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NEW ASPECTS OF THE MICHAELIS-ARBUZOV AND PERKOW REACTIONS

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DECLARATION

While registered as a candidate for the degree of Ph.D. for which this submission is made, I have not been registered as a candidate for any other award.

In partial fulfilment of the requirements for the degree, an evening course of MSc lectures on Structural Methods (uv, ir, nmr, mass spectometry and X-ray crystallography) and research colloquia have been attended in the School of Chemistry.

Mrs L. Powroznyk

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ABSTRACT

NEW ASPECTS OF THE MICHAELIS-ARBUZOV AND PERKOW REACTIONS

Lubomyra Powroznyk

The work presented in this thesis has involved an investigation of the thermal decomposition of the Michaelis-Arbuzov intermediates $(PhO)_3PMeBr$, $(PhO)_3PMeI$, $(\underline{o}\text{-}CH_3C_6H_4O)_3PMeBr$, and $(\underline{o}\text{-}CH_3C_6H_4O)_3PMeI$, in the solid state and in deuterochloroform. Formation of aryl halide has been shown to occur by nucleophilic substitution in the unactivated benzene ring rather than by a benzyne mechanizm. In addition, a novel disproportionation reaction gave the quasiphosphonium salts $(ArO)_2PMe_2X$, $ArOPMe_3X$, and Me_4PX, and their corresponding Arbuzov-cleavage products. The quasiphosphonium intermediates and the tetramethylphosphonium salt which were obtained from disproportionation and the trimethylphosphine oxide were isolated and identified by ^1H, ^{31}P, and ^{13}C n.m.r. spectroscopy. In certain circumstances a substantial proportion of an intermediate containing a P-O-P linkage was also observed. The mechanisms of these reactions and the spectroscopic features of the reactive intermediates and of the end products have been studied. The P-O-P intermediate was isolated in very small amount, and was found to be stable in deuterochloroform in a sealed tube, but not as a solid.

Using sterically hindered phosphorus (III) esters, viz. $(RO)_3P$, $(RO)_2PPh$, and $ROPPh_2$ ($R = Me_3CCH_2$), the first examples of identifiable intermediates, $(RO)_3P^+CH_2COPhBr^-$, $PhP^+(OR)_2CH_2COPhBr^-$, $Ph_2P^+(OR)CH_2COPhBr^-$, and $Ph_2P^+(OR)OC(:CH_2)PhCl^-$ have been obtained in the reactions of these esters with α-bromo- and α-chloro-acetophenone. The structures of the intermediates have been investigated by ^{31}P, and ^1H n.m.r. spectroscopy and the mechanisms of their decomposition to Arbuzov and Perkow products have been elucidated. The intermediates $PhP^+(OR)_2CH_2COPhBr^-$ and $Ph_2P^+(OR)CH_2COPhBr^-$ were stable at room temperature in $CDCl_3$. On heating in sealed tubes (0.5 h at 100 ^oC) the dilute solutions decomposed completely to give pure products of $PhP(O)(OR)CH_2COPh$ and of $Ph_2P(O)CH_2COPh$ respectively. Neopentyl bromide was formed in each case.

Additional studies on the reactions of the phosphorodiamidite $ROP(NMe_2)_2$ ($R = Me_3CCH_2$) with the halogenomethanes, CH_3X ($X = Cl$, Br, or I) have established the identity of the phosphonium intermediates obtained and have also revealed a competing process of P-N cleavage, the extent of which can be correlated with the hardness of the halide present.

CHAPTER I, HISTORICAL

I.1 MICHAELIS-ARBUZOV REACTION

The interaction of trialkyl phosphites and alkyl halides,[1] referred to as the Michaelis-Arbuzov reaction, was first reported by Michaelis[2] and later exploited extensively by Arbuzov[3] and many other workers.

$$(RO)_3P + R'X \longrightarrow (RO)_2P(O)R' + RX$$

A stable 1:1 intermediate was obtainable in certain instances from triaryl phosphites[4-8] and in other special cases involving trialkyl phosphites and α,β-dihaloalkyl ethers.[9-12]

The first step in this type of reaction was made by Michaelis and Kähne, who reported in 1898 that the reaction of triphenyl phosphite with iodomethane at 100 °C for 48 h yielded 1:1 adduct as crystalline needles, m.p. 70-75 °C.[14]

$$(C_6H_5O)_3P + CH_3I \longrightarrow (C_6H_5O)_3PCH_3I$$

Adducts of this type are generally known as quasiphosphonium intermediates[8,13] and are readily hydrolysed to give the phosphonate, phenol, and hydrogen iodide.

$$(C_6H_5O)_3PCH_3I + H{\cdot}OH \longrightarrow HI + C_6H_5OH + CH_3PO(OC_6H_5)_2$$

Michaelis and Kähne prepared a number of other intermediates e.g. from tri-m-tolyl or tri-p-tolyl phosphite and iodomethane by heating the reactants together on a water bath. Tri-m-tolyl phosphite was thus heated for 5 h to give a dark brown oily liquid, which became crystalline after cooling, and after washing with dry ether it gave a hygroscopic crystalline product.[2]

The product from tri-p-tolyl phosphite, obtained after 12 h, remained however as a viscous liquid.[2,14]

Triphenyl phosphite and benzyl chloride gave a syrupy liquid on heating at 150-175 °C, instead of the expected crystalline phosphonium compound.

A number of aromatic intermediates were also produced by Arbuzov[3] in 1906, but both Michaelis and Arbuzov failed to obtain intermediates from trialkyl phosphites and alkyl halides. They showed that the final products in these reactions were usually phosphonates and alkyl halides, although Michaelis and Kähne obtained methylphosphonic acid, ethyl iodide and ethene by heating triethyl phosphite with methyl iodide at 110-220 °C for 12 h.

$$(C_2H_5O)_3PCH_3I \longrightarrow CH_3PO(OH)_2 + C_2H_5I + C_2H_4$$

They assumed from the beginning that a phosphonium intermediate was involved:

$$(RO)_3P + R'X \longrightarrow [(RO)_3PR'X]$$

The thermal decomposition of triphenyl phosphite-alkyl halide adducts was investigated by Arbuzov[26] in 1905, by heating the compounds in sealed tubes at 210-220 °C. Some tar formation occurred, especially with the higher members, along with free iodine, and the following decomposition products were isolated.

Adduct	Temp. °C	Time (h)	Yield (%)	
			PhI	$RP(O)(OPh)_2$
$(PhO)_3PMeI$	220	20	74	56 [a]
$(PhO)_3PEtI$	220	20	71	60 [b]
$(PhO)_3PCH_2PhI$	208	20	15	-

[a] b_{12} 196-9 °C, n_D^{20} 1.5520

[b] b_{12} 200-4 °C, n_D^{20} 1.5454

The isobutyl iodide adduct, however, gave only iodine as the isolated product after 15 h at 210 °C.

The Michaelis-Arbuzov reaction[16] takes place with any derivative of trivalent phosphorus that carries an ester group (OR):

$$>P{-}OR + R'X \longrightarrow >P(OR)R'\ X \longrightarrow P(O)R' + RX$$

and most varied selection of organic halides R'X are able to participate in the reaction. The chief requirement of the structure of the organic halide is that the halogen atom must be capable of nucleophilic displacement, this occurring most easily if it is attached to the terminal carbon atom of an aliphatic chain. It must not be directly connected to an aromatic ring.

The above reaction is merely one instance of the more general Michaelis-Arbuzov rearrangement,[17] or isomerisation. If the radical R' of the alkyl halide is identical with the radical R of the ester group the reaction takes on the aspect of a true isomerisation,[18] which can be performed with minute amounts of the halide R'X.

Landauer and Rydon thus showed that isomerisation[8] of trimethyl phosphite occurred with methyl iodide (0.1 mol) by heating the reactants under reflux at 100 °C. After a brief induction period, a vigorous reaction set in and was complete within 5 min. Distillation then gave methyl iodide and dimethyl methylphosphonate:

$$(MeO)_3P + MeI \longrightarrow (MeO)_2P(O)Me + MeI$$

Although customarily used with tertiary phosphites, $(RO)_3P$, from which the reaction product is an ester of a primary phosphonic acid $R'P(O)(OR)_2$ i.e. a PHOSPHONATE,[16] the reaction may also be carried out with esters of phosphonous acids,[20] $RP(OR)_2$, in which case esters of secondary phosphonic acids $R'RP(O)OR$, i.e. PHOSPHINATES are formed.

$$RP(OR)_2 + R'X \longrightarrow R'RP(O)OR + RX$$

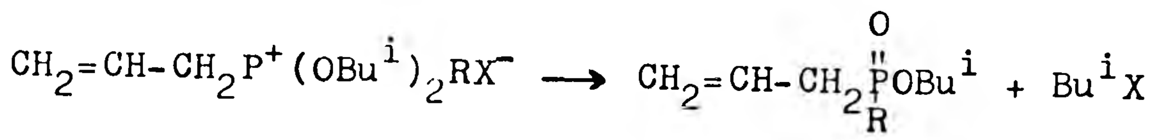
Esters of phosphinous acids, R_2POR, form tertiary phosphine oxides $R_3P{=}O$ as follows:

$$R_2POR + R'X \longrightarrow R_2R'P{=}O + RX$$

The reactivity of phosphorus (III) esters increases from phosphites to phosphonites and again to phosphinites, in accord with a general increase in reactivity upon approach to the tertiary phosphine structure.[3,19,20]

Although the reaction is frequently conducted by mixing the reactants and warming the mixture to the required temperature,[16] most often 100-150 °C, the most reactive combinations enter the reaction at room temperature, this being especially true of reactions with acyl halides.

Crystalline quasiphosphonium salts[20] have in some cases been prepared by the addition of methyl iodide to unsaturated phosphonous diesters containing branched ester radicals, such as $CH_2{=}CH{-}CH_2P(OBu^i)_2$, although the adducts decompose to secondary phosphonic esters on mild heating:



$$CH_2{=}CH{-}CH_2P^+(OBu^i)_2RX^- \longrightarrow CH_2{=}CH{-}CH_2\underset{R}{\overset{\overset{O}{\|}}{P}}OBu^i + Bu^iX$$

The phosphonous diesters are also more susceptible to self-isomerisation than the trialkyl phosphites, but in a truly pure state they isomerize with difficulty. Esters of aromatic phosphonous acids isomerize at 250 °C, but the aliphatic compounds are stable to 300 °C.[21]

Aromatic esters[20] of phosphonous acids interact with alkyl halides to form extremely stable quasiphosphonium salts that are not decomposed under the normal conditions of the Michaelis-Arbuzov reaction.[22]

The salts can, however, be decomposed by drasting heating[23] or by alcoholysis[25] or hydrolysis. The thermal decomposition has further been shown to be complicated by redistribution of the alkyl and phenoxy groups in the products that are obtained.[24]

I.2 QUASIPHOSPHONIUM COMPOUNDS IN THE PREPARATION OF ALKYL HALIDES

Landauer and Rydon in 1953 reported a new method for the preparation of alkyl halides from phosphonium intermediates and alcohols.[8] They heated triphenyl phosphite with methyl iodide under reflux to obtain the methiodide, $(PhO)_3PMeI$, and in an attempt to determine the nature of the phosphorus-iodide bond in this compound, they treated it with alcoholic silver nitrate. Precipitation of silver iodide was slow and not instantaneous as with methyltriphenylphosphonium iodide.

In view of the relatively slow rate at which silver iodide was formed from the triphenyl phosphite methiodide the possibility of a penta-coordinate structure for the phosphorus compound was accepted.

In order to exclude the possibility that the time - dependent production of silver iodide was due to reaction of the silver nitrate with methyl iodide formed by dissociation, the compound was treated with cold ethanol and methyl iodide was sought in product. Surprisingly enough, ethyl iodide was formed together with phenol and diphenyl methylphosphonate, thus:

$$(PhO)_3PMeI + ROH \longrightarrow RI + PhOH + (PhO)_2P(O)Me$$

The experiment thus led to a new method for the preparation of alkyl iodides.

The reaction appeared to be quite general and gave excellent yields of alkyl iodides from a wide variety of saturated and unsaturated alcohols, including cholesterol, glycols and hydroxyesters. Landauer and Rydon also found that it was not necessary to isolate the methiodide and that alkyl chlorides could be prepared similarly from triphenyl phosphite and benzyl chloride.

Hydrogen halides were also shown to react analogously.

$ROH + (PhO)_3P + HHal \longrightarrow RHal + PhOH + (PhO)_2P(O)H$

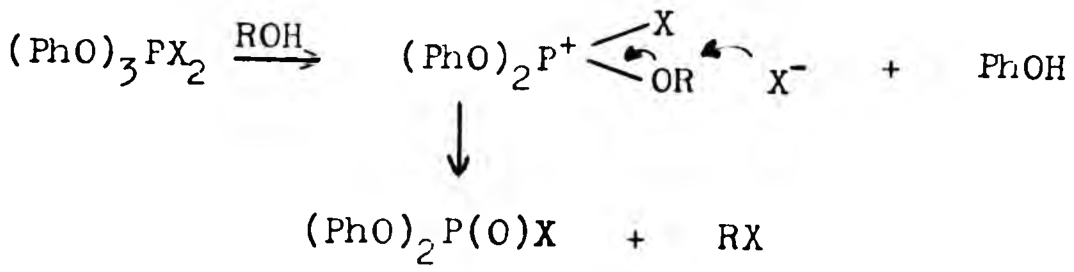
Alkyl halides may thus be prepared by a general procedure which involves refluxing a mixture of an alcohol, triphenyl phosphite, and an alkyl, hydrogen, or other halide, thus: $ROH + (PhO)_3P + R'Hal \longrightarrow RHal + PhOH + (PhO)_2P(O)R'$ (R' = alkyl, H, NH_4, Li, Na).

The new method gave excellent results with sterically hindered alcohols which are difficult to convert into halides by conventional methods, i.e. neopentyl iodide was obtained from the alcohol in 74% yield.

I.3 TRIARYL PHOSPHITE DIHALIDES AND THEIR DISPROPORTIONATION

In 1954 Landauer and Rydon[27] prepared triaryl phosphite dihalides, $(ArO)_3PHal_2$, as crystalline solids. Triphenyl phosphite dichloride, dibromide, di-iodide, bromo-chloride, bromo-iodide and chloro-iodide were obtained, the dichloride being obtained as analytically pure, colourless prisms, m.p. 80-81 °C. Earlier workers had described most of these substances as oils or unstable liquids.

The triphenyl phosphite dihalides were shown to react very readily with alcohols to form alkyl halides, which were assumed to be formed in an Arbuzov-type reaction by halide ion attack on the ester - exchanged intermediate.



$$(PhO)_3PX_2 \xrightarrow{ROH} (PhO)_2P^+ \begin{smallmatrix} X \\ OR \end{smallmatrix} \; X^- \; + \; PhOH \quad \downarrow \quad (PhO)_2P(O)X \; + \; RX$$

A simpler procedure was by the direct interaction of the three components:

$$(PhO)_3P + ROH + Hal_2 \longrightarrow RHal + PhOH + (PhO)_2P(O)Hal$$

However in attempts to prepare highly purified specimens of the triphenoxyphosphorus dihalides for conductivity and X-ray investigations, Rydon and Tonge found that these compounds were less stable and more complex in structure than had been supposed.[28] For example, on repeated recrystallisation, triphenyloxyphosphonium dibromide $(PhO)_3PBr_2$ yielded tetraphenoxyphosphonium bromide $(PhO)_4PBr$.

Further investigation showed also that two molecules of triphenyl phosphite reacted with one molecule of halogen in chlorobenzene solution to produce diphenyl phosphorobromidite $(PhO)_2PBr$, and the tetraphenoxyphosphonium bromide $(PhO)_4PBr$, which could be isolated as a crystalline solid.

$$2(PhO)_3P + Hal_2 \longrightarrow (PhO)_2PHal + (PhO)_4PHal$$

Exactly similar results were obtained with chlorine, and iodine.

The mechanism of reaction seems to be[28] that the dihalide is first formed and then exchanges one of its halogens for a phenoxy group from the second phosphite molecule:

$$(PhO)_3P + Hal_2 \longrightarrow (PhO)_3PHal_2$$

$$(PhO)_3PHal_2 + (PhO)_3P \longrightarrow (PhO)_4PHal + (PhO)_2PHal$$

There is some evidence that the reaction between chlorine and diphenyl phosphorochloridite involves an analogous stage.

$$2(PhO)_2PCl + Cl_2 \longrightarrow (PhO)_3PCl_2 + PhO\cdot PCl_2$$

In agreement with the findings of Harris and Payne, there is no increase in the number of ions when further halogen is added in a solvent of sufficient ionising power, and the reaction may take the following course:

$$(PhO)_4P^+ + Hal^- + (PhO)_2PHal + Hal_2 \longrightarrow$$
$$[(PhO)_4P]^+ + [(PhO)_2PHal_4]^-$$

In a non-ionising solvent this second stage may involve covalent species:

$$(PhO)_4PHal + (PhO)_2PHal + Hal_2 \longrightarrow (PhO)_4PHal + (PhO)_2PHal_3$$

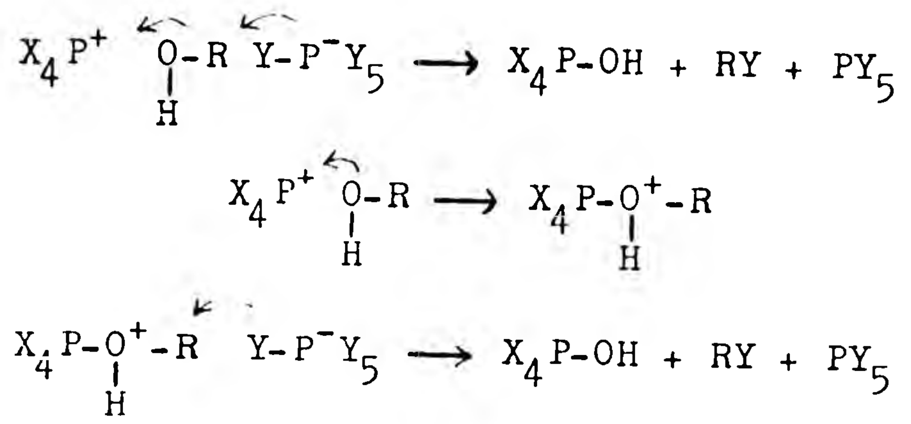
Halogen transfer may then give rise to the ions $[(PhO)_4P]^+$ and $[(PhO)_2PHal_4]^-$ or the exchange of halogen and phenoxy may give the covalent form of the triphenoxydihalide $(PhO)_3PHal_2$.

The mechanism previously advanced[27,8] for the action of the phenoxy-halides on alcohols requires modification in the light of the dimeric ionic structures.

The reactions of compounds of the general type

$$[PX_4]^+ [PY_6]^-$$

with alcohols are most reasonably regarded as involving attack by the oxygen atom of the alcohol on the phosphonium cation, and attack on the alkyl group of the alcohol by one of the nucleophilic halogen atoms of the anion. These processes may be simultaneous or sequential:



$$X_4P^+ \;\; \overset{\curvearrowleft}{\underset{\underset{H}{|}}{O}}\text{-}R \;\; \overset{\curvearrowleft}{Y}\text{-}P^-Y_5 \longrightarrow X_4P\text{-}OH + RY + PY_5 \quad \text{or}$$

$$X_4P^+ \;\; \overset{\curvearrowleft}{\underset{\underset{H}{|}}{O}}\text{-}R \longrightarrow X_4P\text{-}\underset{\underset{H}{|}}{O^+}\text{-}R$$

$$X_4P\text{-}\underset{\underset{H}{|}}{O^+}\text{-}\overset{\curvearrowleft}{R} \;\; Y\text{-}P^-Y_5 \longrightarrow X_4P\text{-}OH + RY + PY_5$$

The process will be completed by loss of HX from the hydroxylated cation: $X_4P\text{-}OH \longrightarrow X_3PO + HX$

Alcoholysis of the dimeric forms of the tetraphenoxymonochloride and monobromide, may occur in two steps as follows:

$$\left[(PhO)_4P\right]^+ \left[(PhO)_4PHal_2\right]^- + ROH \longrightarrow$$

$$(PhO)_3PO + PhOH + RHal + (PhO)_4Hal$$

$$(PhO)_4Hal + ROH \longrightarrow RHal + (PhO)_3PO + PhOH$$

The overall reaction is thus:

$$\left[(PhO)_4P\right]^+ \left[(PhO)_4PHal_2\right]^- + 2ROH \longrightarrow$$

$$2(PhO)_3PO + 2PhOH + 2RHal$$

The disproportionation reactions of the triaryl phosphite dihalides probably occur via a series of exchange reactions between halide and aryloxide ions, involving phosphonium and phosphorane structures.

$$(ArO)_3P^+Cl\;Cl^- \rightleftharpoons (ArO)_3PCl_2 \rightleftharpoons (ArO)_2P^+Cl_2\;OAr^-$$

$$(ArO)_3P^+Cl\;OAr^- \rightleftharpoons (ArO)_4PCl \rightleftharpoons (ArO)_4P^+\;Cl^-$$

A whole range of salts of the general type $[(PhO)_nPX_{4-n}]^+$ $[(PhO)_mPX_{6-m}]^-$ can thus be formed.

I.4 DISPROPORTIONATION OF QUASIPHOSPHONIUM SALTS

In 1967 Nesterov reported disproportionation of methyl and phenoxyl groups in the decomposition of certain quasiphosphonium salts.[24] He thus showed that the thermal decomposition of $MePh_nP(OPh)_{3-n}I$ (n = 1 or 2) was accompanied by a restribution of Me and PhO groups, as a result of which the products containing the phosphoryl group were freed of methyl groups, the other reaction product being the salt of a tetra-substituted phosphonium ion. Equimolar mixtures of MeI and $PhP(OPh)_2$ or of MeI and $Ph_2P(OPh)$ were heated in sealed tubes to give the crystalline quasiphosphonium salts. Further heating in $PhNO_2$ vapour (208 °C) then brought about a slow decomposition of the diphenoxy derivative to give three main products: iodobenzene, diphenyl phenylphosphonate, and phenyltrimethylphosphonium iodide, together with unidentified materials (43%).

$$MePhP(OPh)_2I \xrightarrow[\text{56 hours}]{208\ ^{\circ}C} \underset{55\%}{PhI} + \underset{71.5\%}{(PhO)_2P(O)Ph} + \underset{27\%}{PhPMe_3I}$$

Similar heating of $MePh_2P(OPh)I$ gave little decomposition even at 350 °C, hence the salt was heated in a flask with an open flame yielding a distillate of iodobenzene, phenyl diphenylphosphinate and diphenyldimethylphosphonium iodide:

$$\mathrm{MePh_2P(OPh)I} \xrightarrow{\text{flame}} \underset{14\%}{\mathrm{PhI}} + \underset{95\%}{\mathrm{Ph_2P(O)OPh}} + \underset{-}{\mathrm{Me_2Ph_2PI}}$$

The possible mechanisms by which these processes occurred were not, however, discussed.

An anomalous reaction between triphenyl phosphite and methyl bromide, discovered by Weekes in 1972, led to formation of the unexpected dimethyldiphenoxyphosphonium bromide $(PhO)_2P^+Me_2Br^-$, and suggested that a similar disproportionation might have occurred.[15]

The product was obtained when triphenyl phosphite was heated with an excess of methyl bromide at <u>ca</u>. 180 °C. Then, after removal of the volatile materials (mainly bromobenzene and a small amount of methyl bromide) the ^1H n.m.r. spectrum of the residue showed the presence of two phosphorus compounds by virtue of sharp signals for two P-Me doublets in the aliphatic region at δ 2.69 and 1.77.

