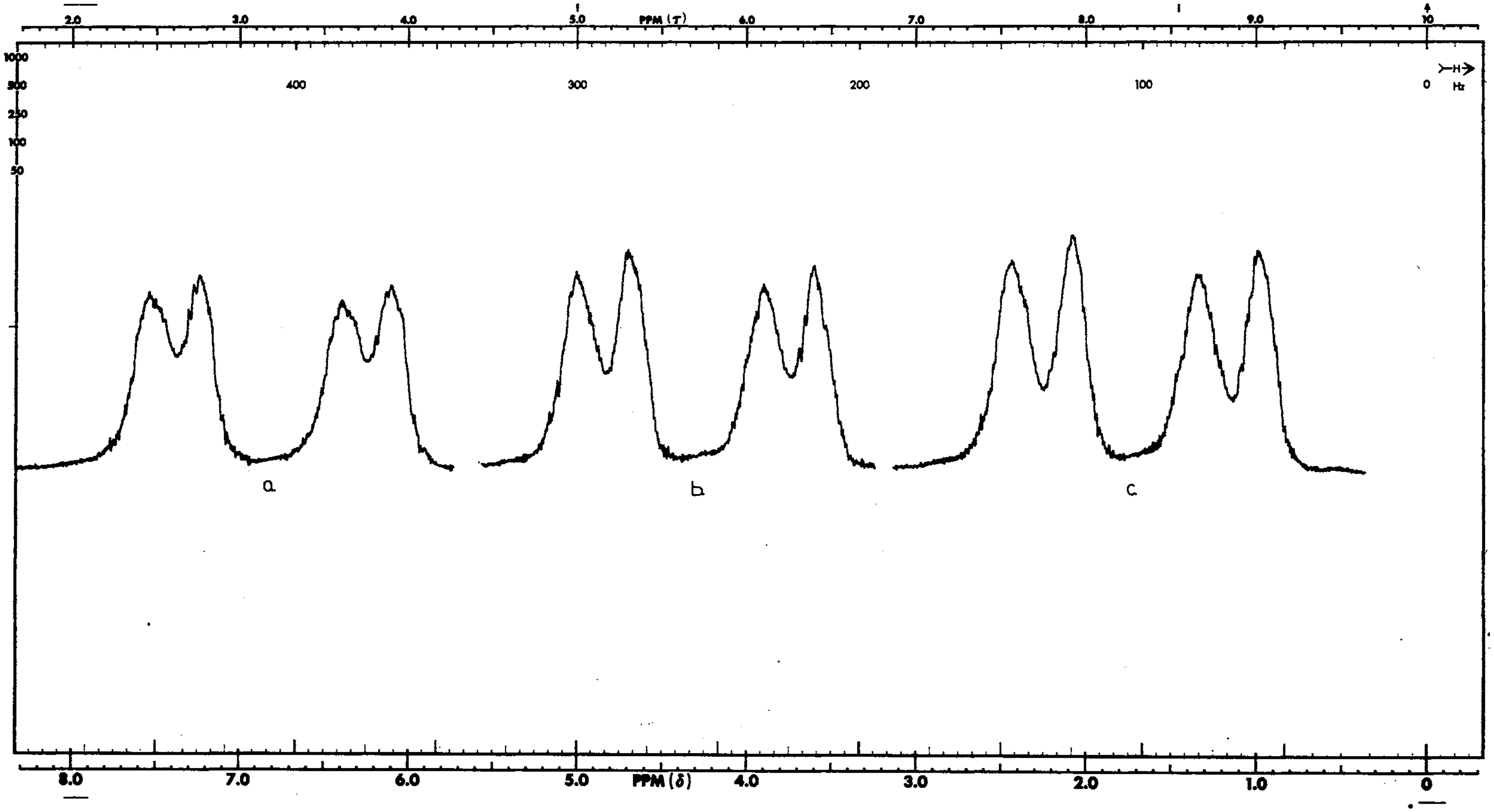
Plate XXIX



^{31}P Spectrum of Diisopropyl 4-Methylbenzoylphosphonate (7)

Solvent. . . . . . Neat	R.F. . . . . . 76 dB	S.W. . . . . . . 25 Hz	S.A. 16
F.B. . . . . . . 2.0 Hz	S.T. . . . . .250 sec	S.O. . . . . 88,919 Hz	O.F. . . . 40.5 MHz

Plate XXX

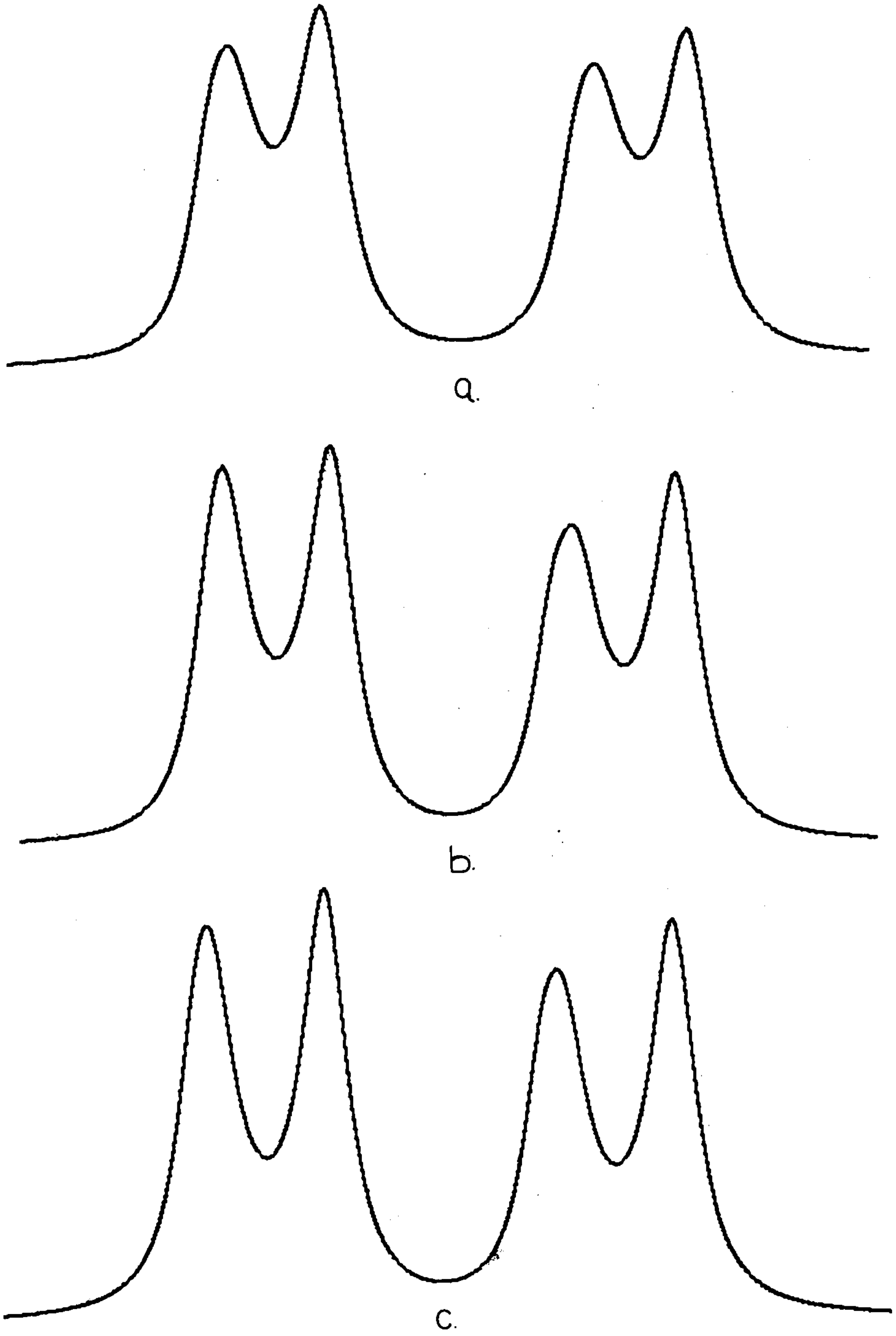


Diisopropyl 4-Methylbenzoylphosphonate (7), Isopropyl-methyl Protons

Solvent. . . . . . CS_2 R.F. . . . . . . 0.025 S.W. . . . . . . 50 Hz S.A. 2.0

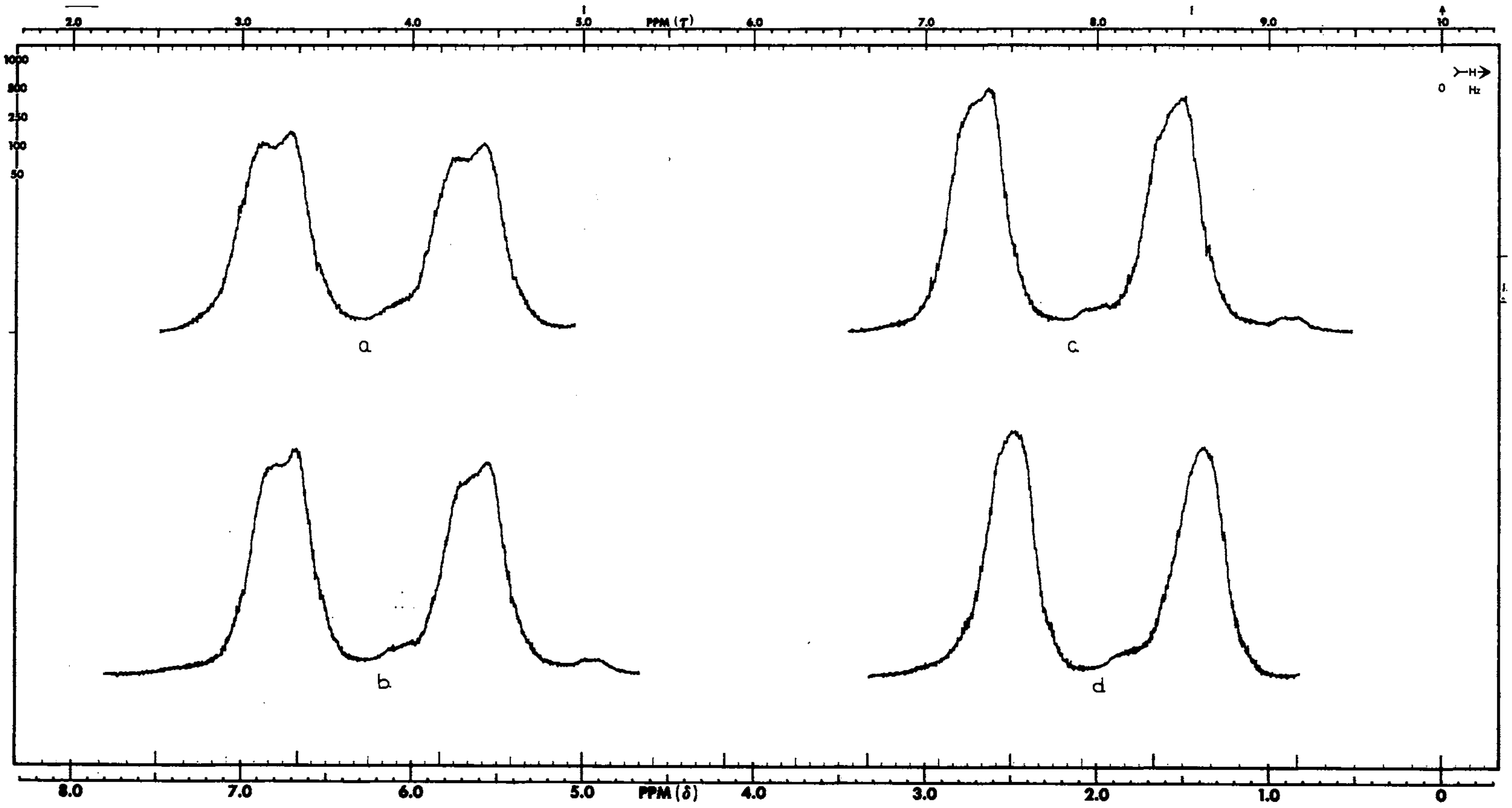
F.B. . . . . . . 4.0 Hz S.T. . . . . . 250 sec Temperature (^{o}K) (a) 273.0 (b) 263.5 (c) 250.2

Plate XXXI



Simulated Spectra, Diisopropyl 4-Methylbenzoylphosphonate (7), Isopropyl-methyl Protons, Rate constants . . . . (a) 1.625. . . . . (b) 1.275. . . . . (c) 0.75