Anhydrous ether was then added to the residue to give a white solid which was recrystallised from Analar acetone and identified as dimethyldiphenyloxyphosphonium bromide, $(PhO)_2P^+Me_2Br^-$, by elemental analysis and n.m.r. spectroscopy.

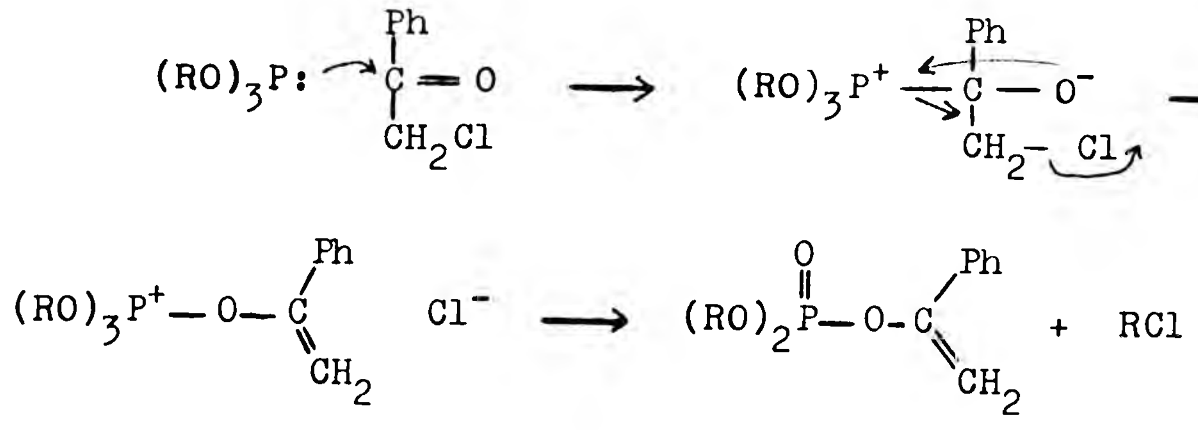
^1H n.m.r. spectrum in deuterochloroform showed τ 7.0 (Me doublet, 3H, J_{PCH} 14.6 Hz); τ 2.48 (phenoxy protons, singlet, 5H) and the ^{31}P spectrum ($CDCl_3$) showed a multiplet, δ 95 ppm.

The evidence suggested that at elevated temperatures and in the presence of an excess of methyl bromide an extra methyl group can be combined into the phosphonium molecule at the expense of the loss of a phenoxy group. No further investigations of these processes have, however been carried out.

I.5 PERKOW REACTIONS

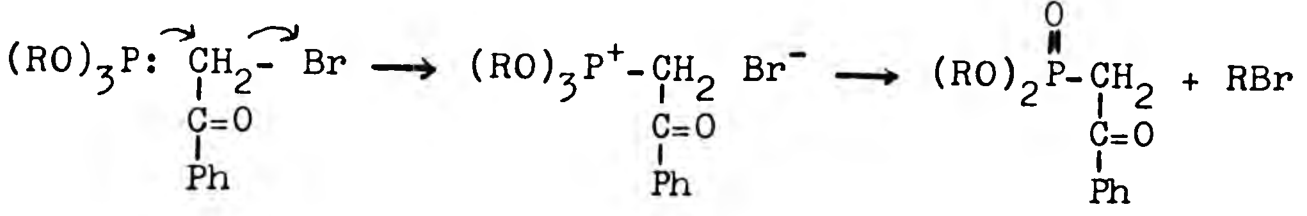
Trialkyl phosphites are known to react with α-halogenocarbonyl compounds to give two products the proportions of which depend on the nature of the halogen and the reaction conditions.[37] The usually accepted mechanisms for these reactions are as follows:

(1) Perkow Reaction



The essential characteristic of this reaction is the formation of a vinyloxyphosphonium intermediate which undergoes dealkylation to form the definitive vinyl phosphate.

(2) Arbuzov Reaction



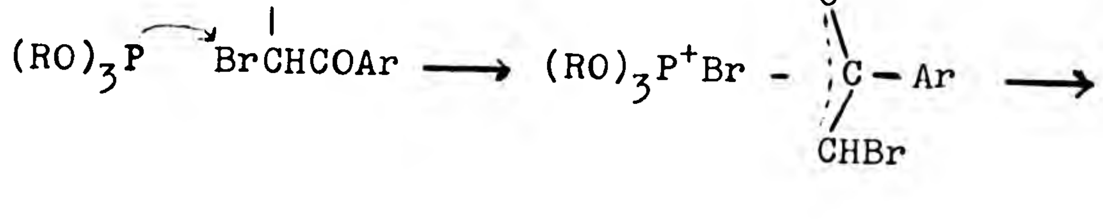
This reaction is characterised by the formation of a ketophosphonium intermediate which also undergoes dealkylation to form the phosphonate product.

The essential difference between the two reactions is the manner in which the initial attack of the phosphorus atom on the α-halogenoketone takes place.

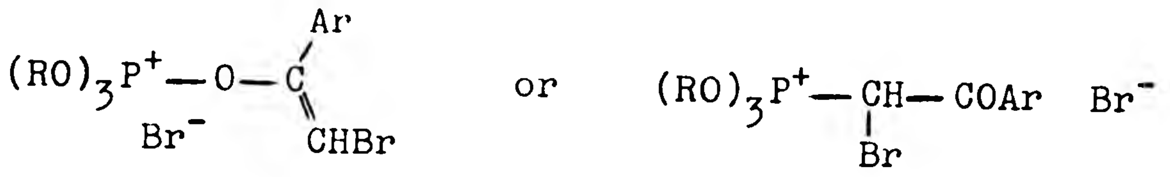
In the Perkow reaction electrons are donated by the phosphorus atom to the carbon atom of the carbonyl group to form a betaine which then undergoes rearrangement so that a halide ion is released with the formation of a vinyl group.

In the Arbuzov reaction, the electrons are initially donated to the α-CH_2 group and a halide ion is released directly.

In the both reactions a phosphonium intermediate is formed and this subsequently undergoes dealkylation to yield the corresponding products. Other modes of reaction may also be possible in certain circumstances, i.e. attack by phosphorus on the halogen atom to give a halophosphonium enolate which then rearranges to give either the ketophosphonium or vinyloxyphosphonium intermediate. A sequence of this type has been proposed in reactions involving α, α-dibromoketones and in those cases in which the carbonyl carbon atom is difficult to attack because of steric hindrance.[38,39]

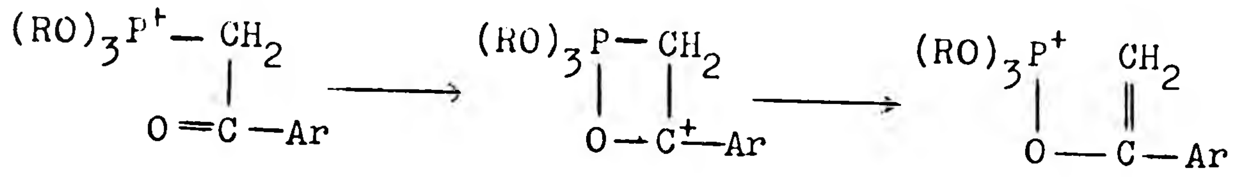


$$(RO)_3P \quad Br\overset{Br}{C}HCOAr \longrightarrow (RO)_3P^+Br^- \; \overset{O}{C}(-Ar)\underset{CHBr}{} \longrightarrow$$



$$(RO)_3P^+\!-\!O\!-\!C(Ar)\!=\!CHBr\ \ Br^- \quad \text{or} \quad (RO)_3P^+\!-\!CH(Br)\!-\!COAr\ \ Br^-$$

It has also been suggested that the vinoxyphosphonium intermediate could be formed from the ketophosphonium species by rearrangement via a four-membered cyclic phosphorane.[40]



The intermediates proposed have however been hypothetical species whose existence was inferred in all cases from kinetic or other studies.

CHAPTER II RESULTS AND DISCUSSION

INTRODUCTION

The work described in this thesis consists of the systematic study and investigation of two aspects of the reactions of phosphorus (III) esters with halogeno-compounds. The first concerns some aspects of the Michaelis-Arbuzov reaction of triaryl phosphites with alkyl halides and the second a study of stabilised intermediates obtained in the Arbuzov and Perkow reactions of neopentyl esters with α-halogeno-compounds and alkyl halides.

II.1 THE MICHAELIS-ARBUZOV REACTION OF TRIARYL PHOSPHITES

Two aspects in particular have been considered:

1. The mechanism of formation of aryl halides (ArX) and the possible formation of benzyne intermediates.

2. The disproportionation of triphenoxyphosphonium intermediates. Intermediates from the reactions of triphenyl phosphite with methyl iodide and methyl bromide were prepared by a described method,[15] as shown below:

$$(ArO)_3P + MeI/Br \longrightarrow (ArO)_3P^+MeI^-/Br^-$$

II.1.1 MECHANISM OF ARYL HALIDE FORMATION

The mechanism of dearylation and formation of ArX in the second stage of the Arbuzov reaction, where the phosphonium intermediate decomposes to ArX and phosphonate was investigated.

$$(ArO)_3P^+MeI^- \longrightarrow ArX + (ArO)_2P(O)Me$$

This process is most simply regarded as occurring <u>via</u> nucleophilic attack of halide ion. However, the formation of ArX by nucleophilic attack on the benzene ring by a halide anion in the absence of an activating group, i.e. NO_2 is unusual.

Electrophilic substitutions in the benzene ring[34] are promoted by OH, NR_2, or alkyl groups etc., which will direct incoming electrophiles predominantly to the ortho and para positions, whereas electron-attracting substituents i.e. NO_2, CN and COOEt direct the electrophiles to the meta position.

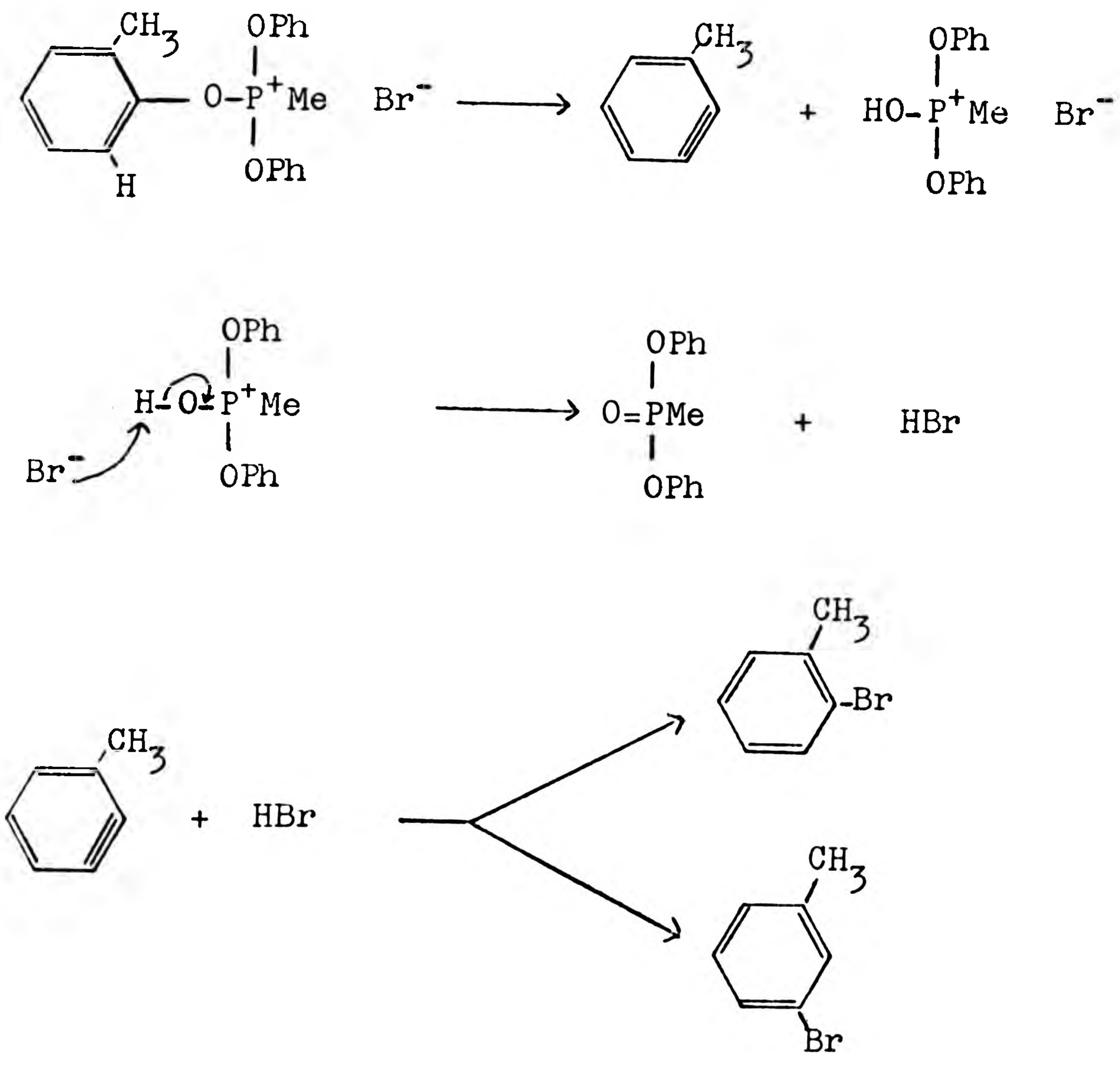
Nucleophilic substitutions[34] in aromatic rings occur more readily when the electron density in the aromatic system is diminished by the presence of one or more strongly electron-attracting groups - most often nitro groups.

Substitution in non-activated rings may occur at elevated temperatures but under these conditions a benzyne mechanism frequently contributes to the reaction pathway.

To investigate this possibility, methyltri-o-tolyloxyphosphonium bromide $(CH_3C_6H_4O)_3P^+MeBr^-$ was thermally decomposed at 200 °C. The products of decomposition were distilled under a high vacuum of 0.05 mmHg, and were collected in a cold trap at -80 °C. They were identified by ^1H n.m.r. spectroscopy and gas-liquid chromatography (g.l.c.).

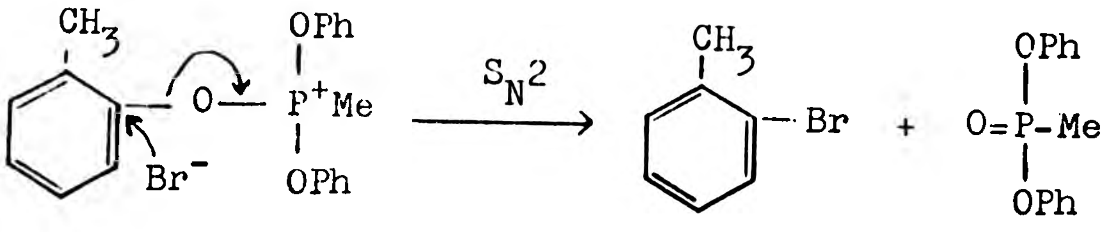
It was found that only o-tolyl bromide was present. No traces of either m- or p-tolyl bromide were detected, although the benzyne intermediate scheme predicts the formation of the ortho and meta isomers.

Mechanism of Benzyne Intermediates

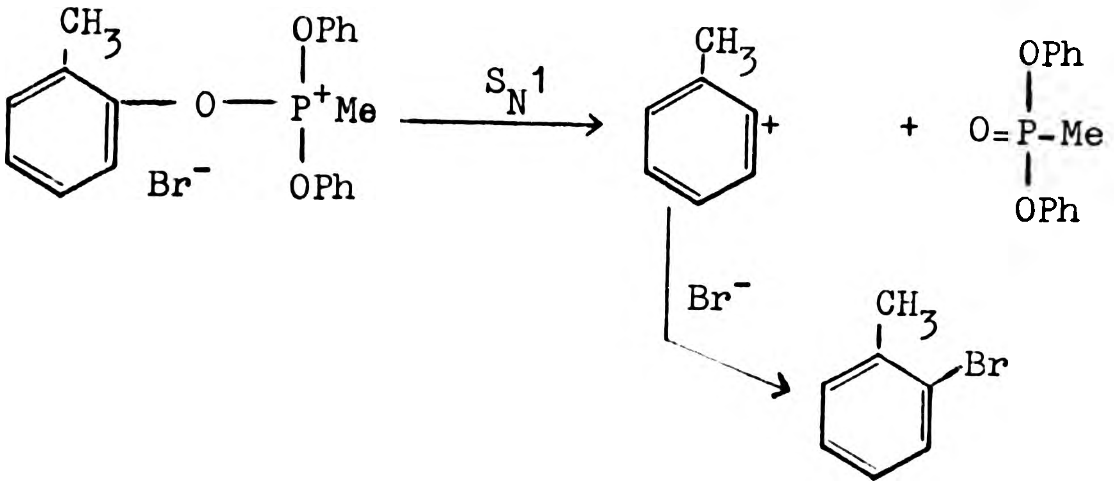


This means that the benzyne intermediate hypothesis must be rejected.

Two mechanisms for nucleophilic substitution remain, the bimolecular S_N2 Ar mechanism as follows in which the benzene ring is attacked by the nucleophilic Br^- ion to form bromobenzene and the stable phosphonate $(PhO)_2P(O)Me$:



and the unimolecular S_N1 Ar mechanism.



The latter is not common but can occur with a very good leaving group e.g. N_2 in the case of aryldiazonium salts.

$$Ph{-}N_2^+ \longrightarrow Ph^+ + N_2$$

It should be noted that the positively charged quarternary phosphorus atom is itself strongly electrophilic, so that it may cause withdrawal of electrons from the PhO-P bond, causing an inherent tendency for dearylation to the phosphonate.

II.1.2 DISPROPORTIONATION OF MICHAELIS-ARBUZOV INTERMEDIATES

The thermal decomposition of triaryl phosphite-alkyl halide adducts as described above is slow. Competitive processes can therefore occur and it has now been shown that disproportionation may be involved to a significant extent.

DISPROPORTIONATION is generally defined as a reaction in which a single substance undergoes change to produce products, one of which is in a higher oxidation state and the other in a lower oxidation state. The term is also frequently used to describe the redistribution of ligands attached to a particular atom.

It can happen that a substance is unstable because it readily disproportionates, or in other case the single substance reacts as both oxidant and reductant, i.e. part of it is reduced and part is oxidised in the process. A familiar example is decomposition of hydrogen peroxide which can be written as: $H_2O_2 \longrightarrow 2H_2O + O_2$.

Examples from the field of phosphorus chemistry are as follows:

1) Primary phosphine oxides disproportionate[29] at about room temperature to primary phosphines and the corresponding phosphinic acids:

$$2RP(O)H_2 \longrightarrow RPH_2 + RPH(O)OH$$

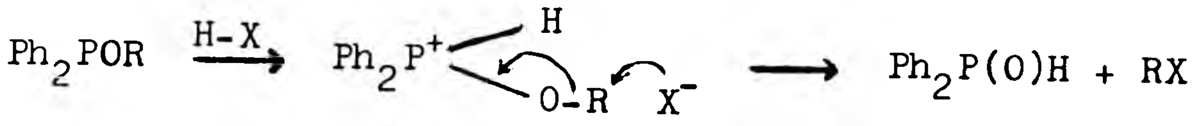
2) The phosphinic acid RPH(O)OH also undergoes a characteristic redox[29] reaction when heated alone to about 150 °C, one mole of primary phosphine being formed for every 2 moles of phosphonic acid:

$$3RPH(O)OH \longrightarrow RPH_2 + 2RP(O)(OH)_2$$

3) Phenyldichlorophosphine disproportionates on heating into diphenylchlorophosphine and phosphorous trichloride:[30]

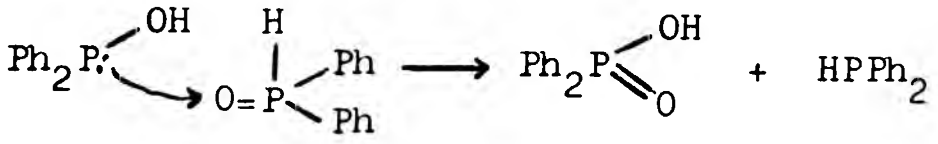
$$2PhPCl_2 \xrightarrow{300\ ^{\circ}C} Ph_2PCl + PCl_3$$

4) From the reactions of hydrogen halides with alkyl diphenylphosphinites the expected phosphorus containing product $Ph_2P(O)H$ is not isolated as such but yields the disproportionation products, diphenylphosphine and diphenylphosphinic acid:[31]



$$2Ph_2P(O)H \longrightarrow Ph_2PH + Ph_2P(O)(OH)$$

In the above example disproportionation probably could be written, as below:



Examples of disproportionation involving phosphonium intermediates have been described in detail by H.N. Rydon in 1956[28] in which the exchange of ArO and X anions in the triaryl phosphite dihalides leads to complex types of salt (see Introduction).

The rapid exchange of ArO anions has also been shown to account for the disproportionation of aryloxyphosphoranes in ionising media such as CH_3CN.[36]

The only reported example of disproportionation involving the restribution of methyl groups on phosphorus is that which occurs during the pyrolytic decomposition of the methyl iodide adducts of diphenyl phenylphosphonite and phenyl diphenylphosphinite at temperatures in excess of 200 °C.[24]

These quasiphosphonium salts are unusually stable to heat and resist the normal Arbuzov cleavage. Exchange of methyl and phenoxy groups is seen to have occurred in the products (see Introduction), although the stage at which exchange occurs is not clear. The unexpected formation of dimethyldiphenoxyphosphonium bromide during the heating of triphenyl phosphite with an excess of methyl bromide appears to be due to a related process,[15] although it has not been investigated further. The effect of heat on methyltriphenoxyphosphonium bromide, previously thought to decompose directly to bromobenzene and diphenyl methanephosphonate, has therefore been re-examined.

The investigations carried out concentrated on the following five main aspects:

1. Thermal decomposition (in the absence of solvent) of methyltriphenoxyphosphonium halides to dimethyldiphenoxyphosphonium halides and higher order products.

2. Thermal disproportionation (in the absence of solvent) of isolated dimethyldiphenoxyphosphonium bromide to trimethylphenoxyphosphonium bromide.

3. Attempted deoxygenation of phosphonate by triphenyl phosphite.

4. Thermal decomposition (in $CDCl_3$) of methyltriphenoxy-

phosphonium halides and the detection and isolation of a new intermediate containing a P-O-P linkage.

5. Hydrolysis of disproportionation products.

1. Thermal decomposition (in the absence of solvent) of methyltriphenoxyphosphonium halides.

In the first experiment the crystalline intermediate methyltriphenoxyphosphonium bromide was heated without solvent in a sealed ^{1}H n.m.r. tube at 175 °C. After heating for 86.5 hours a stable clear liquid was formed, which after cooling did not crystallise immediately but remained as a clear, viscous mass. The ^{1}H n.m.r. (neat) spectrum at this stage (Fig. 1) showed the phosphonium bromide $(PhO)_3P^+MeBr^-$, (41.6%), the phosphonate $(PhO)_2P(O)Me$, (30.0%) and phenoxy protons.

There was also an additional signal at δ 3.23 (Me doublet) J_{PCH} 15.6 Hz, assigned to $(PhO)_2P^+Me_2Br^-$ (28.3%), as a product of disproportionation.

Similar results were obtained after heating for 96 hours at 175 °C. The ^{1}H n.m.r. spectrum of an approximately 10% solution in deuterochloroform (Fig. 2) showed all signals as in the previous experiment, but with slightly different chemical shifts in the solvent, as shown in Table I.