Plate XXXII

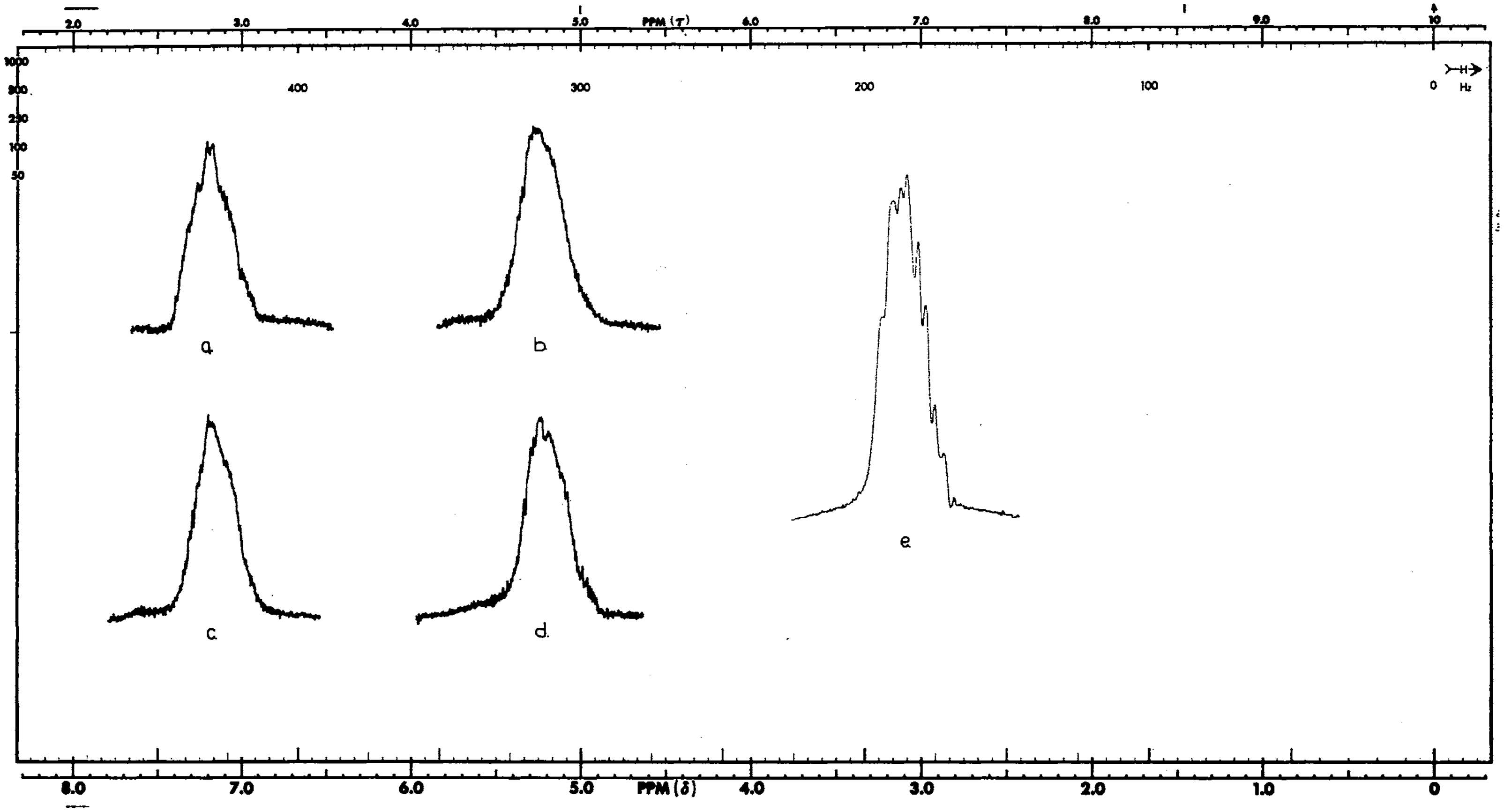


Diisopropyl 4-Methylbenzoylphosphonate (7), Isopropyl-methyl Protons

Solvent. . . . . . Neat   R.F. . . . . . 0.025   S.W. . . . . 50 Hz   F.B. . . . . . 4.0 Hz

S.T. . . . . . 250 sec   Temperature (^{o}K)   (a) 314.16   (b) 319.60   (c) 326.20   (d) 331.15

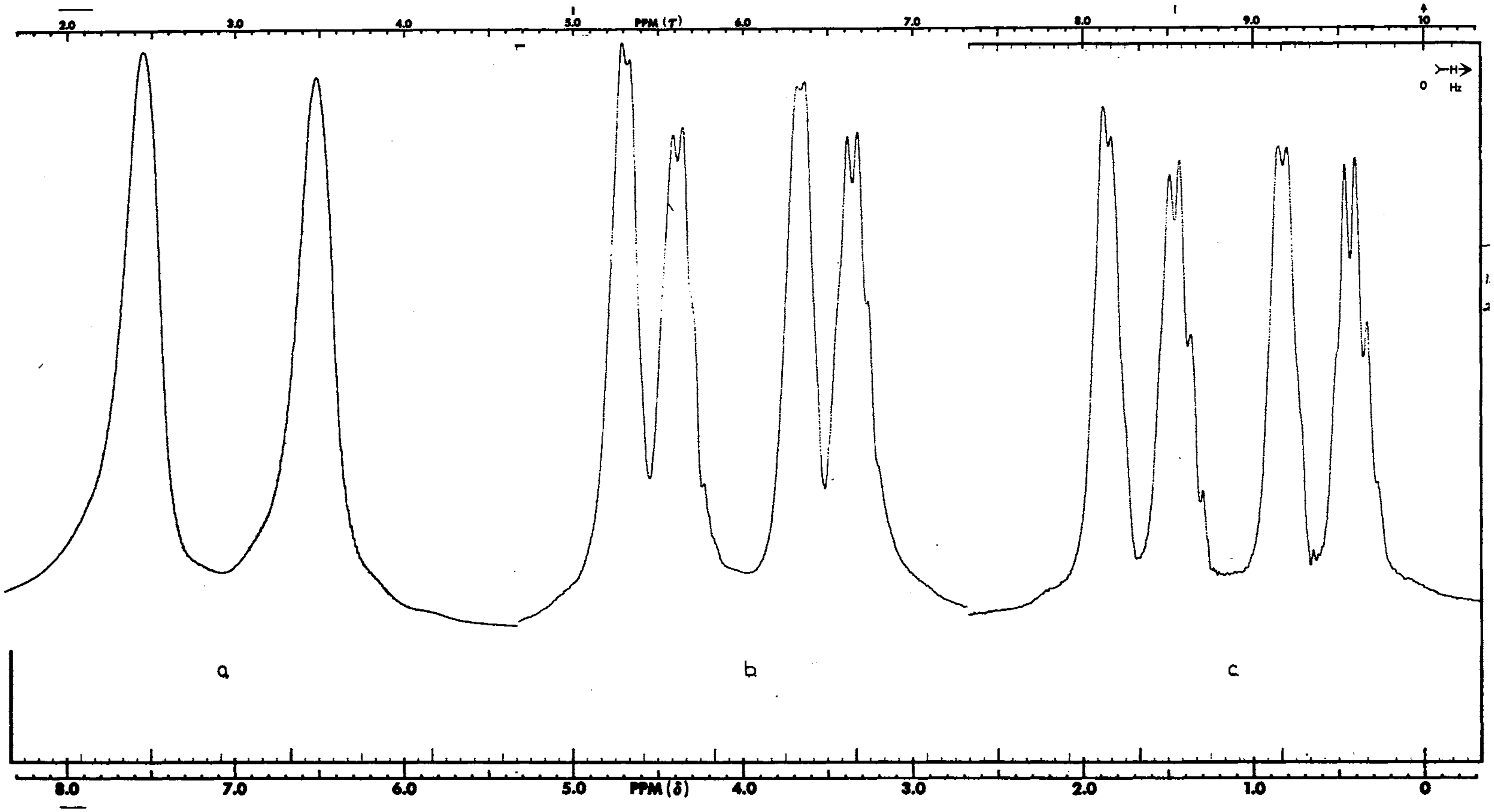
Plate XXXIII



Diisopropyl 2-Methylbenzoylphosphonate (6), Ar-methyl Protons

Solvent. . . CS_2 (a,b,c,d), Neat (e). . . S.W. . . . 50 Hz. . . O.F. . . (a,b,c,d,) 60 MHz. . . (e) 100 MHz. . . Temperature (°C). . . (a) 26.0 (b) -3.4 (c) -15.4 (d) -22.0 (e) 150.0