Confirmation of the disproportionation and that a new carbon bond was formed in a product with two methyl groups attached to the phosphorous atom was obtained from the ^{31}P n.m.r. spectrum which showed a singlet at δ -17.58 ppm due to triphenyl phosphate, $(PhO)_3PO$, a quartet at δ +24.07 ppm, due to phosphonate, and quartet at δ +41.8 ppm, due to

Fig. 1

^{1}H n.m.r. (Neat) spectrum of disproportionation products from $(PhO)_3P^+MeBr^-$ at 175 °C (86.5 h) in the absence of solvent.

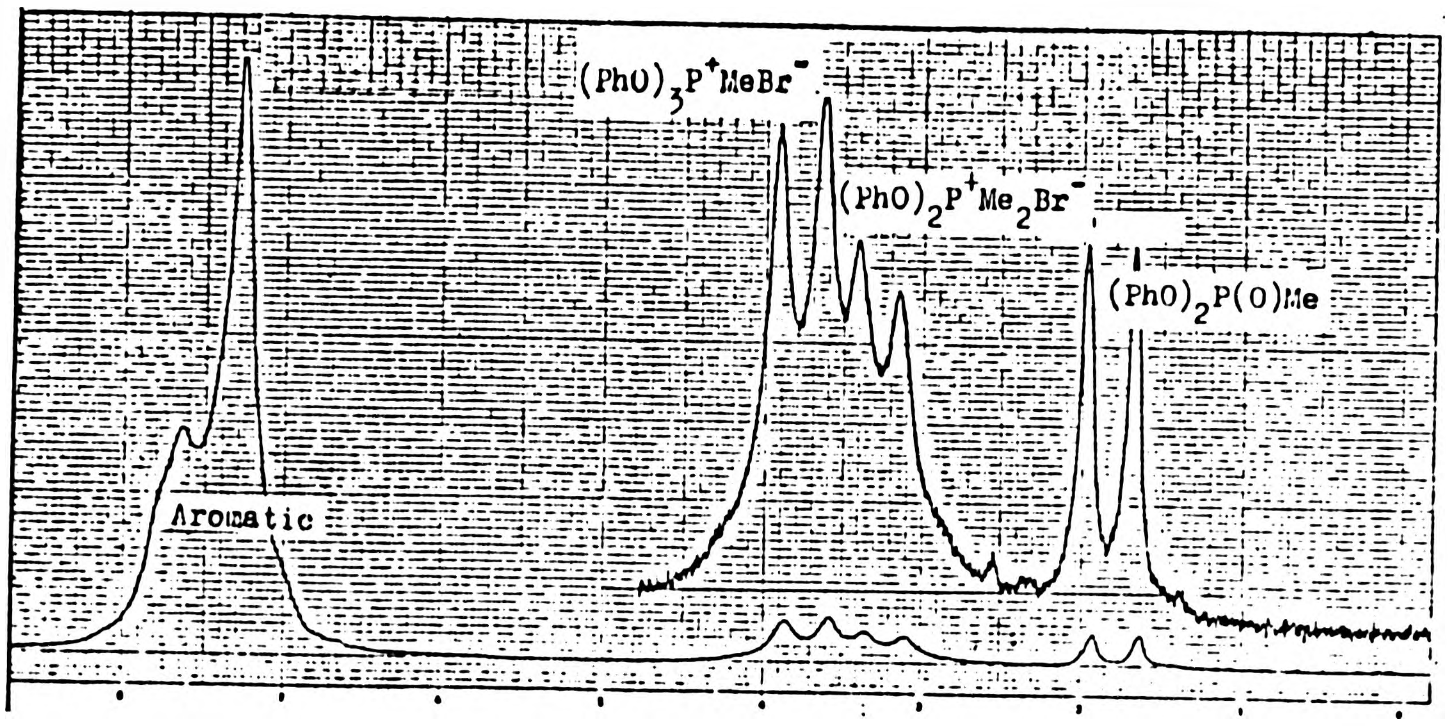
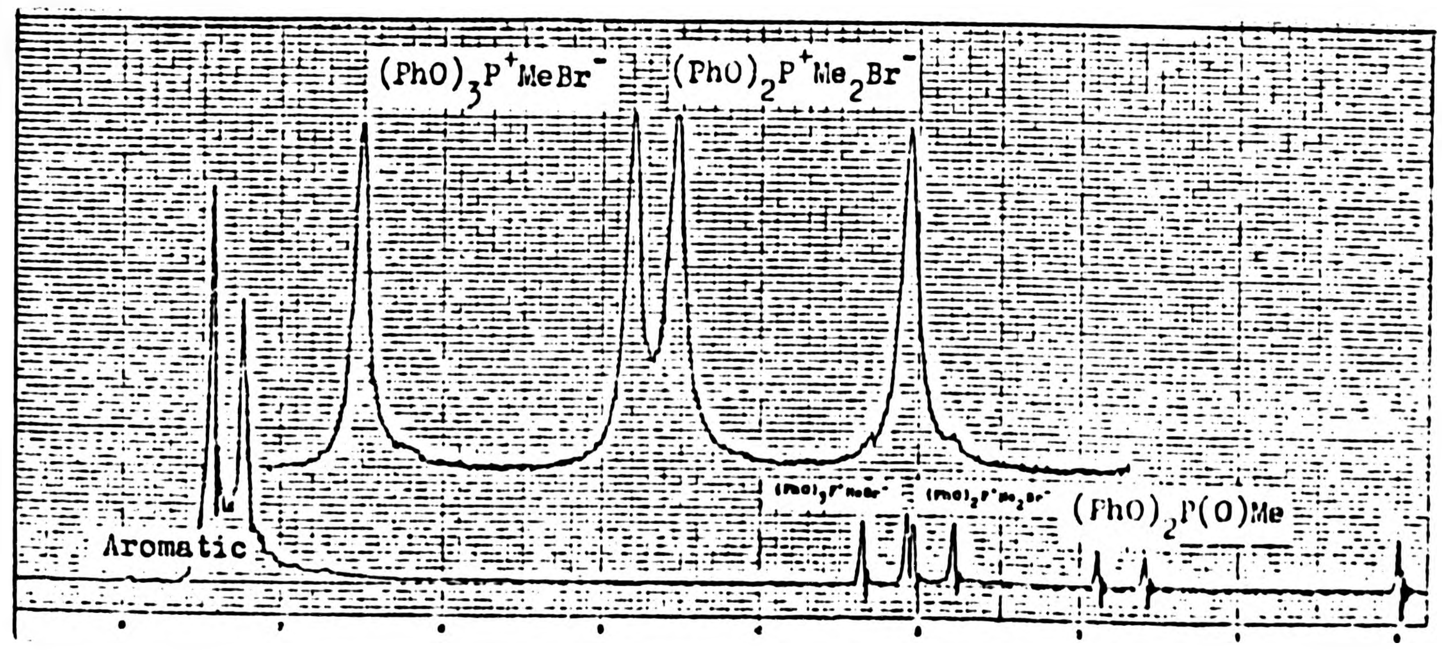


Fig. 2

^{1}H n.m.r. ($CDCl_3$) spectrum of disproportionation products from $(PhO)_3P^+MeBr^-$ at 175 °C (96 h) in the absence of solvent.



unreacted methyltriphenoxyphosphonium bromide. A septet at δ +96.17 ppm confirmed the presence of dimethyldiphenoxyphosphonium bromide, and a small signal at δ +33.98, probably due to a P-O-P component (see later), was also observed.

Overall, a sequence of the following type appears to occur.

$$(PhO)_3P^+MeBr^- \longrightarrow (PhO)_2P(O)Me + PhBr$$

$$2(PhO)_3P^+MeBr^- \longrightarrow (PhO)_2P^+Me_2Br^- + (PhO)_4P^+Br^-$$

$$(PhO)_4P^+Br^- \longrightarrow (PhO)_3PO + PhBr$$

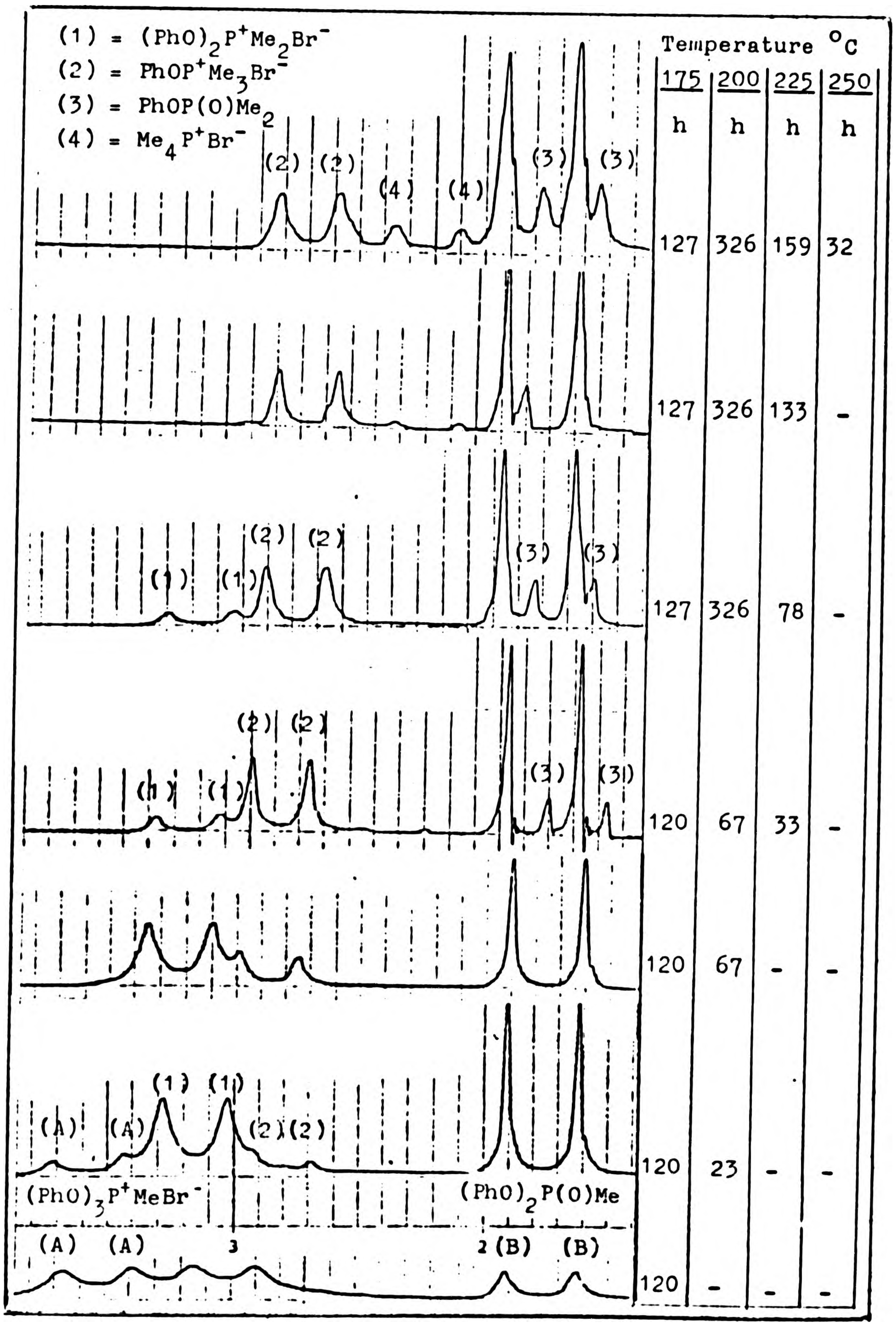
It now also seems likely that an unidentified ^{31}P n.m.r. peak (δ -25 ppm), recorded previously during the heating of triphenyl phosphite with certain alkyl halides,[15] was due to the tetraphenoxyphosphonium ion,[56] formed in this way.

A further investigation of the disproportionation was carried out to study the effect of prolonged heating at higher temperatures up to 250 °C.

The ^{1}H n.m.r. spectra were recorded at different intervals of time (without $CDCl_3$ in this case) and are shown in Fig. 3. It can be seen that the methyltriphenoxyphosphonium bromide signals (A) disappeared after heating at 200 °C for 67 hours. Confirmation of the identity of the various products of disproportionation and decomposition was then obtained by ^{31}P n.m.r. in $CDCl_3$ which showed triphenyl phosphate at δ -17.6 (s), diphenyl methanephosphonate δ 23.9 (quartet), dimethyldiphenoxyphosphonium

Fig. 3

^1H n.m.r. spectra (without solvent) of disproportionation of methyltriphenoxyphosphonium bromide.

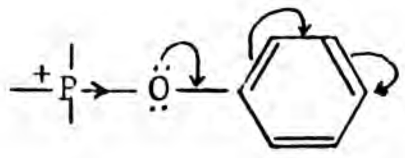


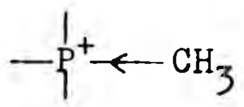
Temperature °C			
175	200	225	250
h	h	h	h
127	326	159	32
127	326	133	-
127	326	78	-
120	67	33	-
120	67	-	-
120	23	-	-
120	-	-	-

bromide δ 96 (septet), and trimethylphenoxyphosphonium bromide δ 102.4 (multiplet).

Further heating then caused an increase in trimethylphenoxyphosphonium bromide (2), and also the formation of additional products at 225-250 °C labelled (3) and (4), which were considered to be tetramethylphosphonium bromide $Me_4P^+Br^-$, and the phosphinate, $PhOP(O)Me_2$, formed by Arbuzov cleavage of the salt (1).

These three salts are clearly much more thermally stable than methyltriphenoxyphosphonium bromide, a fact which can be attributed to the replacement of electron-attracting phenoxy groups by electron-releasing methyl groups.



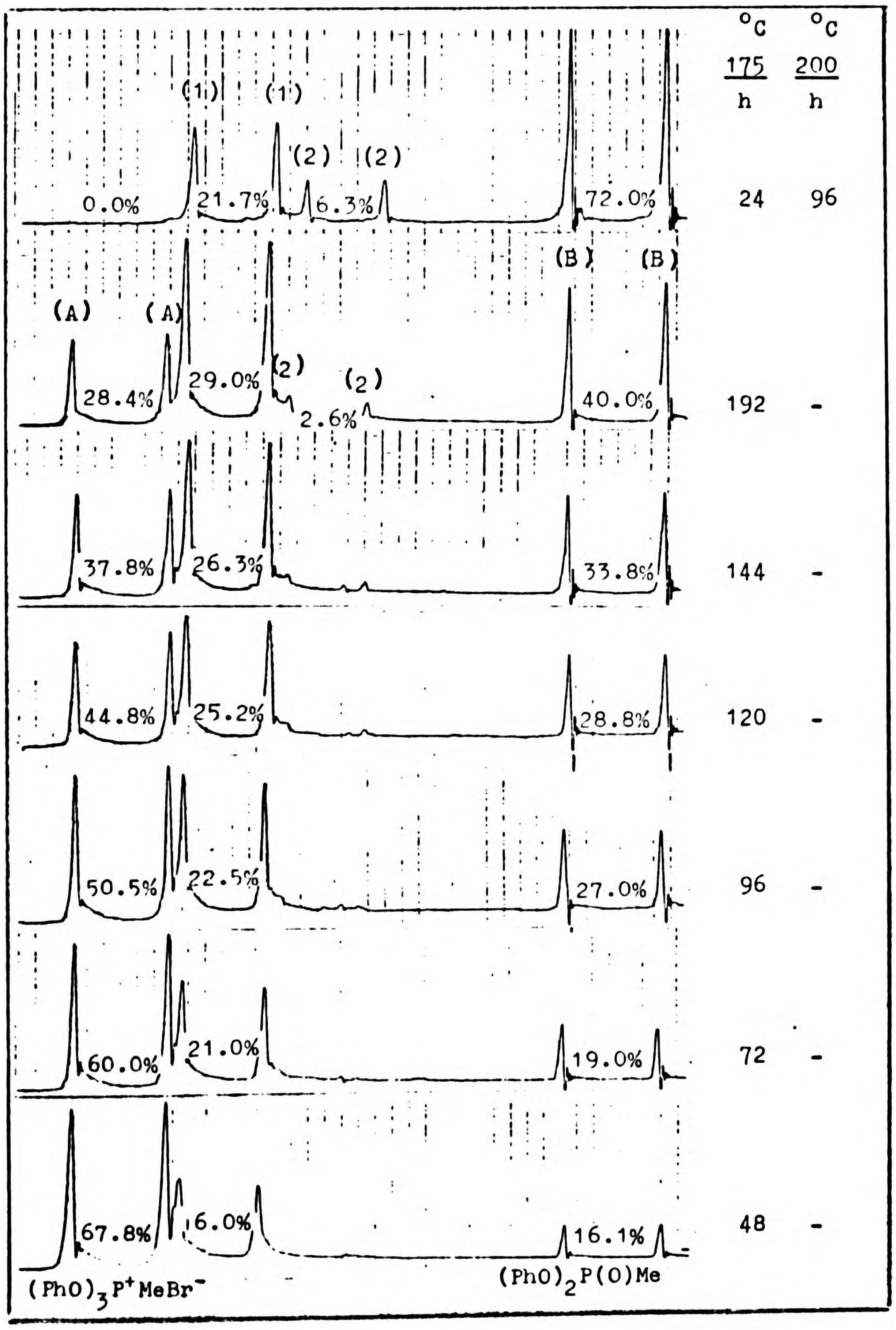


To follow the course of reaction in more detail some ^1H n.m.r. tubes were sealed with $(PhO)_3P^+MeBr^-$, and then heated at 175 °C from 2 to 8 days, and one for an additional period at 200 °C (24 hours at 175 °C and 96 hours at 200 °C). Each tube was opened in a N_2 atmosphere, deuterochloroform was added, and the ^1H n.m.r. spectra recorded.

The collected ^1H n.m.r. spectra (Fig. 4) show a picture of reaction in which the proportion of the phosphonium salt, $(PhO)_3P^+MeBr^-$ (A), fell to 67.8% after two days of heating and gradually, after 8 days, to 28.4%, whilst the disproportionation product, $(PhO)_2P^+Me_2Br^-$ (1), and the phosphonate $(PhO)_2P(O)Me$ (B), correspondingly increased

Fig. 4

^{1}H n.m.r. spectra ($CDCl_3$) of thermal decomposition without solvent of methyltriphenoxyphosphonium bromide (A), to dimethyldiphenoxyphosphonium bromide (1), to trimethylphenoxyphosphonium bromide (2) and to diphenyl methanephosphonate (B).



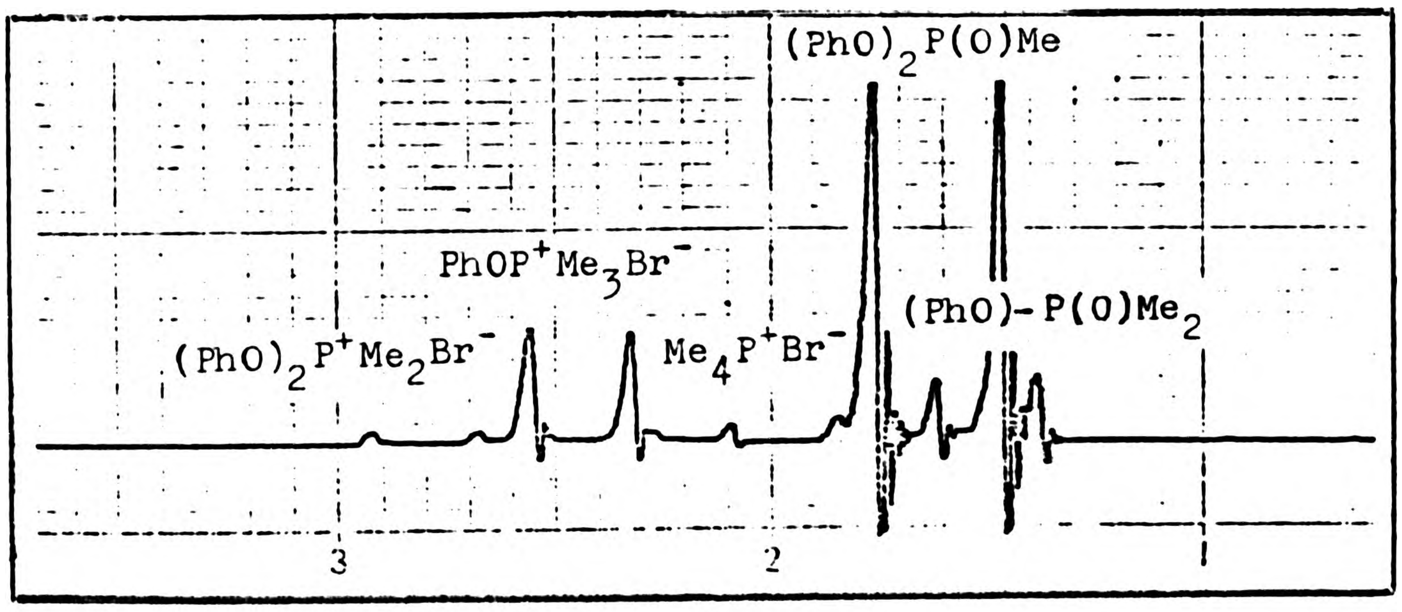
in concentration. The collected results of the above experiments are shown in Table I.

It can also be seen that after five days of heating a further disproportionation product, trimethylphenoxyphosphonium bromide, $PhOP^{+}Me_3Br^{-}$ (2), began to appear. This product reached a level of 6.3% by the time the original phosphonium salt had completely decomposed (one day at 175 °C and four days at 200 °C). The composition at this stage was as follows:

$(PhO)_3P^{+}MeBr^{-}$	$(PhO)_2P^{+}Me_2Br^{-}$	$PhOP^{+}Me_3Br^{-}$	$(PhO)_2P(O)Me$
0 %	21.7%	6.3%	72.0%

It can also be seen (Fig. 5) that methyltriphenoxyphosphonium bromide heated (without solvent) at a higher temperature up to 260 °C for 36 hours disproportionated to three phosphonium intermediates: dimethyldiphenoxyphosphonium

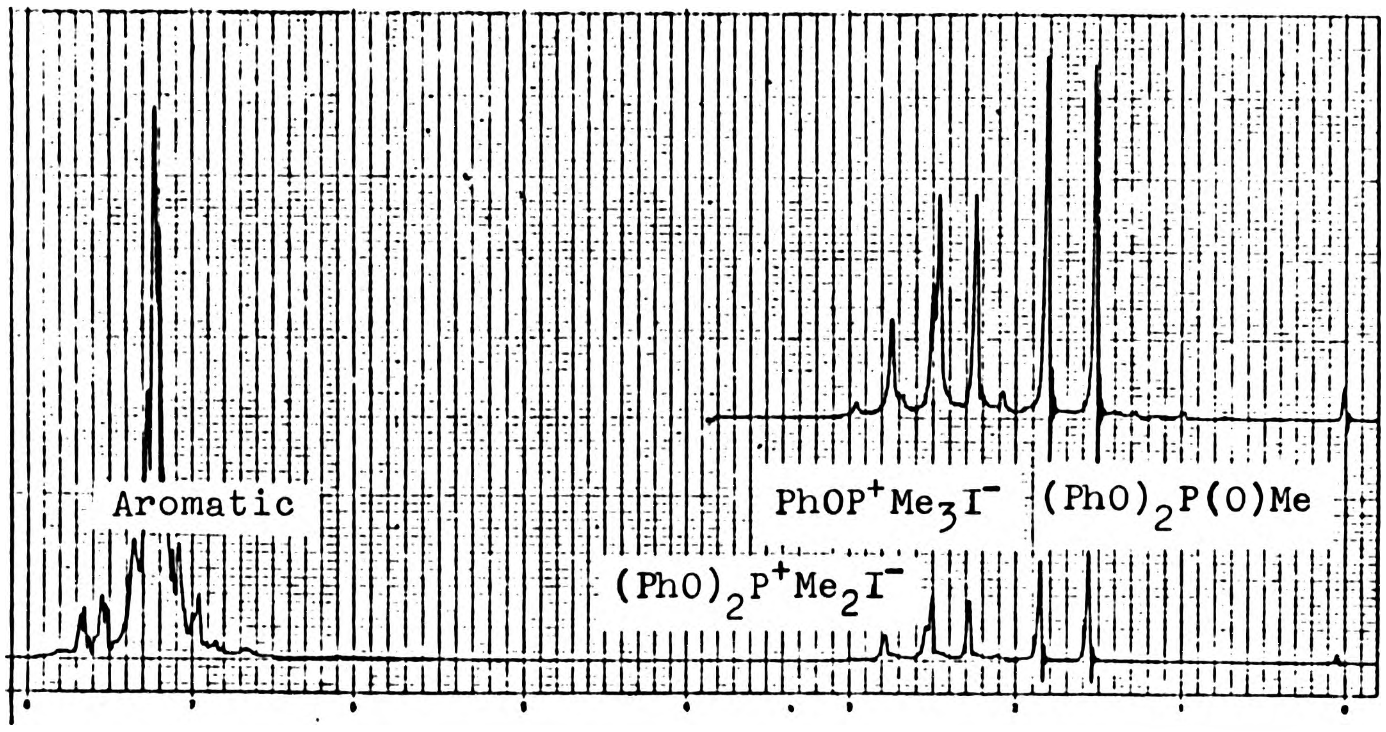
Disproportionation of $(PhO)_3P^{+}MeBr^{-}$ at 260 °C (Fig. 5)



bromide $(PhO)_2P^+Me_2Br^-$ (1.3%), trimethylphenoxyphosphonium bromide $PhOP^+Me_3Br^-$ (6.7%), and tetramethylphosphonium bromide $Me_4P^+Br^-$ (1.4%), and to two phosphonates: diphenyl methanephosphonate $(PhO)_2P(O)Me$ (85%) and phenyl dimethylphosphinate $PhOP(O)Me_2$ (6.0%) (see Table I).

Methyltriphenoxyphosphonium iodide similarly disproportionated to dimethyldiphenoxyphosphonium iodide (11.3%), and to trimethylphenoxyphosphonium iodide (14.8%) (Fig. 6), whilst undecomposed methyltriphenoxyphosphonium iodide (3.9%) remained (Table II).

^{1}H n.m.r. spectrum in $CDCl_3$ of methyltriphenoxyphosphonium iodide after the solid had been heated at 210 °C for two days. It had decomposed completely to dimethyldiphenoxyphosphonium iodide, some of which had decomposed to trimethylphenoxyphosphonium iodide. (Fig. 6)



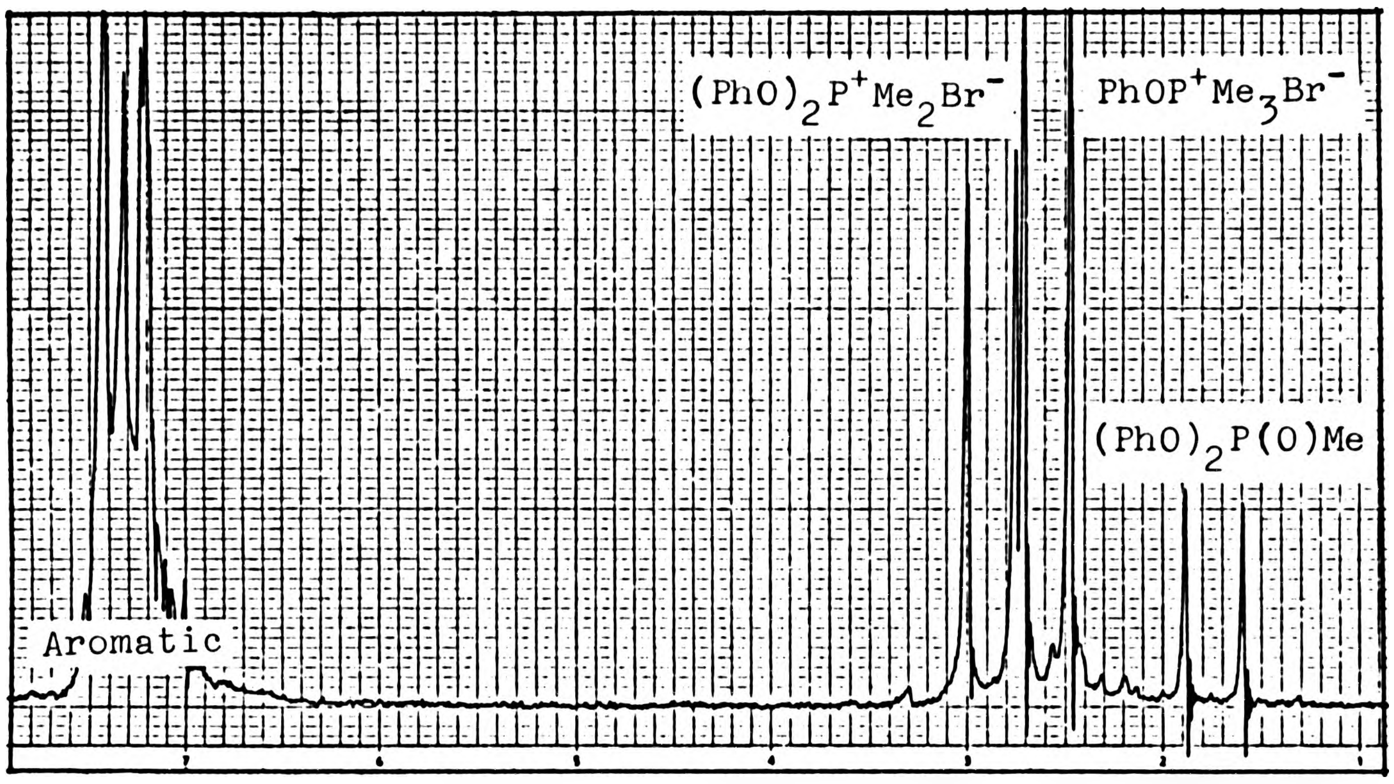
Methyltri-o-tolyloxyphosphonium bromide heated at 200 °C in absence of solvent for 38.5 hours showed disproportionation to dimethyldi-o-tolyloxyphosphonium bromide and to trimethyl-o-tolyloxyphosphonium bromide the results being confirmed by ^{31}P n.m.r. and in some cases by ^{13}C n.m.r. spectra for hydrolysed products (Table III).

2. Thermal disproportionation (in the absence of solvent) of dimethyldiphenoxyphosphonium bromide

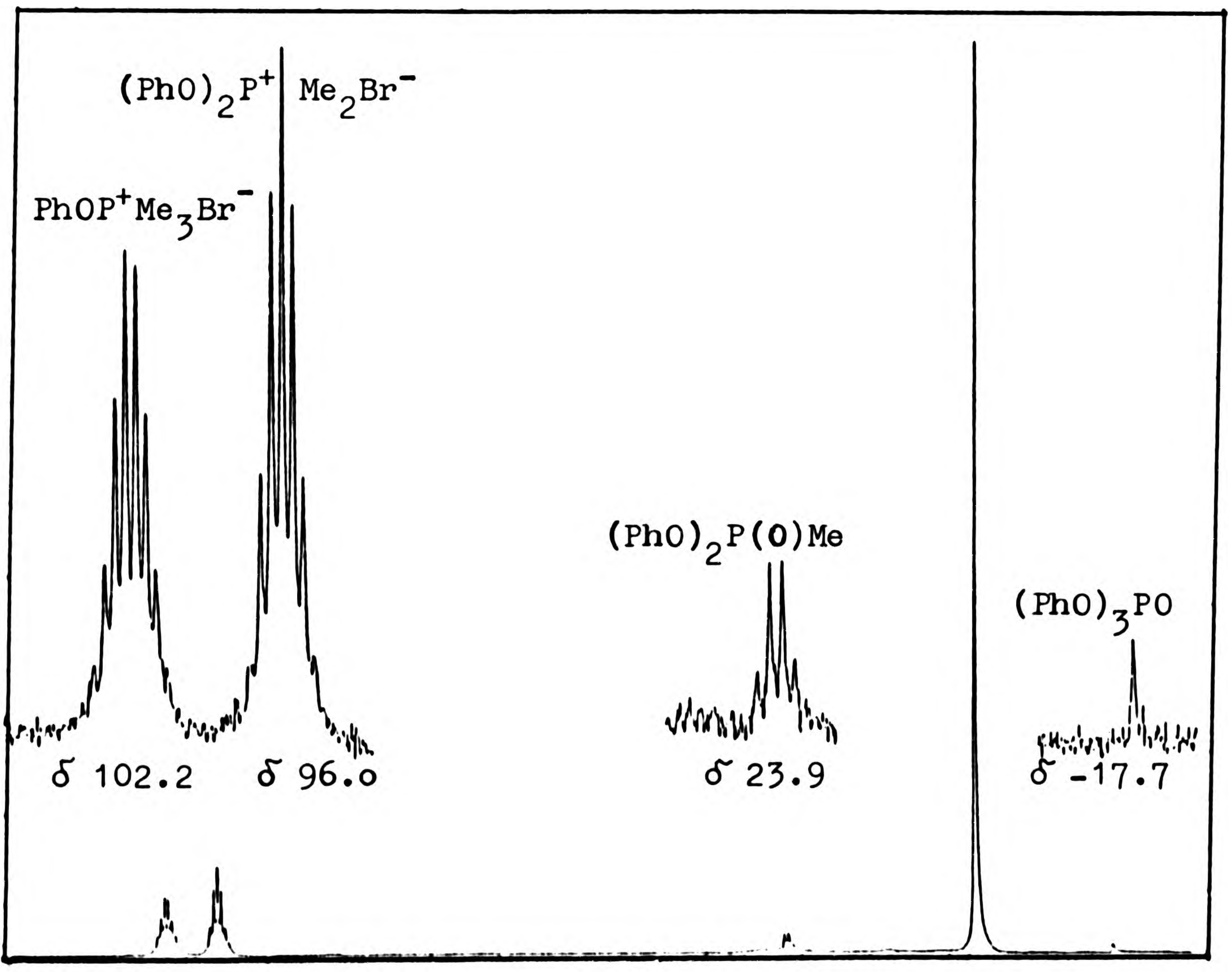
In order to gain further information on the disproportionation reactions the first disproportionation product, dimethyldiphenoxyphosphonium bromide, which had been isolated previously as a crystalline solid was heated in a sealed ^{1}H n.m.r. tube at its melting point (210 °C) for 190 hours. The ^{1}H n.m.r. spectrum (Fig. 7) in deuterochloroform then showed signals of the starting material, dimethyldiphenoxyphosphonium bromide (36.5%), of trimethylphenoxyphosphonium bromide (35.3%) as a product of disproportionation, and diphenyl methanephosphonate (28.2%). The ^{31}P n.m.r. spectrum (Fig. 8) in deuterochloroform showed signals at δ -17.7 due to triphenyl phosphate, δ 23.9 (quartet) due to diphenyl methylphosphonate, δ 96.0 (septet) due to unreacted dimethyldiphenoxyphosphonium bromide and δ 102.2 (decet) due to trimethylphenoxyphosphonium bromide. A very weak signal at 125.1 was probably due to triphenyl phosphite, formed by dissociation of the triphenyl phosphite complex.

The most interesting observation is that none of the expected Arbuzov product which would be derived directly from the starting material was obtained, but only those, i.e. $(PhO)_3PO$, and $(PhO)_2P(O)Me$, which would be obtained after disproportionation to yield phosphonium ions containing three of four phenoxy groups. The other disproportio-

^{1}H n.m.r. (CDCl$_3$) spectrum of disproportionation products from (PhO)$_2$P$^+$Me$_2$Br$^-$ at 210 °C. (Fig. 7)



^{31}P n.m.r. (CDCl$_3$) spectrum of disproportionation products from (PhO$_2$P$^+$Me$_2$Br$^-$ at 210 °C. (Fig. 8)



nation product, $PhOP^+Me_3Br^-$, did not undergo decomposition under the conditions of the experiment.

A similar experiment in which dimethyldiphenoxyphosphonium bromide was strongly heated up to 290 °C for 46 hours showed further disproportionation to trimethylphenoxyphosphonium bromide (24.0%), and to tetramethylphosphonium bromide ($Me_4P^+Br^-$) (12.5%), δ 2.12 (Me, d, J_{PCH} 14.7 Hz), and also gave the Arbuzov products diphenyl methanephosphonate (48.5%), and phenyl dimethylphosphinate $PhOP(O)Me_2$ (14.9%), δ 1.78 (Me, d, J_{PCH} 14.4 Hz) (Fig. 9). The ^{31}P n.m.r. spectrum confirmed the products of disproportionation with signals at δ 23.9 (quartet) due to $(PhO)_2P(O)Me$, 22.6 (small) due to $Me_4P^+Br^-$, 60.3 (multiplet) due to $PhOP(O)Me_2$, and 101.9 (multiplet) due to $PhOP^+Me_3Br^-$, whilst the ^{13}C n.m.r. spectra showed doublets for methyl group attached to phosphorus as follows.

Compounds	δ_C	J_{PC} (Hz)
$PhOP^+Me_3Br^-$	13.3	64.6
$Me_4P^+Br^-$	10.6	55.5
$(PhO)_2P(O)Me$	11.5	144.7

From the disproportionation products of dimethyldiphenoxyphosphonium bromide, two components were separated, which the ^1H n.m.r. spectrum (DMSO) showed to be tetramethylphosphonium bromide, and trimethylphosphine oxide (Fig. 10).

Fig. 9

^{1}H n.m.r. spectrum in $CDCl_3$ of thermal decomposition of $(PhO)_2P^+Me_2Br^-$ at 190-290 °C

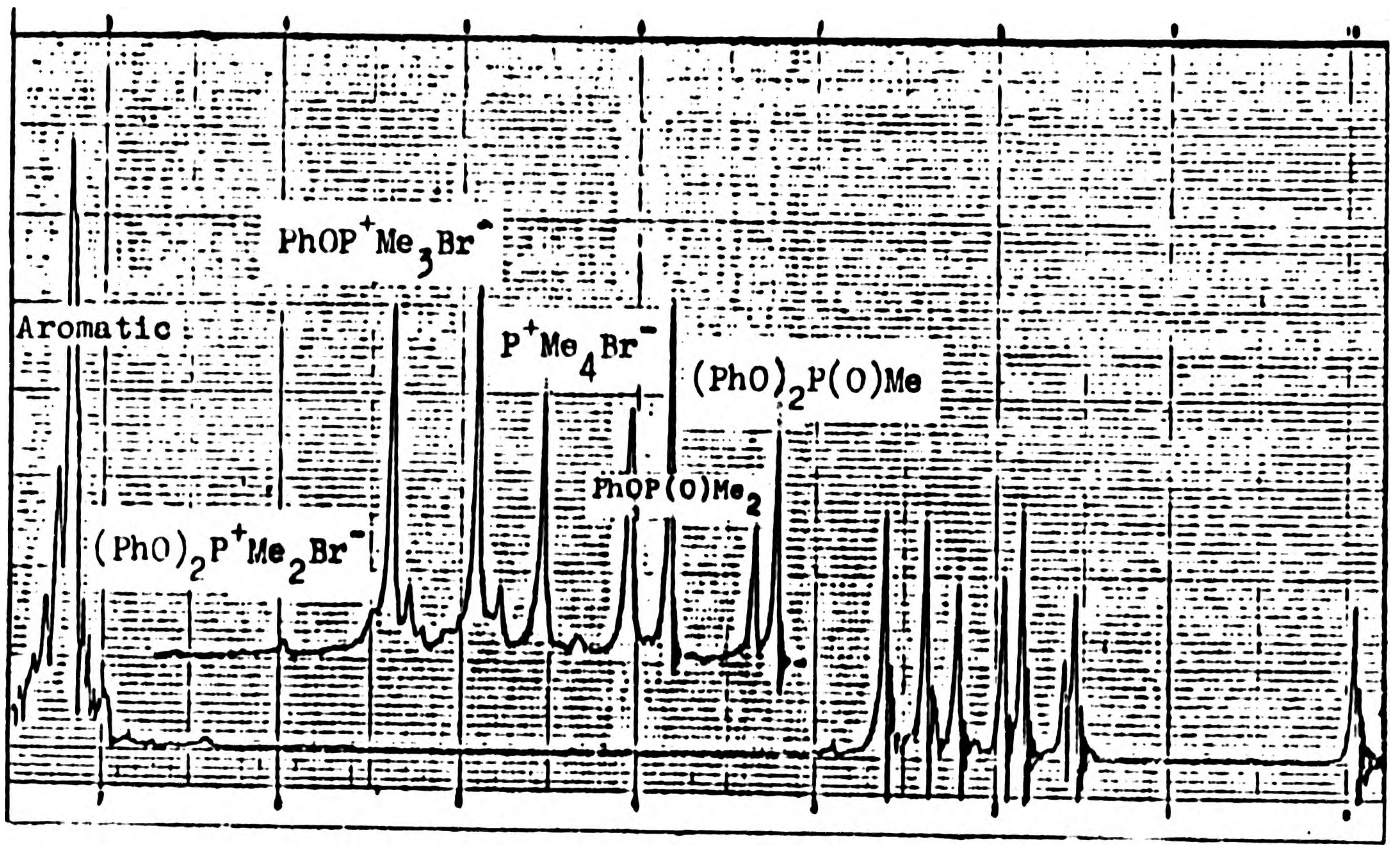
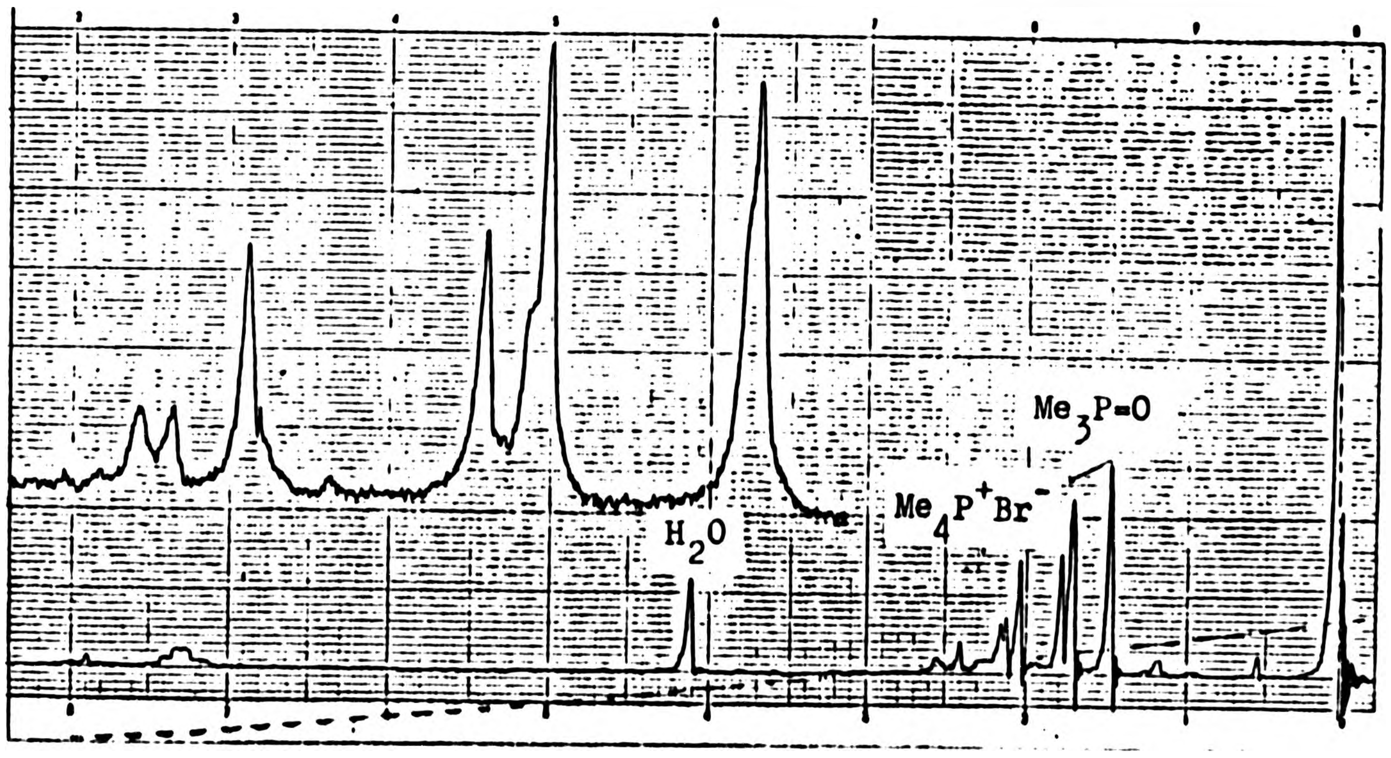


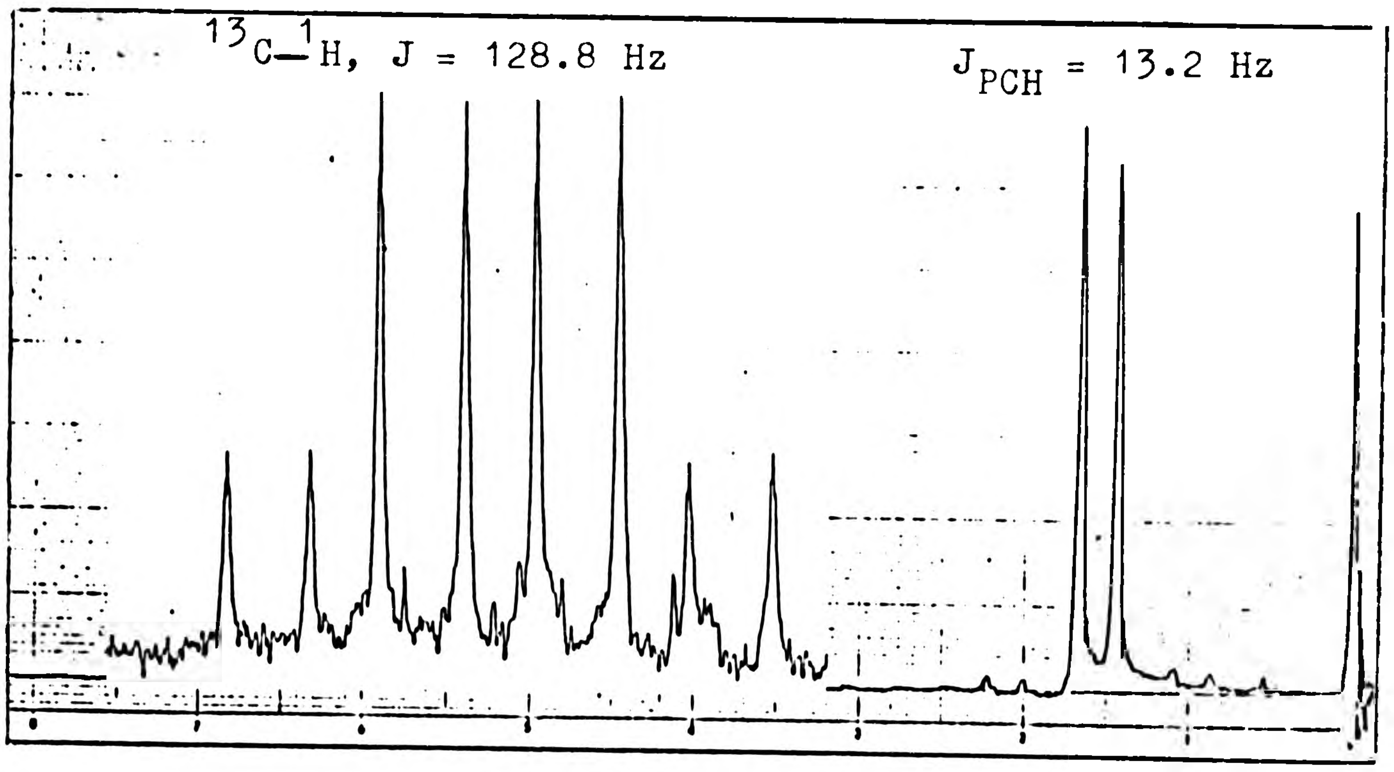
Fig. 10

^{1}H n.m.r. spectrum in DMSO of $Me_4P^+Br^-$ and Me_3PO separated from reaction mixture



Trimethylphosphine oxide was also obtained by hydrolysis of trimethylphenoxyphosphonium bromide and trimethylphenoxyphosphonium iodide, and was identified by its characteristic $^{13}C-^{1}H$ coupling constant, 128.8 (D_2O) (Lit.[43] 129.0 in D_2O), and its ^{1}H n.m.r. spectrum in DMSO (δ 1.50, J_{PCH} 13.2 Hz) (Lit.[42] δ_H 1.39, J_{PCH} 13.2 Hz), (see Fig. 11).