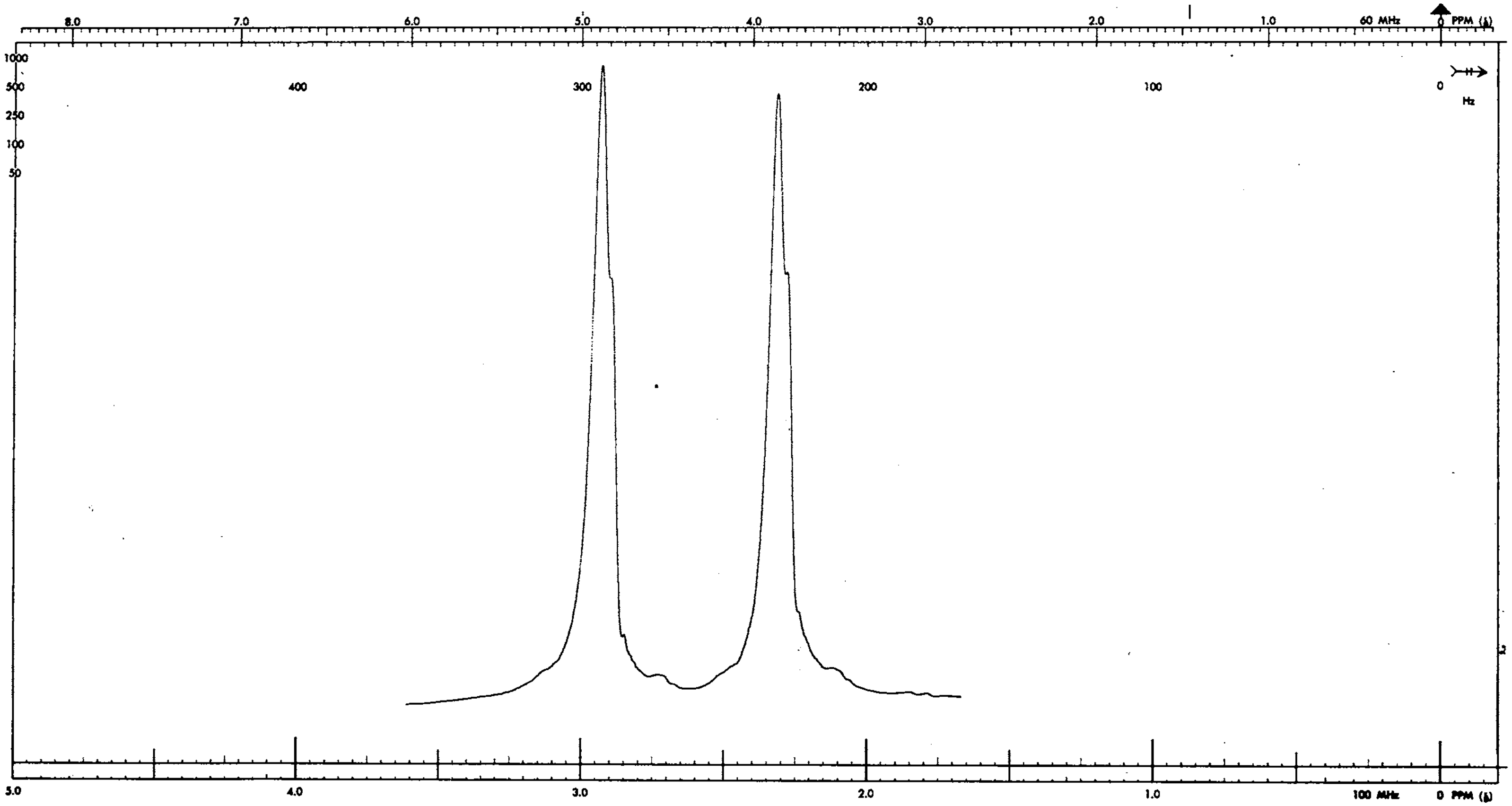
Plate XXXIV



100 MHz Spectra of Diisopropyl 2-Methylbenzoylphosphonate (6), Isopropyl-methyl Protons

Solvent. . . Neat S.W. . . . 50 Hz Temperature (°C). . (a) R.T. (b) 110.0 (c) 150.0