^{1}H n.m.r. (DMSO) and $^{13}C-^{1}H$ (D_2O) spectra of isolated trimethylphosphine oxide (Fig. 11).



Conclusions

The systematic investigation of the disproportionation of methyltriphenoxyphosphonium bromide described above confirmed that this compound gives dimethyldiphenoxyphosphonium bromide $(PhO)_2P^+Me_2Br^-$, when heated at high temperature in a sealed tube.

A similar result was also obtained with the methyltriphenoxyphosphonium iodide, as shown:

$$2(PhO)_3P^+MeBr^- \longrightarrow (PhO)_2P^+Me_2Br^- + (PhO)_4P^+Br^-$$

$$2(PhO)_3P^+MeI^- \longrightarrow (PhO)_2P^+Me_2I^- + (PhO)_4P^+I^-$$

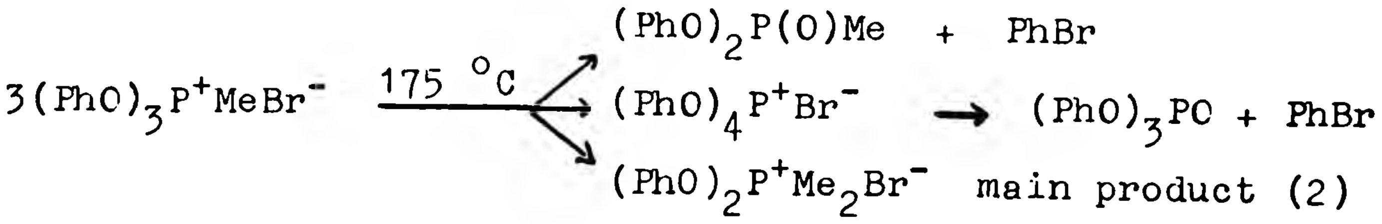
In this way the two phosphonium intermediates $(PhO)_2P^+Me_2Br^-$ and $(PhO)_2P^+Me_2I^-$ were isolated as pure crystalline solids. It was also found that the dimethyldiphenoxyphosphonium halides disproportionated to give the trimethylphenoxyphosphonium salts on strong heating, both the bromide and the iodide being isolated in small amounts as crystalline solids from their reaction mixtures.

$$2(PhO)_2P^+Me_2Br^- \longrightarrow PhOP^+Me_3Br^- + (PhO)_3P^+MeBr^-$$

$$2(PhO)_2P^+Me_2I^- \longrightarrow PhOP^+Me_3I^- + (PhO)_3P^+MeI^-$$

Therefore the overall reactions of disproportionation which are proposed are as in the equations below:

$$(PhO)_3P^+MeBr^- \xrightarrow{175\ ^{o}C} (PhO)_2P^+Me_2Br^- \quad \text{main product} \quad (2)$$



$$3(PhO)_3P^+MeBr^- \xrightarrow{175\ ^{o}C} \begin{cases} (PhO)_2P(O)Me + PhBr \\ (PhO)_4P^+Br^- \longrightarrow (PhO)_3PO + PhBr \\ (PhO)_2P^+Me_2Br^- \quad \text{main product} \quad (2) \end{cases}$$

$$(PhO)_2P^+Me_2Br^- \xrightarrow{210\ ^{o}C} (PhO)P^+Me_3Br^- \quad \text{main product} \quad (3)$$

phenoxyphosphonium iodide, as shown:

$$2(PhO)_3P^+MeBr^- \longrightarrow (PhO)_2P^+Me_2Br^- + (PhO)_4P^+Br^-$$

$$2(PhO)_3P^+MeI^- \longrightarrow (PhO)_2P^+Me_2I^- + (PhO)_4P^+I^-$$

In this way the two phosphonium intermediates $(PhO)_2P^+Me_2Br^-$ and $(PhO)_2P^+Me_2I^-$ were isolated as pure crystalline solids. It was also found that the dimethyldiphenoxyphosphonium halides disproportionated to give the trimethylphenoxyphosphonium salts on strong heating, both the bromide and the iodide being isolated in small amounts as crystalline solids from their reaction mixtures.

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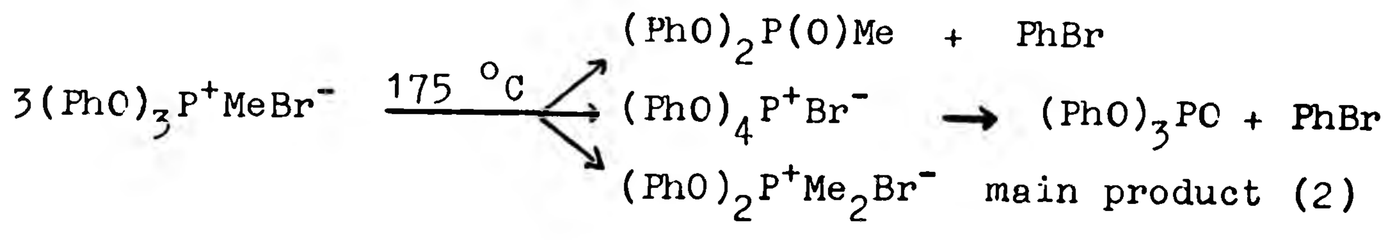


$$3(PhO)_3P^+MeBr^- \xrightarrow{175\ ^\circ C} \begin{cases} (PhO)_2P(O)Me + PhBr \\ (PhO)_4P^+Br^- \longrightarrow (PhO)_3PO + PhBr \\ (PhO)_2P^+Me_2Br^- \quad \text{main product (2)} \end{cases}$$

$$(PhO)_2P^+Me_2Br^- \xrightarrow{210\ ^\circ C} (PhO)P^+Me_3Br^- \quad \text{main product (3)}$$

$$\begin{tikzcd}[column sep=small] & 2(PhO)P^+Me_3Br^- & \text{main product (3)} \\ 4(PhO)_2P^+Me_2Br^- \arrow[ur] \arrow[dr] & & \\ & 2(PhO)_3P^+MeBr^- \arrow[r, "\text{partly}"'] & (PhO)_2P(O)Me \end{tikzcd}$$

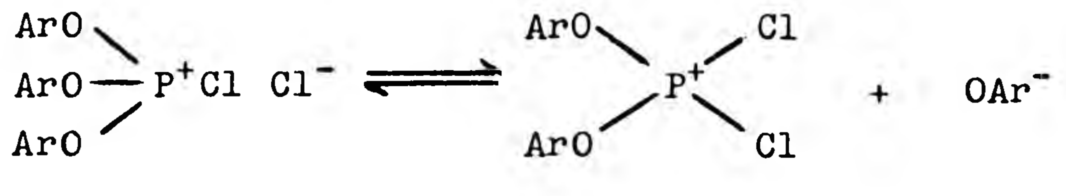
$$\begin{tikzcd}[column sep=small] & (PhO)_4P^+Br^- \arrow[r] & (PhO)_3PO + PhBr \\ 2(PhO)_3P^+MeBr^- \arrow[ur] \arrow[dr] & & \\ & (PhO)_2P^+Me_2Br^- \quad \ldots & \text{involved in further reaction} \end{tikzcd}$$

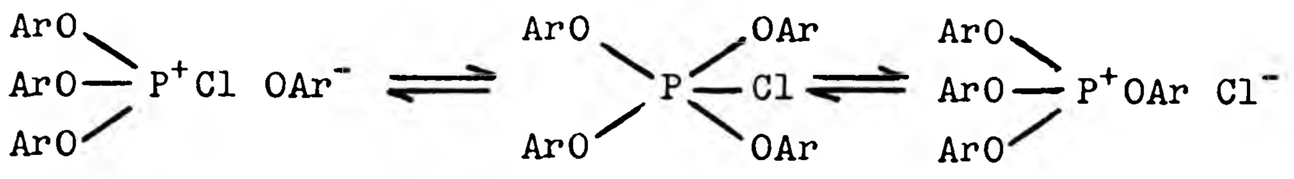
All the above products of decomposition were identified and determined by ^{31}P and ^{1}H n.m.r. spectroscopy, and some by the ^{13}C n.m.r. The exception was $(PhO)_4P^+Br^-$ which is probably not stable at the high temperatures used, although the decomposition products $(PhO)_3P(O)$ and PhBr were found.

To explain the mechanism of disproportionation it is important to compare the results with those of Rydon in 1956,[28] who showed that $(ArO)_4PCl$ was obtained on recrystallisation of $(ArO)_3PCl_2$.

$$2(ArO)_3PCl_2 \longrightarrow (ArO)_4PCl + (ArO)_2PCl_3$$

Although the mechanism of this process has not been investigated in detail, it is reasonable to suppose that the transfer of phenoxide and halide anions occurs by a series of reactions as shown:



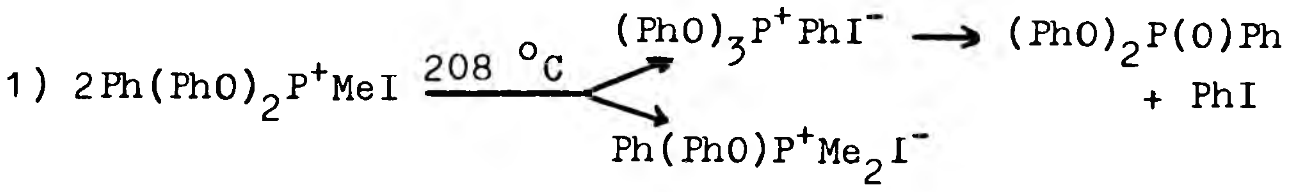


Quite recently this interpretation was confirmed by I.S. Sigal[36] in 1979, who investigated the disproportionation of aryloxyphosphoranes, in which a rapid redistribution of aryloxy groups between all possible phosphoranes and aryloxyphosphonium intermediates were observed. The only previous experiment was reported by Nesterov, who showed that disproportionation of methyl and phenoxy groups occurred in the thermal decomposition of certain quasiphosphonium salts as follows:[24]

1) $MePPh(OPh)_2I \xrightarrow{208\ ^{o}C} PhI + (PhO)_2P(O)Ph + PhPMe_3I$

2) $MePPh_2(OPh)I \xrightarrow{flame} PhI + Ph_2P(O)(OPh) + Ph_2PMe_2I$

The intermediate stages of the process were not studied although it is likely that a sequence such as the following occurred:



1) $2Ph(PhO)_2P^+MeI \xrightarrow{208\ ^{o}C}$ $(PhO)_3P^+PhI^- \rightarrow (PhO)_2P(O)Ph + PhI$; $Ph(PhO)P^+Me_2I^-$

Then 2 mol of $Ph(PhO)P^+Me_2I^- \rightarrow Ph(PhO)_2PMeI + PhPMe_3I$

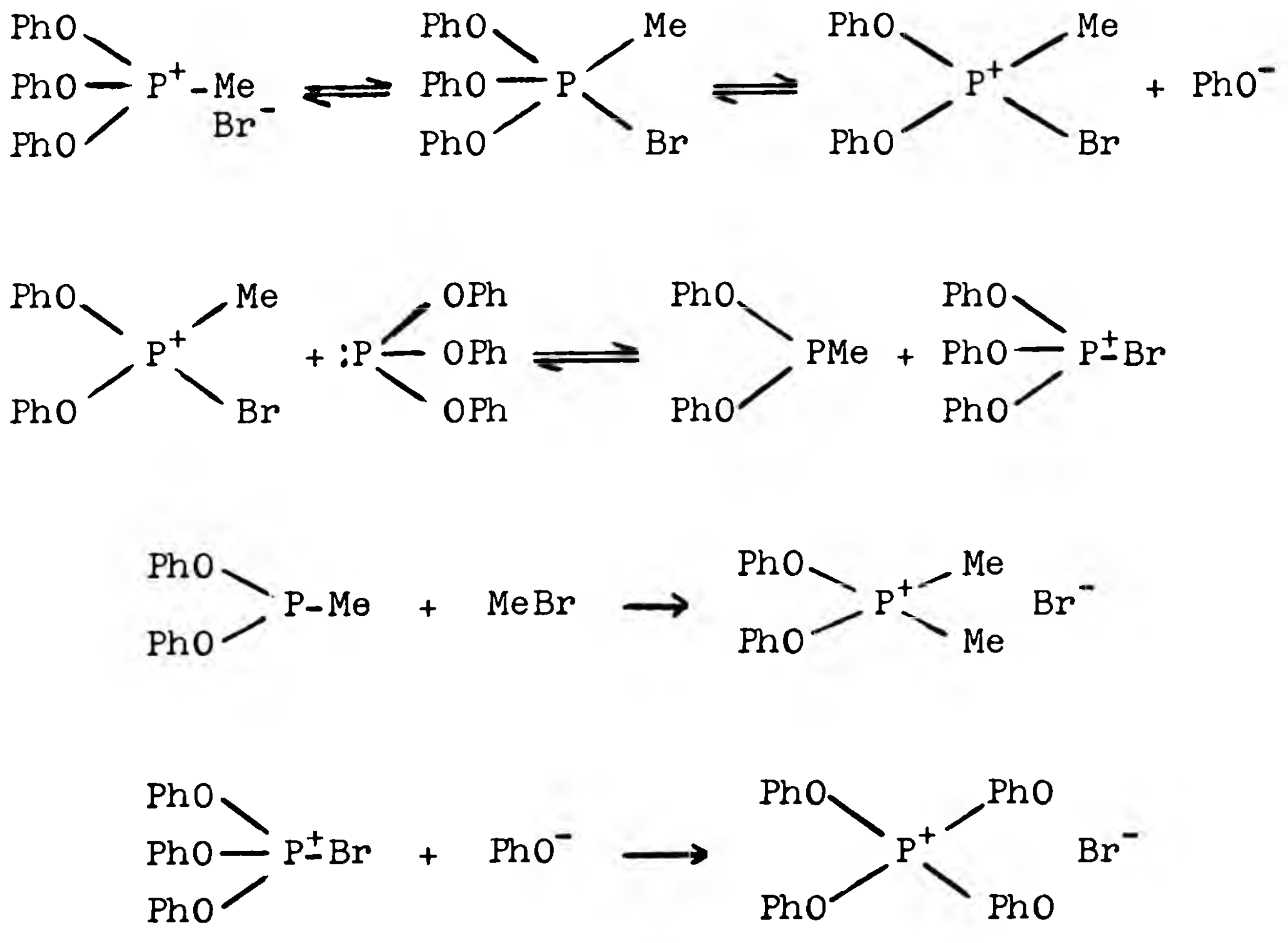
2) $2Ph_2(PhO)PMeI \xrightarrow{flame} Ph(PhO)_2P^+PhI^- + Ph_2PMe_2I$

$Ph(PhO)_2P^+PhI^- \rightarrow Ph_2(PhO)P{=}O + PhI$

The disproportionation of phenoxy groups and methyl groups is however less easy to understand in terms of anion exchange.

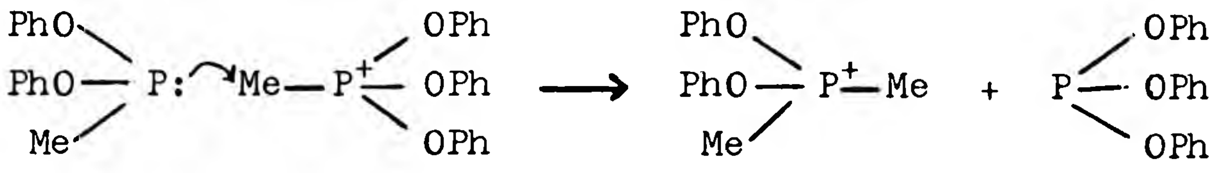
A possible mechanism which may be proposed for the disproportionation of methyltriphenoxyphosphonium bromide (as shown below) involves ligand exchange[35] between bromide and phenoxy, the transfer of Br^+ from the so-formed bromophosphonium intermediate to a molecule of phosphorus III ester (formed by simple dissociation), and further reaction of the newly formed phosphorus (III) ester with methyl halide, as shown:

$$(PhO)_3P^+MeBr^- \xrightleftharpoons{\text{high temp.}} (PhO)_3P + MeBr$$



$$(PhO)_4P^+Br^- \longrightarrow (PhO)_3P{=}O + PhBr$$

It is also possible that the diphenyl methylphosphonite may be converted to dimethyldiphenoxyphosphonium bromide by direct removal of methyl from another molecule of the starting material, rather than by reaction with methyl bromide.



The transfer of methyl from quasiphosphonium salts to phosphorus (III) esters in this way has been reported by other workers.[57]

3. Attempted deoxygenation of phosphonate by triphenyl phosphite

An alternative possible route for the formation of the tervalent ester, diphenyl methylphosphonite, was thought to be the deoxygenation of the normal Arbuzov product (the phosphonate) by triaryl phosphite as follows:

$$(PhO)_3P + O{=}P(OPh)_2Me \xrightarrow{\text{high temp.}} (PhO)_3P{=}O + (PhO)_2PMe$$

An example of deoxygenation of phosphine oxides by triphenyl phosphite has been claimed to give the corresponding phosphines.[58]

To investigate this possibility, triphenyl phosphite and diphenyl methylphosphonate (1:1 mol. ratio) were heated in sealed ^{1}H n.m.r. tubes, the temperature being gradually increased from 60 °C to 210 °C in the time interval 10 - 24 hours, and then for up to 4 weeks at 210 °C, but no change was observed.

The tube was then opened and 1 mol. equiv. of MeI was added and the tube reheated. The only product obtained was methyltriphenoxyphosphonium iodide, which was identified by hydrolysis to the phosphonate $(PhO)_2P(O)Me$.

The negative results obtained for deoxygenation, support the mechanism of disproportionation which has already been described.

4. Thermal decomposition in deuterochloroform of methyltriphenoxyphosphonium halides and methyltri-o-tolyloxyphosphonium halides and the detection and isolation of new intermediate containing a P-O-P linkage

New types of intermediate were observed during the thermal decomposition of methyltriphenoxyphosphonium bromide and iodide, and of methyltri-o-tolyloxyphosphonium bromide and iodide in chloroform or deuterochloroform.

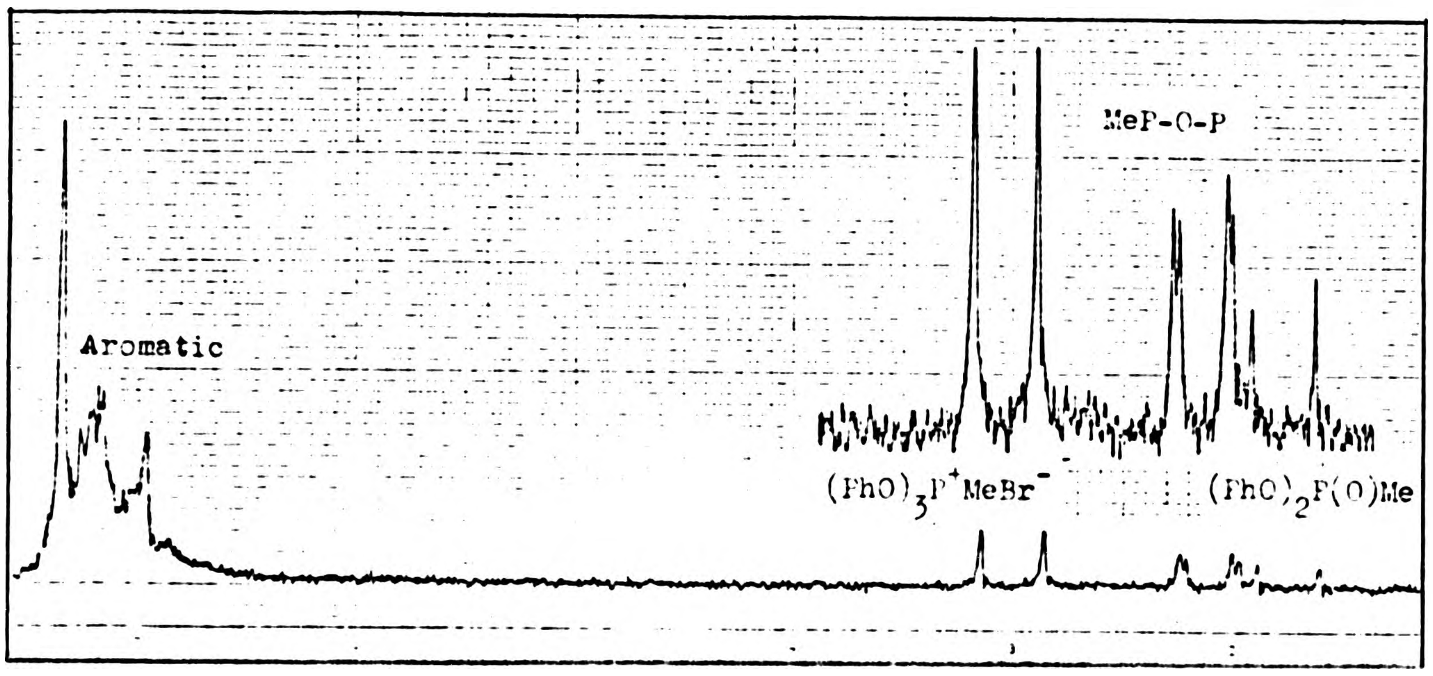
The experiments were carried out in sealed ^1H n.m.r. tubes which were heated at different temperatures (125 °C, 175 °C, 200 °C) and for various length of time (from 0.5 up to 112 hours).

After heating methyltriphenoxyphosphonium bromide for 15 hours in deuterochloroform at 125 °C or 175 °C, unexpected signals appeared at δ 2.15 (two doublets, J_{PCH} 14.4 Hz and _ca_. 2 Hz) (Fig. 12). These signals appeared first, before those for the phosphonate at δ 1.75 (Me doublet, J_{PCH} 17.7 Hz), and reached maximum height after 30 to 60 hours.

In dilute solution they reached 45% maximum, and in concentrated solution, 20 or 28%. Then if the tubes were heated for a longer period the two doublets decreased in intensity and finally disappeared, whereas the phosphonate signals grew taller.

Fig. 12

^{1}H n.m.r. spectrum of thermal decomposition of methyltriphenoxyphosphonium bromide in deuterochloroform at 125 °C



Similar results were obtained in all the above experiments which gave the same doublet of doublets at δ 2.15 ppm varying in intensity from 16 to 45% maximum. Results for methyltriphenoxyphosphonium bromide are shown in Table XII.

The role of $CHCl_3$ or $CDCl_3$ is thought to be simply that of a diluent or suitable medium in which this reaction can occur, since the same intermediate has also been detected (although in trace amounts only) on heating the phosphonium salts alone.

Further information on the possible nature of the intermediate from methyltriphenoxyphosphonium bromide was obtained from the ^{31}P n.m.r. spectrum which suggested the presence of P-O-P linkage. The proton decoupled spectrum (Fig. 13) confirmed the presence of two doublets (δ 77.0 and δ 34.0 ppm) each with J values of about 40 Hz which is in the expected range for P-O-P coupling.[59] The proton coupled spectrum (Fig. 14) further showed that the phosphorus species which gave the signal at 77 ppm had a methyl group attached (appearing as a doublet of quartets) whilst the other, at 34 ppm, did not. Other signals present were at 41.8 (quartet) due to methyltriphenoxyphosphonium bromide, 23.9 (quartet) due to phosphonate, and 96.1 (multiplet) due to dimethyldiphenoxyphosphonium bromide (small). A further weak signal at δ 33.9, overlapping the high field phosphorus doublet, was also present.

The ^{31}P n.m.r. spectrum (Fig. 15) for the P-O-P intermediate derived from methyltri-o-tolyloxyphosphonium bromide is similar. It shows that the two phosphorus atoms appear as doublets: at δ 32.3 (Me-P-O-$\underline{P}$, d, J_{POP} 32.4 Hz) and δ 77.0 ($\underline{Me-P}$-O-P, d, J_{POP} 32.4 Hz and J_{PCH} 16.0 Hz, doublet of quartets), showing that the methyl group (CH_3) is attached to the second phosphorus only.

The structure of the new intermediate is not completely clear but it is reasonable to suppose that it contains the grouping CH_3-P-O-P. The appearance of a doublet of doublets in the ^{1}H n.m.r. spectrum of the phenoxy compound centred at δ 2.15 ppm (J_{PCH} 14.4 Hz) and with

Fig. 13

^{31}P n.m.r. proton decoupled spectrum of thermal decomposition of $(PhO)_3P^+MeBr^-$ in deuterochloroform at 125 °C

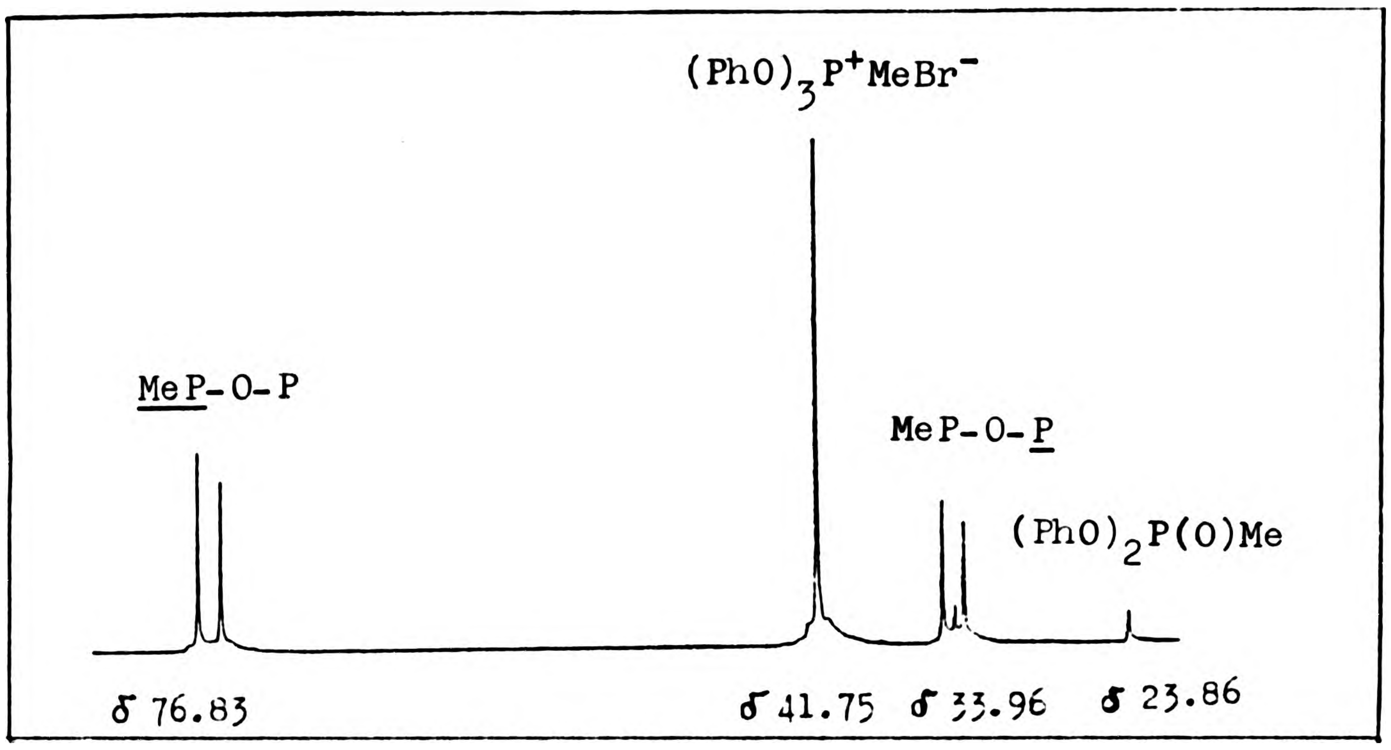


Fig. 14

^{31}P n.m.r. protons coupled spectrum of thermal decomposition of $(PhO)_3P^+MeBr^-$ in deuterochloroform at 125 °C

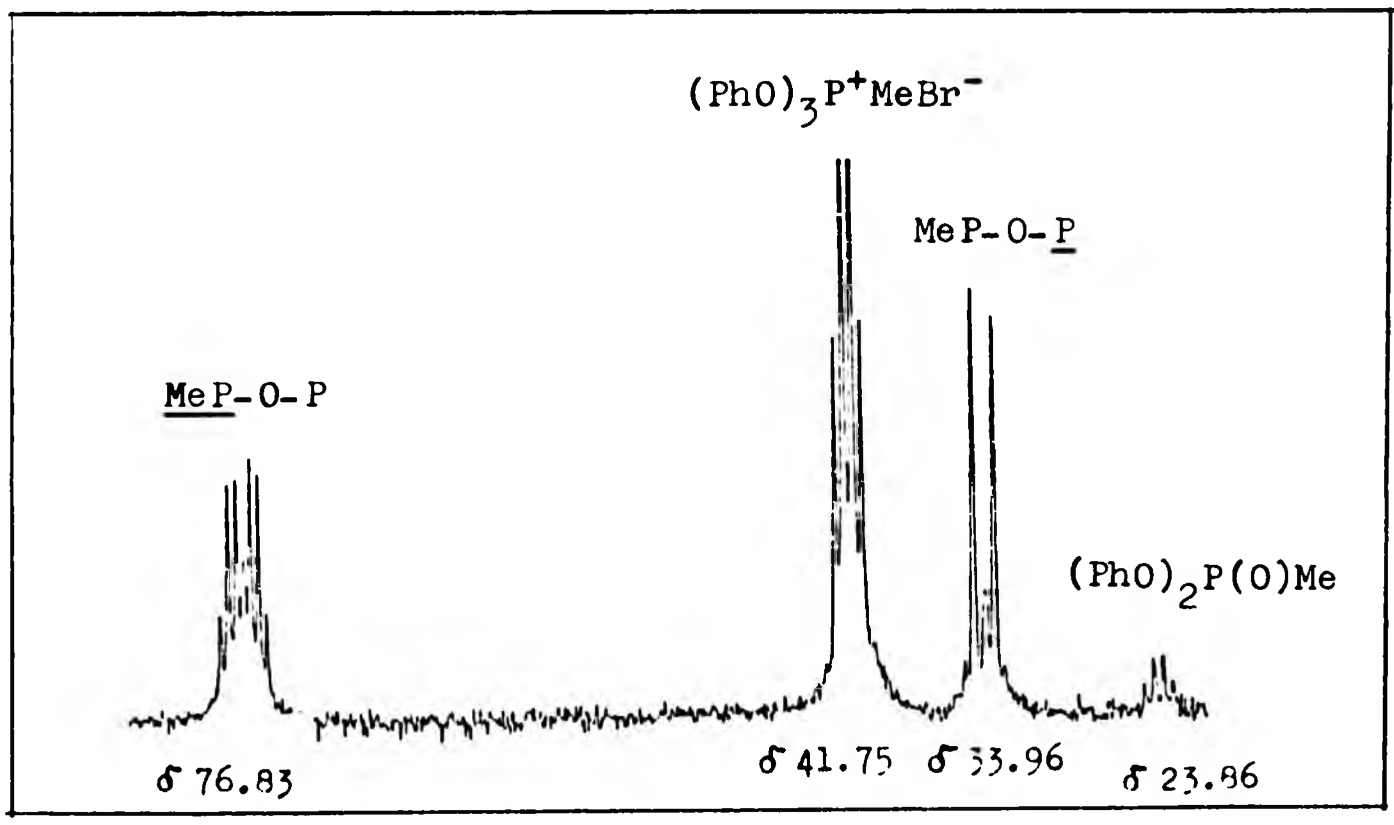
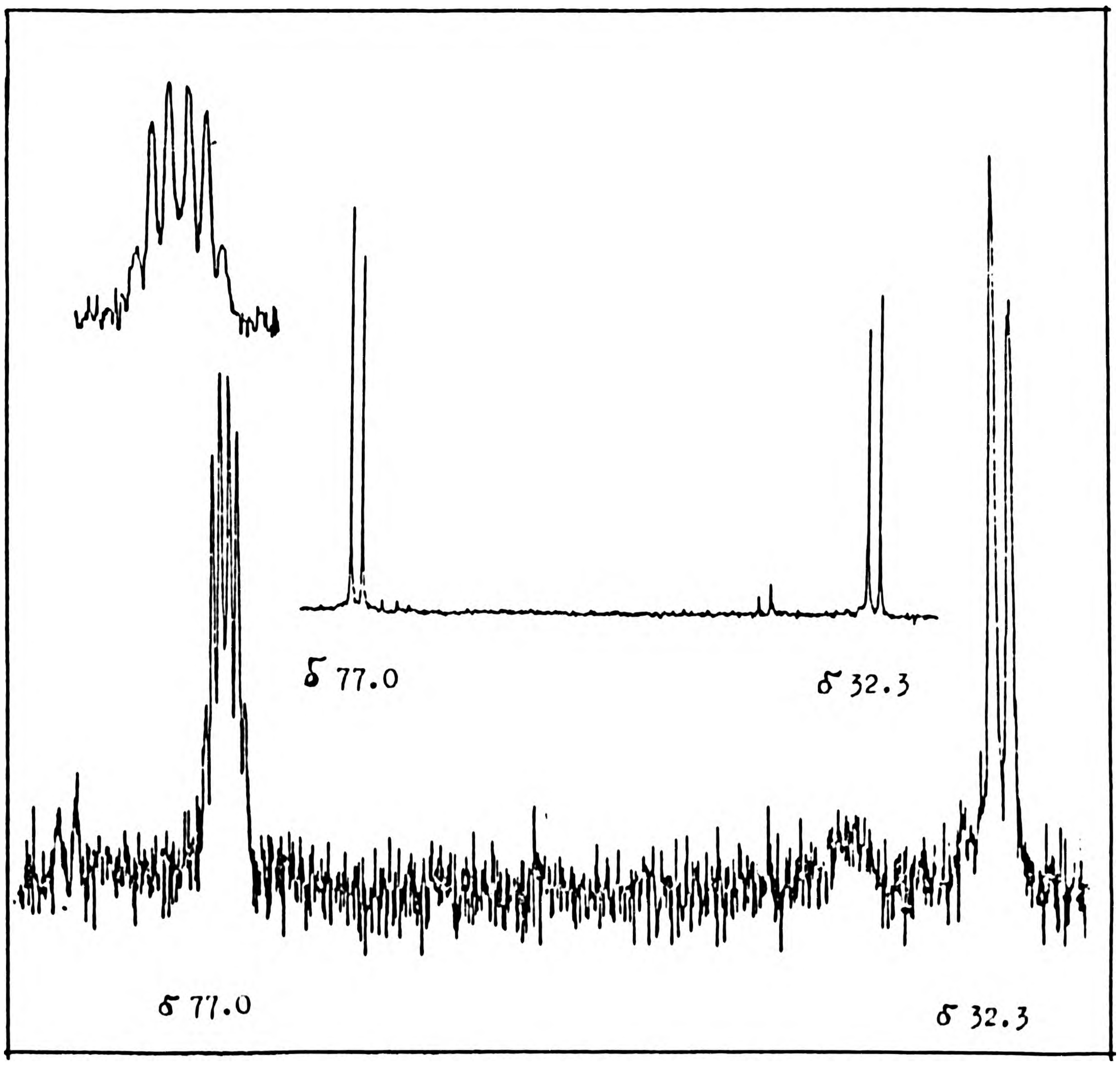
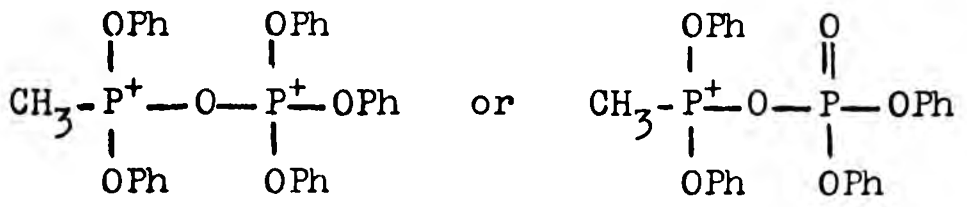


Fig. 15

^{31}P n.m.r. ($CDCl_3$) spectra of MeP-O-P intermediate isolated from thermal decomposition of methyltri-o-tolyloxyphosphonium bromide.

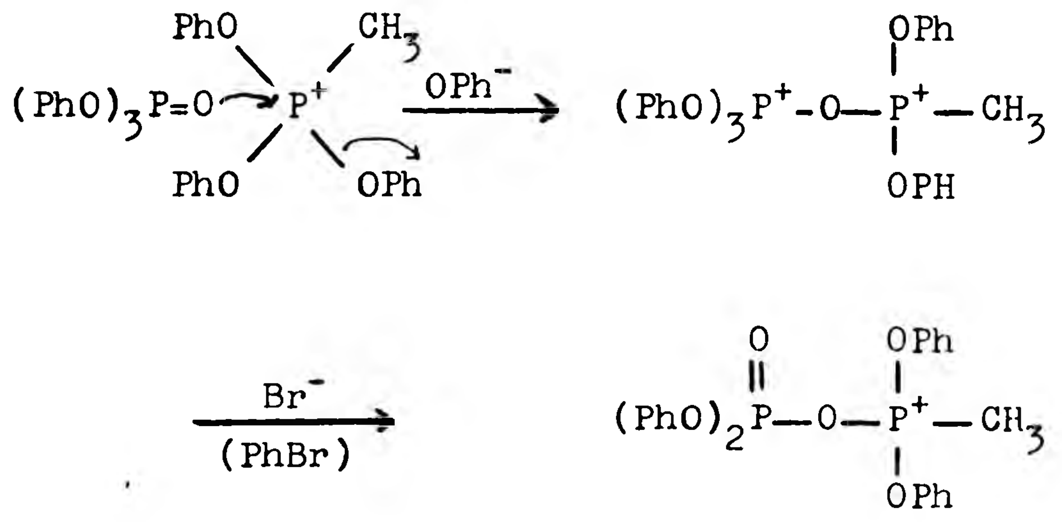


what appears to be coupling also to the more remote phosphorus atom (J ca. 2 Hz) is in accord with this interpretation. The absence of a methyl group on the second phosphorus suggests a structure such as:



$CH_3-\underset{OPh}{\overset{OPh}{P^+}}-O-\underset{OPh}{\overset{OPh}{P^+}}-OPh$ or $CH_3-\underset{OPh}{\overset{OPh}{P^+}}-O-\underset{OPh}{\overset{O}{\overset{\|}{P}}}-OPh$

which could be formed by reaction of triphenyl phosphate (a disproportionation product - see earlier) with methyltriphenoxyphosphonium bromide as follows:



The formation and disappearance of this intermediate is shown in Table XII.

The ^1H n.m.r. spectrum (Fig. 16) of the P-O-P intermediate isolated from the thermal decomposition of methyltri-o-tolyloxyphosphonium bromide showed two similar doublets at δ 2.38 (J_{PCH} 13.9 Hz, J_{POPCH} 1.9 Hz), and additionally two tall signals in ratio 3:2 for the o-tolyl methyl groups attached to the two different phosphorus atoms. These signals appeared as doublets at δ 2.02 (J_{POCCCH} 0.9 Hz, 9H), and δ 2.18 (J_{POCCCH} 0.9 Hz, 6H) respectively.

The evidence therefore is that the intermediate has

Table XII

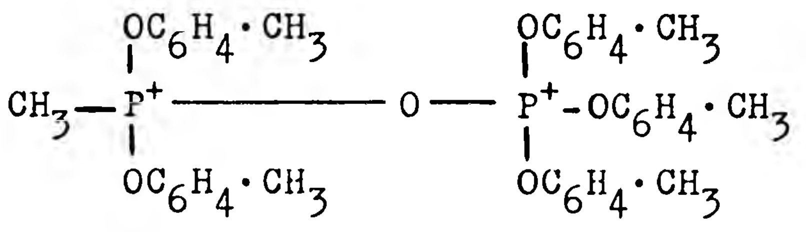
Experimental data on the thermal decomposition of methyltriphenoxyphosphonium bromide in chloroform* and deuterochloroform, and appearance of a new intermediate MeP-O-P

Experiment No.	Temperature °C	Heating time in hours from		to	$(PhO)_3P^+MeBr^-$ (mole %)			MeP-O-P (mole %)			$(PhO)_2P(O)Me$ (mole %)		
8%	100 125	129.5 15.5	37.0	60.0	75.3	66.3	61.2	24.7	33.7	38.8		-	
4.5%	125	48.0	68.0	95.0	45.7	44.2	38.5	36.9	38.5	41.8	17.4	17.3	19.7
8%	125	61.0	81.0	98.0	72.1	65.0	62.6	22.9	28.2	31.0	5.0	6.8	6.4
10%*	125	37.5	60.5	84.5	75.1	73.6	76.0	21.3	20.9	19.0	3.6	5.5	4.7
30%	125	33.5	53.5	112.5**	83.8	82.4	80.0	16.2	17.6	20.0		-	
4.5%	175	10.0	14.0	16.0 a	45.9	22.6	21.5	36.1	49.2	45.4	18.0	25.6	29.8
8%	175	3.0	-	5.5	47.6	-	44.2	45.1	-	45.2	7.2	-	10.6
40%	175	6.0	-	- a	76.6	-	-	19.4	-	-	2.5	-	-
30%	200	0.75	1.5	2.5 a	72.0	67.3	65.7	25.2	28.2	27.2	2.8	4.5	5.7

** Heated at 118 °C for 44 h,

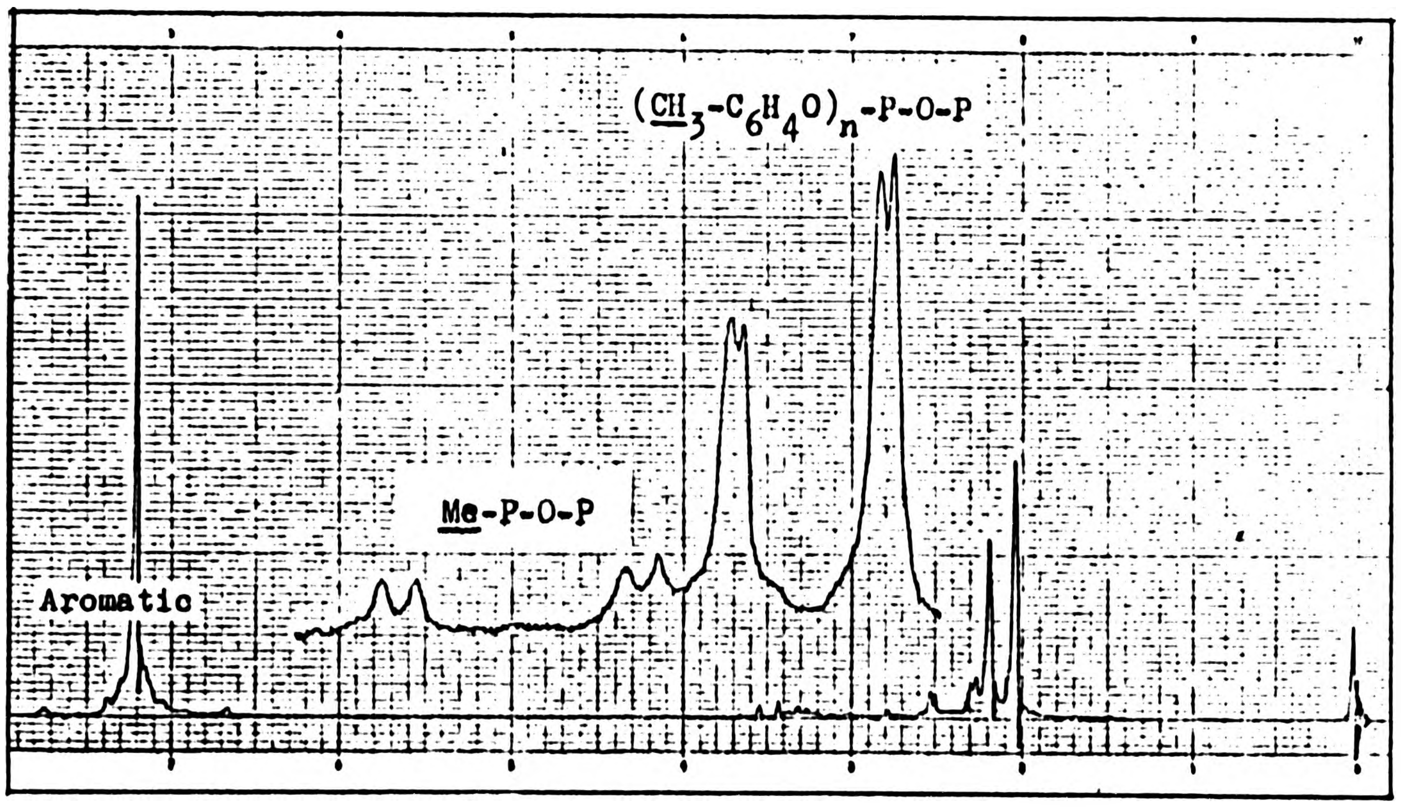
a Appearance of $(PhO)_2P^+Me_2Br^-$ (3.3 mole%), (1.5 mole %), (1.4 mole %) respectively.

two o-tolyloxy groups on one phosphorus atom and three on the other, suggesting the structure shown.



$$\mathrm{CH_3-\overset{\overset{\displaystyle OC_6H_4\cdot CH_3}{|}}{\underset{\underset{\displaystyle OC_6H_4\cdot CH_3}{|}}{P^+}}-O-\overset{\overset{\displaystyle OC_6H_4\cdot CH_3}{|}}{\underset{\underset{\displaystyle OC_6H_4\cdot CH_3}{|}}{P^+}}-OC_6H_4\cdot CH_3}$$

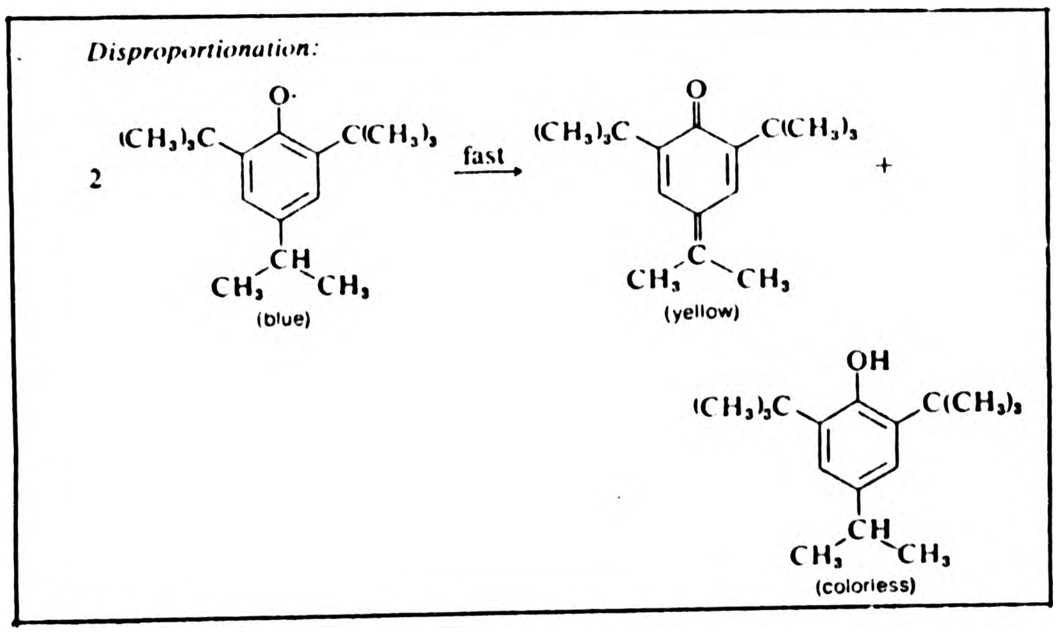
^{1}H n.m.r. ($CDCl_3$) spectrum of MeP-O-P intermediate isolated from thermal decomposition of methyltri-o-tolyloxyphosphonium bromide (Fig. 16).