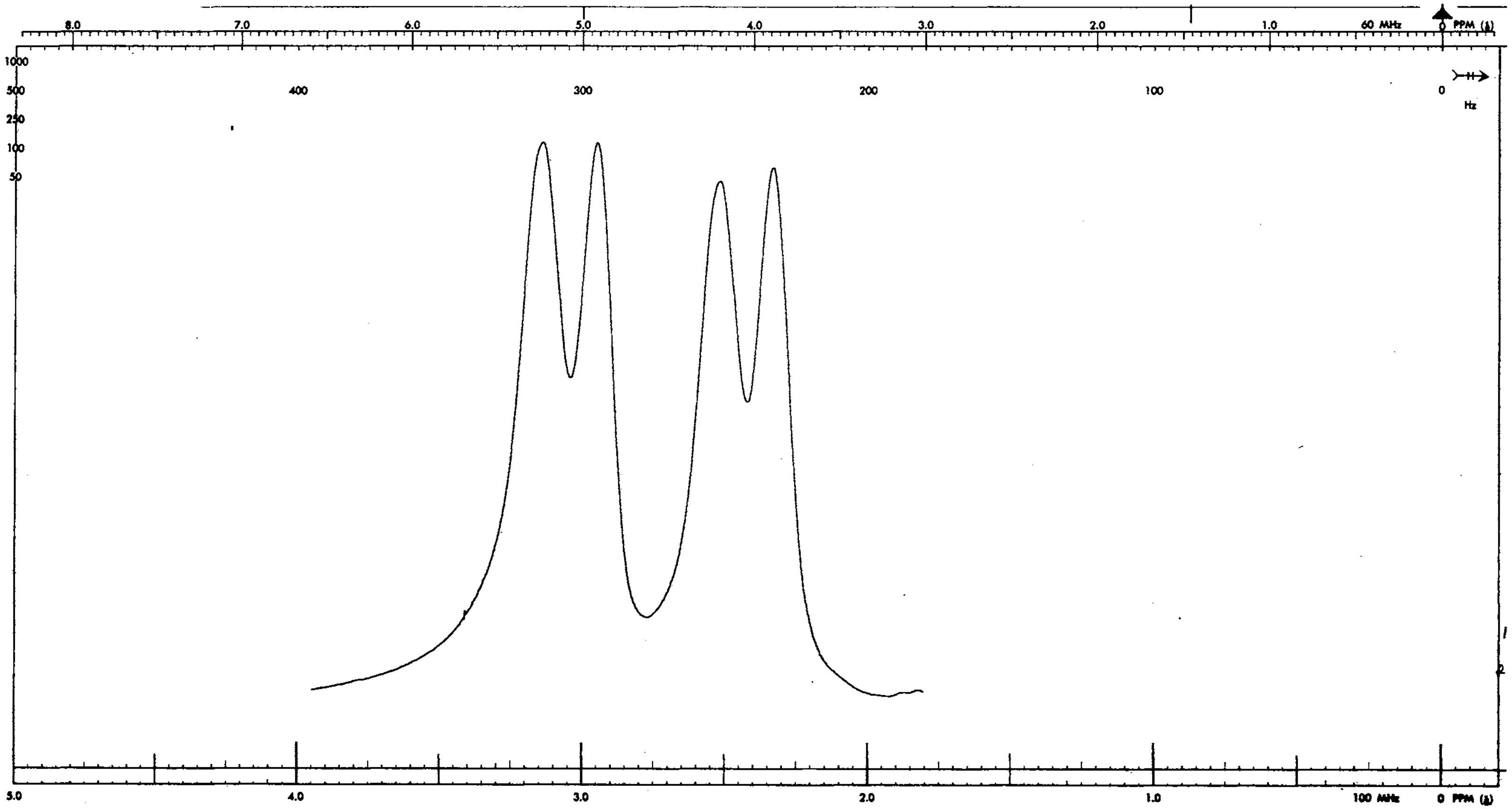
Plate XXXV



100 MHz Spectrum of Diisopropyl Benzoylphosphonate (5), Isopropyl-methyl Protons

Solvent. . . Neat S.W. . . 50 Hz S.T. . . . 500 sec Temperature. . . 120° C

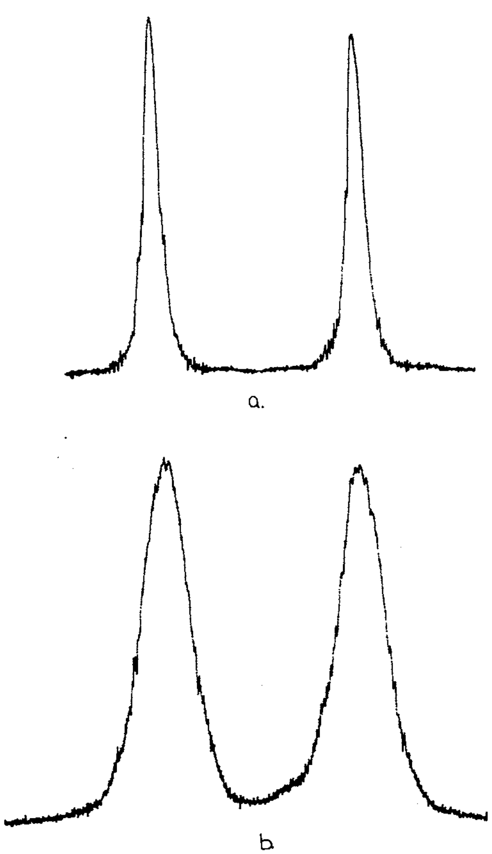
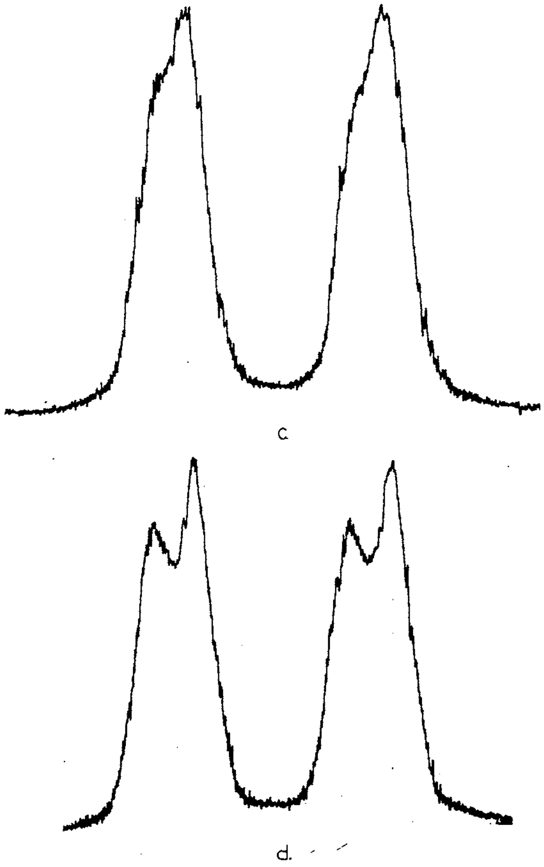
Plate XXXVI



100 MHz Spectrum of Diisopropyl Benzoylphosphonate (5), Isopropyl-methyl Protons

Solvent. . . Neat S.W. . . . 50 Hz S.T. . . . 500 sec Temperature. . . R.T.