The above MeP-O-P intermediate which was isolated in a very small amount was found to be stable in $CDCl_3$ in a sealed tube, but was too unstable to be isolated and stored as a solid even under a vacuum.

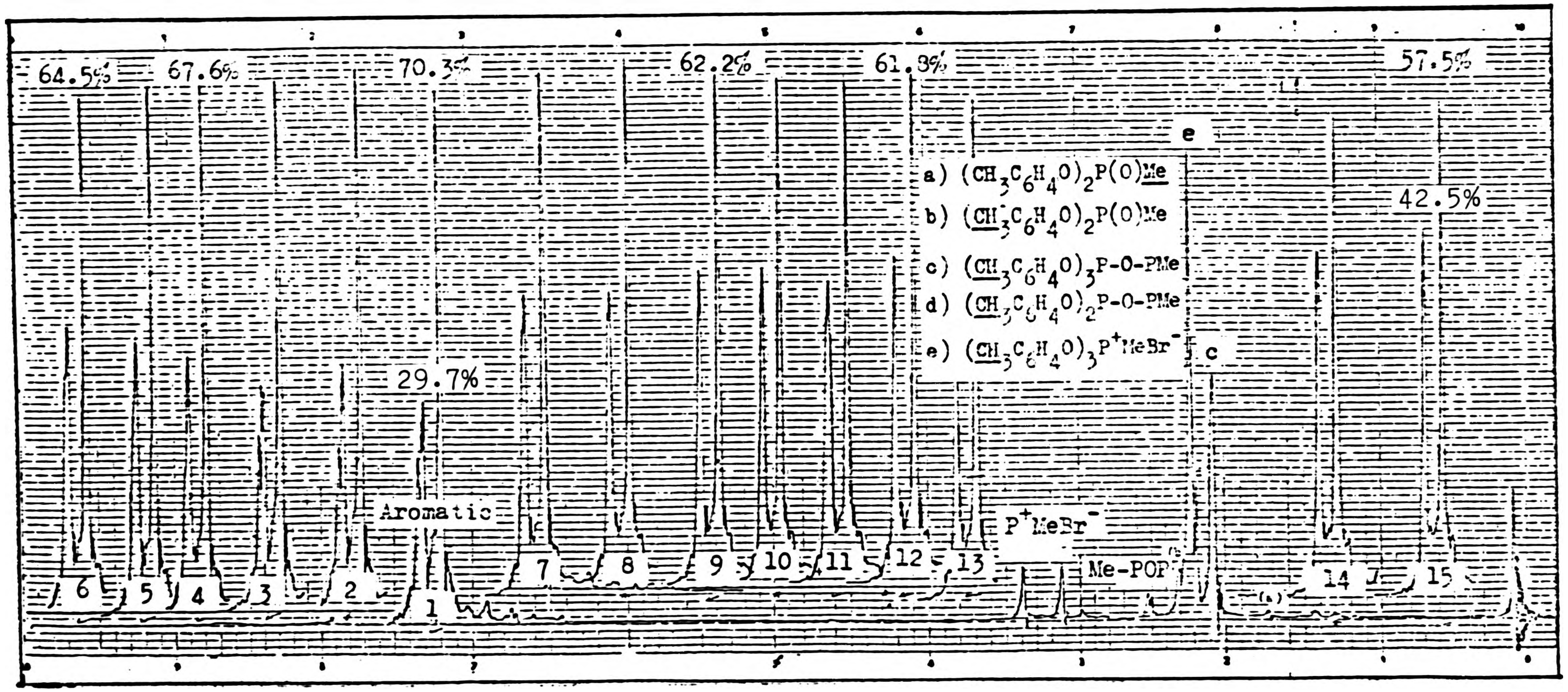
An interesting feature of the thermal decomposition of methyltri-o-tolyloxyphosphonium bromide in deuterochloroform was that the solution became blue when hot, and slowly changed to green and then to light brown or colourless after cooling. (See Table VII). The blue colour was observed when hot only as long as the two doublet signals were present. After these signals had disappeared the colour was changed to brown. Another specific observation was the change in height of two aromatic signals (back reaction) δ 7.33 (s) phosphonium, and δ 7.12 (s) phosphonate. On cooling and changing from blue to green the phosphonium signals increased from 29.7% to 42.5% after 1.25 hours whereas the phosphonate signal decreased in height from 70.3% to 57.5% (Fig. 17).

The blue colour is considered to be a specific indicator for phenoxy radicals.[52]



The possible role of such radicals in the Arbuzov reaction described above is however uncertain.

^1H n.m.r. spectra of thermal decomposition of methyltri-o-tolyloxyphosphonium bromide (ca. 10.0% in $CDCl_3$) at 150 °C. (Dark-blue colour appears on heating. On standing at 33 °C for 1.25 hours changes to green and aromatic signals change in height) (Fig. 17).



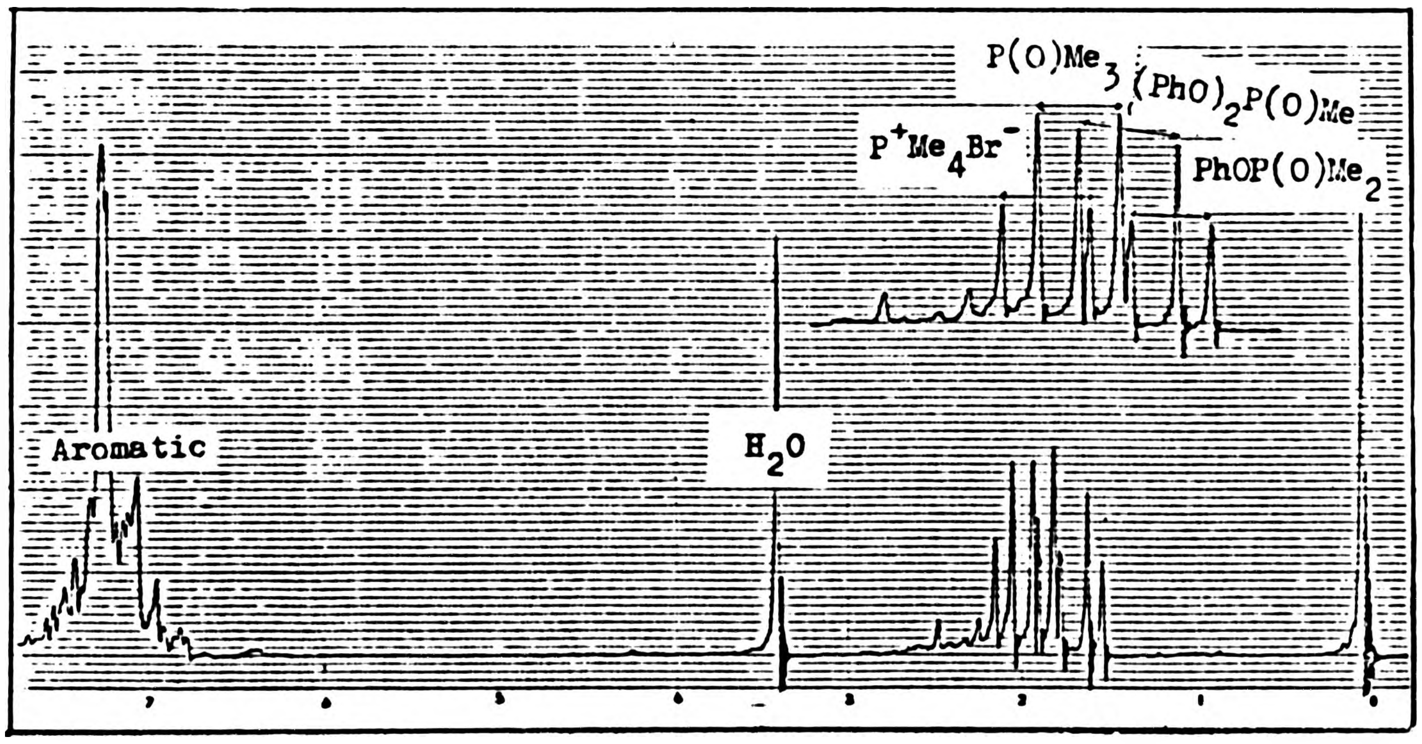
5. Hydrolysis of disproportionation products

The products of thermal decomposition of dimethyldiphenoxyphosphonium bromide (Fig. 9) were hydrolysed by atmospheric moisture to give three phosphonates: Me_3PO, $PhOP(O)Me_2$, and $(PhO)_2P(O)Me$ (Fig. 18). The presence of the last, which was unexpected, supports the mechanism of disproportionation:

$$2(PhO)_2P^+Me_2Br^- \longrightarrow PhOP^+Me_3Br^- + (PhO)_3P^+MeBr^-$$

$$(PhO_3P^+MeBr^- \longrightarrow (PhO)_2P(O)Me$$

^1H n.m.r. ($CDCl_3$) spectrum of hydrolysis of disproportionation products for $(PhO)_2P^+Me_2Br^-$ at 290 °C (Fig. 18).



The formation of several different hydrolysis products when the tube of the P-O-P intermediates was opened to the atmospheric moisture, suggests that the system is complicated. The results of hydrolysis are summarised in Tables IX and X.

Further studies based on ^{31}P n.m.r. spectroscopy showed two stages of hydrolysis. The first stage of hydrolysis showed main, but unidentified signals at δ 4.98 (triplet, J ca. 20.0 Hz) and δ 84.4 (m).

The second stage of hydrolysis showed a change to new unidentified signals at δ 11.7 (triplet, J 23.3 Hz) and δ 47.7 (m) probably two overlapping quartets.

6. Some observations on n.m.r. data

The chemical shift of the Me_3PO peak in the decoupled ^{31}P n.m.r. spectrum was found to vary depending upon which solvent was used and upon the pH of the solution:

Solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	DMSO	D_2O
^{31}P found	76.6 in reaction mixture	40.0	57.3 at pH 4	46.4	53.7
lit.[53]	-	39.0	-	-	-
lit.[54]	-	36.2	-	-	-

Other workers have found similar effect.[55] Thus the ^{31}P chemical shifts of Ph_3PO in some different solvents at concentration of 1:20 mole ratio were as follows:

Solvent	^{31}P (ppm)
1,4-Dioxane	24.8
m-Cresol	36.4
Trifluoroacetic acid	48.1
Sulphuric acid	59.8

The difference between the shifts obtained in highly acidic solvents can be interpreted mostly in terms of a large change in the position of the equilibrium:

$$Ph_3P{=}O + HA \rightleftharpoons Ph_3P{=}O{-}{-}{-}HA \rightleftharpoons Ph_3P^{+}{-}OH\ A^{-}$$

In such solvents the predominant effect responsible for the downfield trend with increasing acidity appears to be that of an increase in the number and strength of solvent-to-solute hydrogen bonds as represented by the hydrogen bonded complex in the above equilibrium.

There is ample evidence in the literature that such interactions are important in systems containing triphenylphosphone oxide and alcohol, phenols, carboxylic acids, or chloroform.

The ^{13}C-^{31}P coupling constants for Arbuzov intermediates and products show large differences, depending on the number of methyl groups attached to phosphorus. With increasing number of methyl groups the value of J_{P-C} decreases significantly as shown and this can be a valuable aid to their identification.

Phenoxyphosphonium bromide intermediates containing P-Me$_n$	$^{13}C-^{31}P$ coupling constant J_{P-C} (Hz)
P^+Me	126.95
P^+Me_2	87.42
P^+Me_3	64.70
P^+Me_4	55.50
Phenoxyphosphonium iodide intermediates	
P^+Me	127.50
P^+Me_2	87.89
P^+Me_3	64.09
Phosphonates	
$(PhO)_2P(O)Me$	144.62
o-$(CH_3C_6H_4O)_2P(O)Me$	145.26
$PhOP(O)Me_2$	95.62
$P(O)Me_3$	68.40

NMR data ($CDCl_3$) for Arbuzov intermediates and products (Table No. XIII)

Structure	^{31}P	^{1}H				^{13}C		
	δ (ppm)	δ (ppm) CH_3-P (d)	J (Hz) PCH	δ (ppm) $CH_3C_6H_4$ (s)	δ Ph	δ (ppm) P-CH (d)	J (Hz) P-C	δ (ppm) $CH_3C_6H_4$ (s)
$(PhO)_3P^+MeBr^-$	41.82	3.24	17.4	-	7.35	10.07	126.95	-
$(PhO)_3P^+MeI^-$	40.86	3.12	16.8	-	7.44	10.89	127.50	-
$(CH_3C_6H_4O)_3P^+MeBr^-$	42.13	3.26	15.8	2.19	7.33	10.94	125.46	16.21
$(CH_3C_6H_4O)_3P^+MeI^-$	41.31	3.16	15.9	2.20	7.32	11.89	126.95	16.35
$(PhO)_2P^+Me_2Br^-$	96.65	2.95	14.7	-	7.41	12.39	87.42	-
$(PhO)_2P^+Me_2I^-$	94.79	2.92	14.0	-	7.43	13.16	87.89	-
$PhOP^+Me_3Br^-$	102.23	2.60	14.0	-	7.48	13.32	64.70	-
$PhOP^+Me_3I^-$	101.34	2.65	13.5	-	7.42	14.08	64.09	-
$P^+Me_4Br^-$ *	22.60	2.12	14.7	-	-	10.60	55.50	-
$P^+Me_4Br^-$ (DMSO) *	25.10[a]	1.87	15.0	-	-	8.93	55.50	-
$P^+Me_4I^-$ *	23.30	2.25	13.5	-	-	not	recorded	-

* Isolated with other product

[a] δ_P (DMSO) 25.2[41]

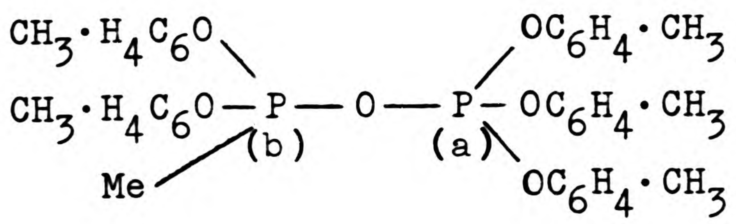
(Table XIII, continued)

Structure	^{31}P		^{1}H			^{13}C		
	δ (ppm)	δ (ppm) CH_3-P (d)	J (Hz) PCH	δ (ppm) $CH_3C_6H_4$ (s)	δ Ph	δ (ppm) P-CH (d)	J (Hz) P-C	δ (ppm) $CH_3C_6H_4$ (s)
$(PhO)_2P(O)Me$	23.79	1.65	17.7	-	7.17	11.43	144.62	-
$(CH_3C_6H_4O)_2P(O)Me$	23.49	1.83	18.0	2.22	7.15	11.47	145.26	16.29
$PhOP(O)Me_2$ **	60.70	1.63	14.4	-	7.19	15.22	95.62	-
Me_3PO **	76.60	1.90[b]	13.5	-	-	15.30	68.40	-
Me_3PO (DMSO) *	53.70	1.55	13.2[c]	-	-	16.30	68.40	-
Isolated Me_3PO	b 40.00[d]	1.47	13.5	-	-			-
Isolated Me_3PO at pH 4	57.30	1.50	13.5	-	-			-
Isolated Me_3PO DMSO	46.4	1.50	13.2	-	-			-
Isolated Me_3PO D_2O	53.6	1.57	13.2	-	-	$J_{C^{13}-H}$ = 128.8 Hz[e]		-

** in reaction mixture [b] δ_H ($CDCl_3$) 2.15, J 13.2 Hz, δ_P ($CDCl_3$) 39.0[53]

[c] δ_H 1.39, J 13.2 Hz[42] [d] δ_P 36.2[54] [e] $J_{C^{13}-H}$ = 129 Hz (D_2O)[43].

NMR data of isolated Me-P-O-P intermediate (Table XIII, continued)

^{31}P (ppm), J (Hz)		^{1}H (ppm), J (Hz)	
Structure		P-Me	CH_3-tolyl
			
P—O—P (a)	δ 32.3(d) J_{POP} 32.4 (Ez)		δ 2.02(d) H9 J_{POCCCH} 0.9 (Hz)
Me —P—O—P (b)	δ 77.0(dq) J_{POP} 32.4 (Hz) J_{PCH} 16.0 (Hz)	δ 2.38(dd) J_{PCH} 13.9 (Hz) J_{POPCH} 1.9 (Hz)	δ 2.18(d) H6 J_{POCCCH} 0.9 (Hz)

II.2 PERKOW AND ARBUZOV INTERMEDIATES

The reactions of trialkyl phosphites with α-halogenocarbonyl compounds may yield two different products, either the ketophosphonate (Arbuzov product) or the vinyl phosphate (Perkow product), depending on the halogen involved and the particular reaction conditions.

There have been several proposed mechanisms for these reactions.

1. Chopard et al. suggest that the Perkow product is formed by initial attack at the carbonyl carbon atom, followed by migration of the phosphorus atom from the carbon to oxygen atoms.
2. Koziara et al. propose the formation of a halogenophosphonium-enolate ion pair, which is common to both the Arbuzov and Perkow intermediates and their products.
3. Marquading and Ramirez also suggest a common intermediate. The ketophosphonium intermediate gives rise to the Arbuzov product directly and to the Perkow product by rearrangement <u>via</u> a four-membered cyclic phosphorane.
4. Petneházy et al. also favour the idea of a common intermediate after work on α-halogenoacetophenones.[60]

However up to now all the evidence for and against the various postulated mechanisms has been of an indirect nature particularly from kinetic studies, because no intermediates have been isolated nor identified, and no direct evidence has been obtained.

In my work I have isolated and identified some of the intermediates during these reactions, and have therefore produced the first direct evidence for and against the postulated mechanisms.

The present work has now shown that identifiable alkyloxyphosphonium intermediates are obtainable by the reaction of neopentyl esters of phosphorus (III) acids with phenacyl halides. Phenacyl bromide gave the ketophosphonium salts,

$$ROP\langle \; + \; PhCOCH_2X \qquad RO\text{-}\overset{|}{\underset{|}{P}}{}^{+}\text{—}CH_2COPh\ X^-$$

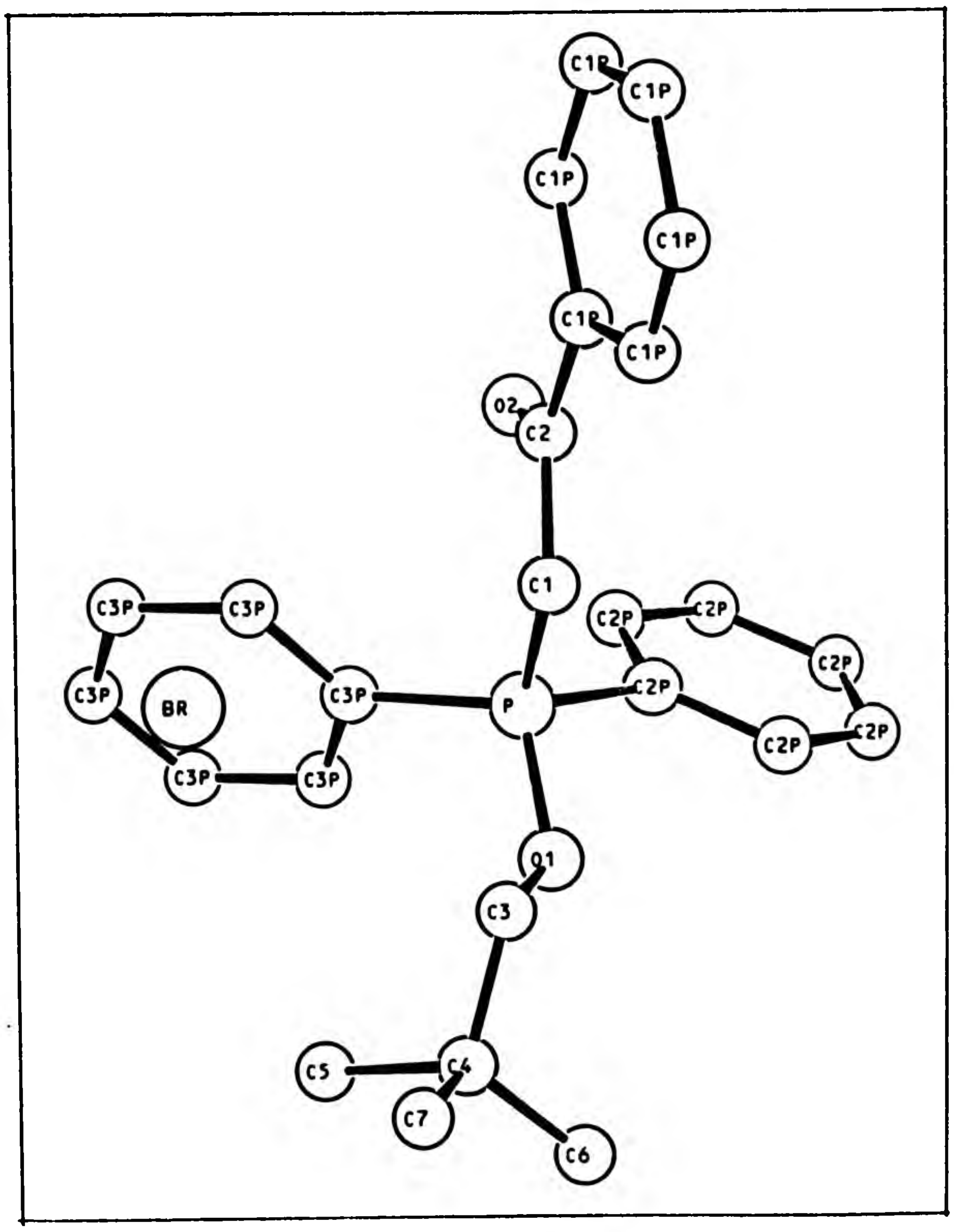
e.g. reaction with trineopentyl phosphite in acetone at room temperature for 2 hours allowed the isolation of the Arbuzov intermediate $(RO)_3P^+CH_2COPhBr^-$ which was washed with ether and obtained as a crystalline solid, m.p. 88 °C, in 21% yield. Similarly, the reaction of dineopentyl phenylphosphonite with phenacyl bromide in ether at room temperature gave the Arbuzov intermediate $(RO)_2P^+(Ph)CH_2COPhBr^-$ m.p. 120 - 122 °C, in 45.8% yield, and the reaction of neopentyl diphenylphosphinite with phenacyl bromide in chloroform at room temperature produced $(RO)P^+Ph_2CH_2COPhBr^-$ m.p. 135 - 136 °C, in 71.4% yield.