Plate XXXVII

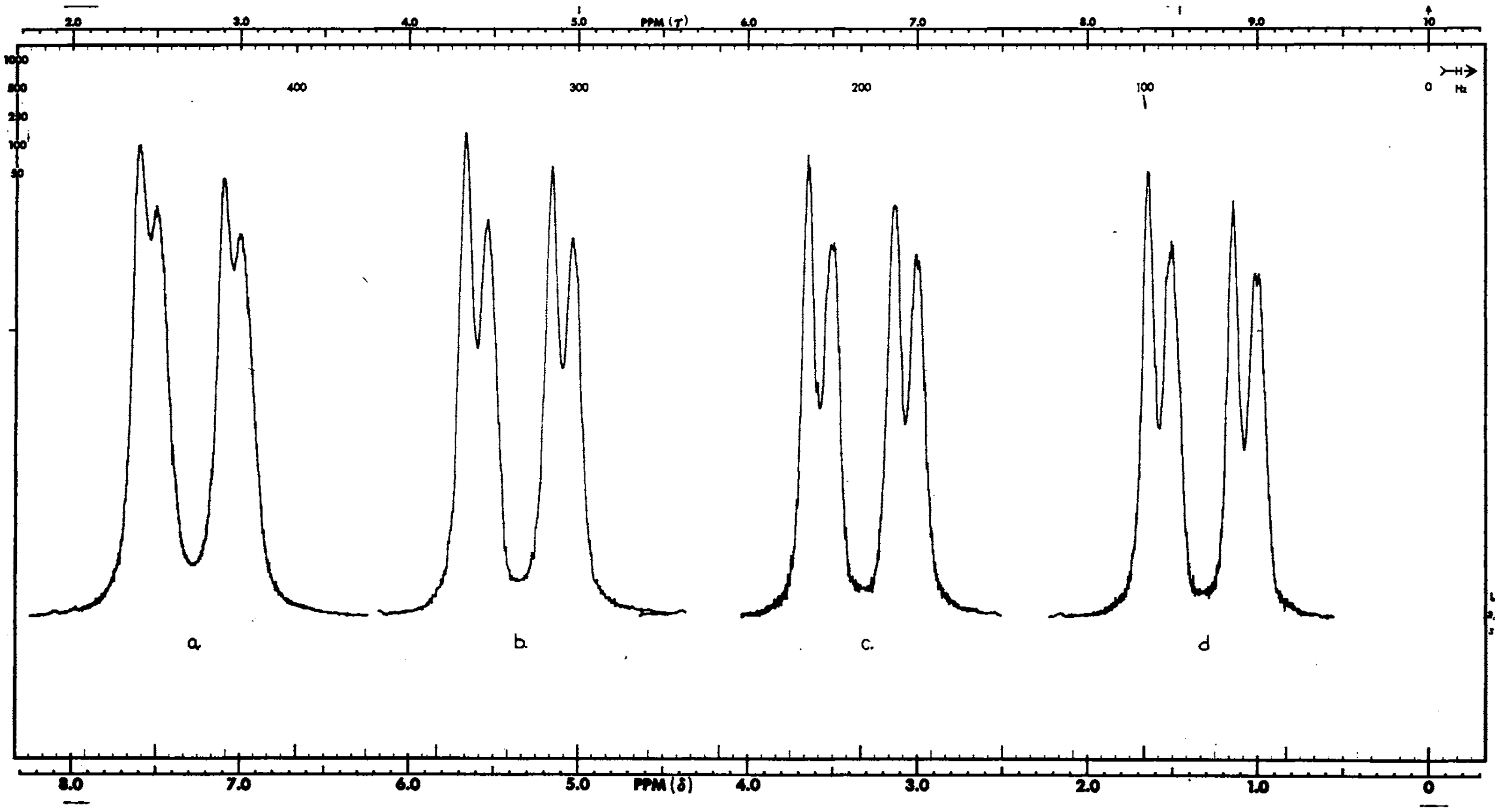



Diisopropyl 2-Methylbenzoylphosphonate ($\underset{\sim}{6}$), Isopropyl-methyl Protons

Solvent. . . . . CS_2 S.W. . . . . . 50 Hz S.T. . . . . 250 Hz

Temperature (^{o}C). . . . (a) 26.0 (b) -3.4 (c) -15.4 (d) -22.0

Plate XXXVIII



Diisopropyl 2-Chlorobenzoylphosphonate (12), Isopropyl-methyl Protons

Solvent. . . Neat   S.W. . . . 100 Hz   S.T. . . . . 250 sec

Temperature (^{o}C). . . (a) 26.0 (b) 47.0 (c) 64.0 (d) 69.0

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2

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