It should, however, be noted that some of the phenacyl intermediates did not precipitate well with ether and for this reason they were precipitated by addition of an excess of chloroform.

The last product was the most stable and was sufficiently resistant to hydrolysis to allow an X-ray structure determination to be carried out in the open laboratory atmosphere without the need for special precautions.

Fig. 19

X-ray crystal structure of $Ph_2P^+(OR)CH_2COPh\ Br^-$ (R = neopentyl)



Important Bond Lengths, and Bond Angles

Bond Lengths (Å)

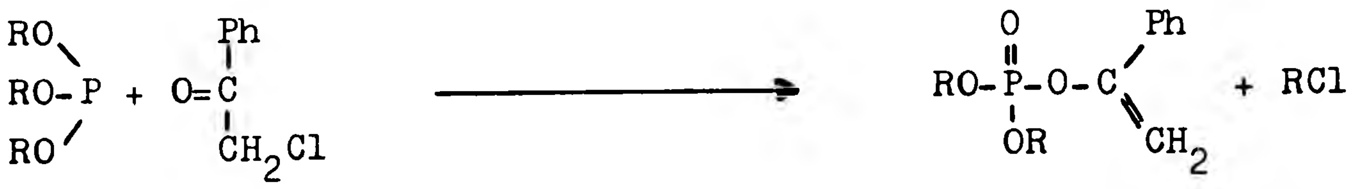
P - C(1)	1.798(11)
P - C(2P)	1.792(11)
P - C(3P)	1.786(12)
P - O(1)	1.573(8)

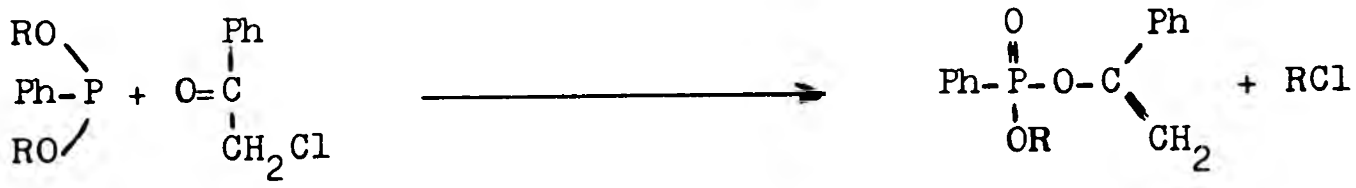
Bond Angles (°)

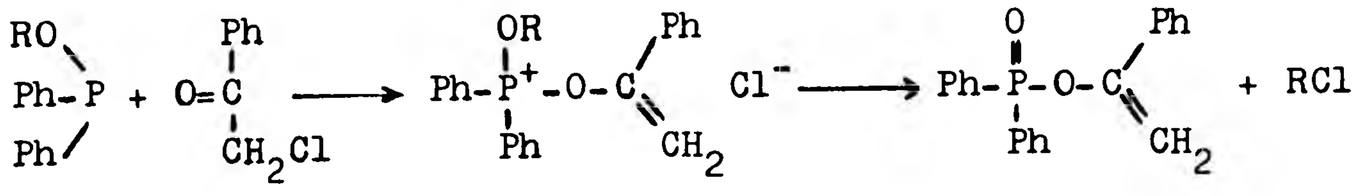
C(2P) - P - C(3P)	111.8(6)
C(3P) - P - O(1)	109.5(5)
C(3P) - P - C(1)	112.3(6)
C(2P) - P - C(1)	113.0(5)
C(1) - P - O(1)	107.8(5)
C(2P) - P - O(1)	102.0(5)

The X-ray diffraction data confirm the phosphonium structure, with bond angles at phosphorus approximating to a tetrahedral arrangement, and with a $P^+....Br^-$ interatomic distance of 4.229 Å. Some double-bond character between phosphorus and oxygen is indicated by the bond length of 1.573 Å. The fact that the stability of these intermediates decreases as the number of alkoxy groups increases, suggests however that the inductive effect (-I) of oxygen is more important than its mesomeric (+M) effect.

When the reaction of $(RO)_3P$, $(RO)_2PPh$ and of $ROPPh_2$ with phenacyl chloride were carried out in $CHCl_3$ at room temperature no Arbuzov intermediates or products were detected by ^1H n.m.r. spectroscopy. With $(RO)_3P$ and $(RO)_2PPh$, only the Perkow products were detectable, but $(RO)PPh_2$ gave both the Perkow intermediate and the vinyl phosphinate as detectable species.







35% (Intermediate)   45% (Product)

Table XIV shows the various Arbuzov and Perkow intermediates that were detectable in solution during the course of this work.

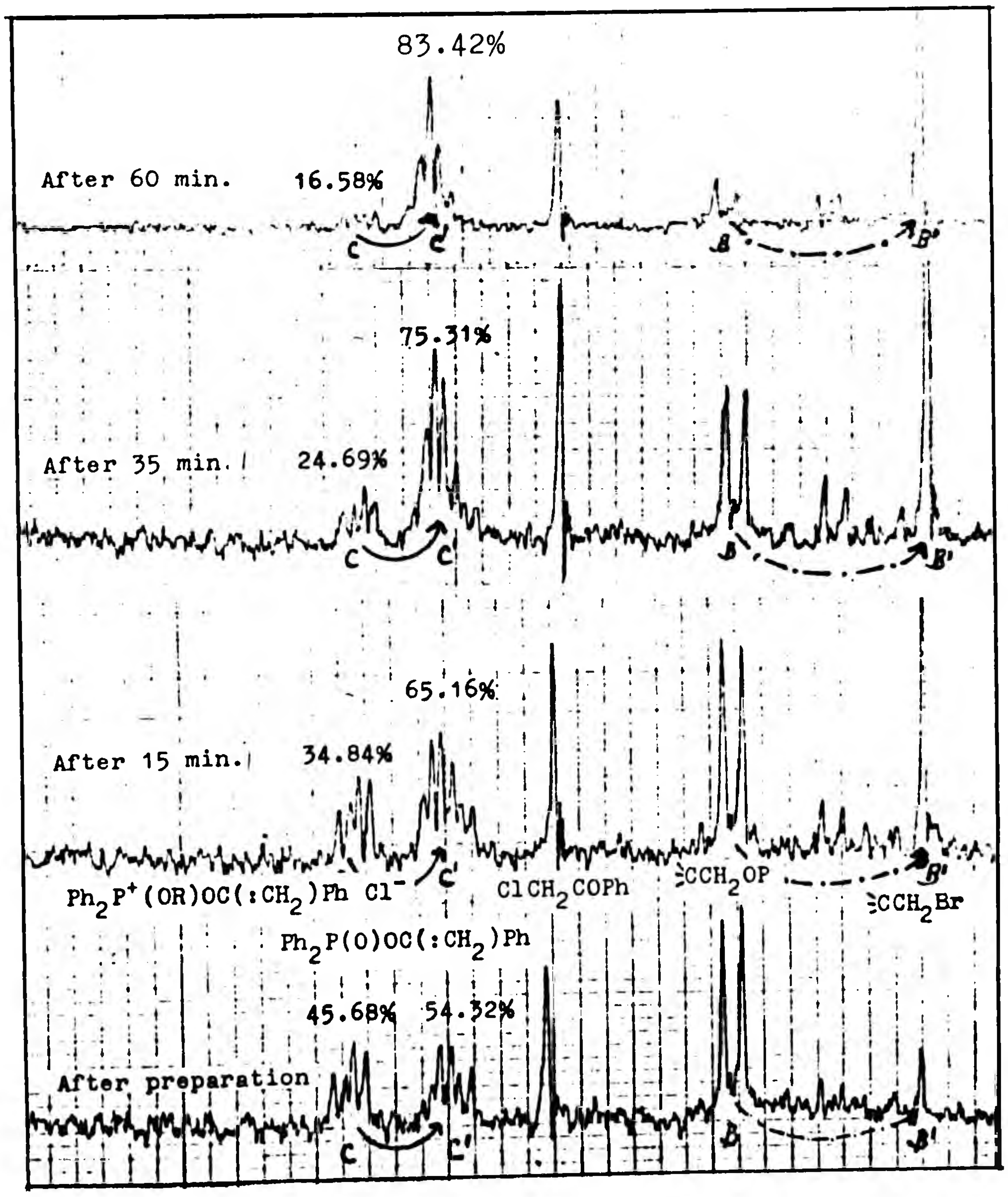
The reaction of phenacyl chloride with $(RO)PPh_2$ was therefore repeated at -5 to 0 °C, when the vinyloxyphos-

The various Arbuzov and Perkow intermediates and products detectable in $CDCl_3$ during the reaction of phosphorus (III) esters with δ-halogenoacetophenones (Table XIV)

Reaction mixture	Time (h)	Starting materials (%)	ARBUZOV		PERKOW	
			Intermediate (%)	Products (%)	Intermediate (%)	Products (%)
$(RO)_3P$			$(RO)_3P^+CH_2COPhBr^-$	$(RO)_2P(O)CH_2COPh$		$(RO)_2P(O)OC(:CH_2)Ph$
with	0.25	57.0	10.6	18.4	-	13.7
$PhC(O)CH_2Br$	4.5	11.4	10.4	34.2	-	44.2
$(RO)_2PhP$	after		$PhP^+(OR)_2CH_2COPhBr^-$			$PhP(O)(OR)OC(:CH_2)Ph$
with	prep.	2.0	41.0	-	-	57.0
$PhC(O)CH_2Br$	1.0	2.0	41.0	-	-	57.0
$ROPPh_2$			$Ph_2P^+(OR)CH_2COPhBr^-$		$Ph_2P^+(OR)OC(:CH_2)PhBr^-$	$Ph_2P(O)OC(:CH_2)Ph$
with	0.25	8.0	68.0	-	10.0	13.0
$PhC(O)CH_2Br$						
$(RO)_3P$						$(RO)_2P(O)OC(:CH_2)Ph$
with	0.17	64.6	-	-	-	35.3
$PhC(O)CH_2Cl$	2.58	6.8	-	-	-	93.2
$(RO)_2PhP$ with	after					$PhP(O)(OR)OC(:CH_2)Ph$
$PhC(O)CH_2Cl$	prep.	-	-	-	-	100.0
$(RO)PPh_2$					$Ph_2P^+(OR)OC(:CH_2)PhCl^-$	$Ph_2P(O)OC(:CH_2)Ph$
with	0.17	20.0	-	-	35.0	45.0
$PhC(O)CH_2Cl$	3.00	13.0	-	-	26.0	61.0

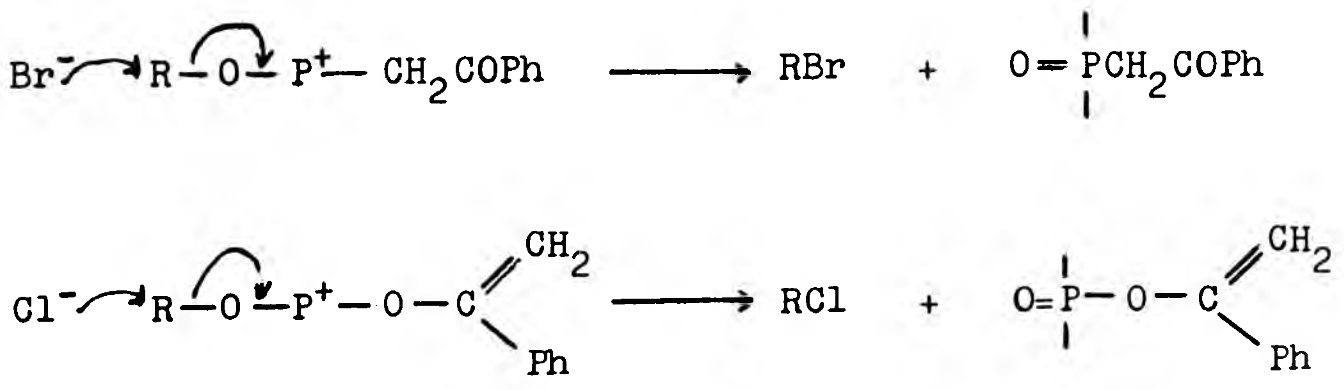
phonium chloride (i. e. The Perkow intermediate) was isolated and purified. Its decomposition at 33 °C in $CDCl_3$ was followed by ^1H n.m.r. spectroscopy, the kinetics being found to be first order with a half life ($t_{\frac{1}{2}}$) of approximately 40 min. (Fig. 20).

The decomposition of neopentyloxydiphenyl-1-phenylvinyloxyphosphonium chloride in $CDCl_3$ to 1-phenylvinyl diphenylphosphinate (Fig. 20).



Perkow intermediates were characterised by the multiplet in the ^{1}H n.m.r. spectrum at δ 5.41-5.54 ppm due to vinyl protons and which was gradually replaced by a corresponding multiplet at δ 5.05-5.25 ppm assigned to the vinyl protons of the product (Fig. 20). Neopentyl chloride was also formed.

The Arbuzov intermediates were considerably more stable than the Perkow intermediates but they decomposed on heating in chloroform or other solvent. It is important to note that in doing this they yielded Arbuzov products exclusively, thus showing that rearrangement to the Perkow intermediates (as suggested elsewhere[40]) can be excluded under the conditions of these experiments. Dealkylation of all intermediates gave neopentyl halides as the only halide products, showing that the reactions occurred by an S_N2 - type cleavage of the R-O bond.



The observed first order kinetics are in accord with the existence of these intermediates as ion-pairs in the organic solvent used.

The isolated Perkow and Arbuzov intermediates and their products of decomposition were identified by the ^{1}H n.m.r. and ^{31}P n.m.r. spectroscopy. (Table XV).

NMR data for Arbuzov and Perkow intermediates and products (Table XV)

Structure	^{31}P δ (ppm)	^1H δ (ppm)					J (Hz)	
		Me_3C	CH_2OP	CH_2-P	CH_2=C	Ph	POCH	PCH
$(RO)_3P^+CH_2COPh\ Br^-$	+ 41.0	1.02(s)	4.35(d)	5.74(d)	-	7.3-8.4(m)	4.8	18.3
$PhP^+(OR)_2CH_2COPh\ Br^-$	+ 67.1	1.07(s)	4.34(m)[a]	5.99(d)	-	7.2-8.4(m)	a	15.6
$Ph_2P^+(OR)CH_2COPh\ Br^-$	+ 68.3	0.99(s)	4.15(d)	6.25(d)	-	7.2-8.3(m)	4.2	12.6
$Ph_2P^+(OR)OC(:CH_2)Ph\ Cl^-$	+ 55.9	0.98(s)	4.04(d)	-	5.48(m)	7.3-8.2(m)	4.8	-
$(RO)_2P(O)CH_2COPh^*$	+ 19.0	0.86(s)	3.72(d)	3.65(d)	-	7.2-8.1(m)	4.8	22.8
$PhP(O)(OR)CH_2COPh$	+ 32.1	0.81(s)	3.52(m)[b]	3.77(dd)[c]	-	7.3-8.3(m)	b	c
$Ph_2P(O)CH_2COPh$	+ 28.2	-	-	4.14(d)	-	7.3-8.5(m)	-	15.6
$(RO)_2P(O)OC(:CH_2)Ph^*$	- 7.0	0.95(s)	3.78(d)	-	5.30(m)	7.2-8.1(m)	4.8	-
$PhP(O)(OR)OC(:CH_2)Ph$	+ 15.0	0.89(s)	3.77(d)	-	5.19(d)	7.2-8.2(m)	5.1	-
$Ph_2P(O)OC(:CH_2)Ph$	+ 29.7	-	-	-	5.15(m)	7.2-8.2(m)	-	-

[a] Dounlet of AB patterns: $\delta(H_A)$ 4.42, $\delta(H_B)$ 4.26 ppm, J_{AB} 8.0, $J_{POCH(A)}$ 4.0, $J_{POCH(B)}$ 4.1 Hz. [b,c] Complex Overlapping signals consisting of a doublet of AB patterns (CH_2OP), $\delta(H_A)$ 3.67, $\delta(H_B)$ 3.37 ppm, J_{AB} 8.9, $J_{POCH(A)}$ 5.1, $J_{POCH(B)}$ 4.8 Hz and a doublet of doublets (CH_2P), $\delta(H_A)$ 3.79, $\delta(H_B)$ 3.74 ppm, J_{AB} 0, $J_{POCH(A)}$ 18.4, $J_{POCH(B)}$ 17.5 Hz. The CH_2P signal could be removed and hence identified by shaking with D_2O for several hours.

* Were not isolated by author, data given from reaction mixtures.

II.3 BISDIMETHYLAMINO(METHYL)NEOPENTYLOXY-PHOSPHONIUM HALIDES

Alkyl phosphorodiamidites $(R_2'N)_2POR$ undergo typical Michaelis-Arbuzov reactions with a number of organic halides, although phosphorus-nitrogen fission may also occur.[61] Few examples of reactions involving simple alkyl halides have been reported[62] and the results are not entirely clear. Thus the ethyl esters (R = Et ; R' = Et or Pr^i) reacted exothermically with iodomethane to give unstable oily adducts which yielded the corresponding alkanephosphonic diamides on standing.

$$(R_2'N)_2POR + R''X \longrightarrow (R_2'N)_2P(OR)R''X \longrightarrow (R_2'N)_2P(O)R'' + RX$$

In addition, the diethylamino derivative (R = R' = Et) gave diethylammonium iodide. The only other phosphonium species reported in reactions of this type was obtained from the phenyl ester (R = Ph, R' = Bu^i) by heating with two equivalents of iodomethane.

Some investigations of the reactions of $ROP(NMe_2)_2$ with MeX (X = Cl, Br, I) were carried out by A.R. Qureshi.[48] Only the MeI gave a pure phosphonium salt. The bromide was contaminated with Me_4NBr and the chloride could not be obtained.

Further studies of these reactions have therefore been carried out.

The reaction of neopentyl N,N,N',N'-tetramethylphosphorodiamidite with iodomethane gave the alkoxyphosphonium iodide as the exclusive product.

$$(Me_2N)_2POR \quad + \quad MeX \xrightarrow{(a)} (Me_2N)_2P^+(OR)MeX^-$$

The corresponding phosphonium halides (X = Br or Cl) were also the major products of reaction with bromomethane and chloromethane but an increasing tendency to quaternization (side reaction) at nitrogen in the order I < Br < Cl led to phosphorus-nitrogen fission and formation of the tetra-alkylammonium halides which were isolated and positively identified by IR and chemical analysis. (See Table below).

Table XVI

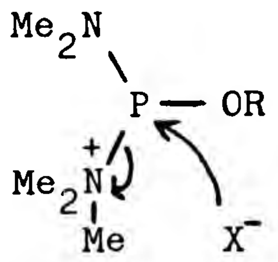
Products from the reactions of neopentyl N,N,N',N'-tetramethylphosphorodiamidite with halogenomethanes

X in MeX	Reaction products (mole %)		
(mol. equiv.)	$(Me_2N)_2P^+(OR)Me\ X^-$	$Me_2NP(OR)X$[a]	Me_4NX[b]
I (1.0)	100[a]	0	0
Br (2.6)	86[a] (88.6)[b]	14	3.9
Cl (2.5)	83[a] (30.1)[b]	17	10.4

[a] Yields by ^1H n.m.r. analysis of product mixtures.
[b] Isolated yields.

The cleavage reactions involve nucleophilic displacement of trialkylamine from trivalent phosphorus by halide ion and give the alkyl phosphoramidohalidites (X = Cl or Br), which were detected in solution by ^{31}P and ^{1}H n.m.r. spectroscopy. Although the ^{31}P chemical shifts of the phosphoramidohalidites ($ROPClNMe_2$ δ_P 178.44 and $ROPBrNMe_2$ δ_P 198.29) are close to those of the corresponding phosphorodihalidites ($ROPCl_2$ δ_P 178.31 and $ROPBr_2$ δ_P 200.44) and cannot be used to distinguish these species with certainty,

$$(Me_2N)_2POR + MeX \xrightarrow[\text{side reaction}]{(b)}$$



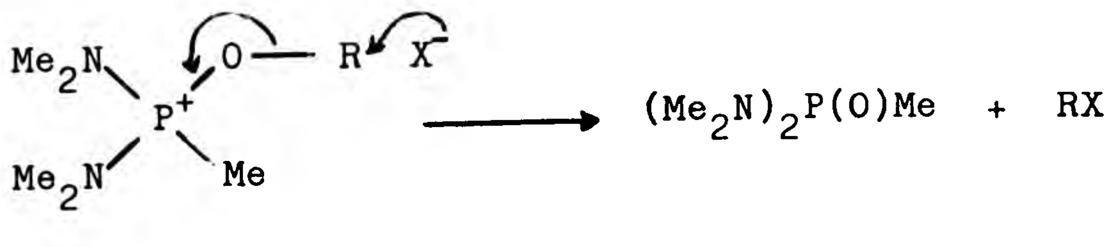
$$Me_2NP(OR)X + Me_3N \quad (\xrightarrow{MeX} Me_4NX)$$

the possible formation of the dihalidites by further cleavage was excluded in separate experiments.

$$Me_2NP(OR)X + MeX \xcancel{\longrightarrow} ROPX_2 + Me_3N$$

The proton n.m.r. spectra of these compounds are distinctive: for $Me_2NP(OR)X$ δ_H 3.65 or 3.55 (J_{POCH} 7.2 Hz), for $ROPX_2$ δ_H 3.83 or 3.88 (J_{POCH} 8.4 Hz). (See Table XVII). The absence of reaction between the phosphoramidohalidites and bromomethane or chloromethane is attributed to the electron-withdrawing effect of the halogen and to a consequent reduction in the tendency of the halidite to undergo quaternization at either phosphorus or nitrogen.

The bisdimethylamino(methyl)neopentyloxyphosphonium halides were thermally stable and were not hydrolysed appreciably at room temperature, the bromide and iodide being well-defined crystalline solids that could be handled in the open laboratory for considerable periods of time without difficulty. The chloride, in contrast, had a relatively low melting point, was difficult to crystallise, and was highly deliquescent; nevertheless, it underwent no detectable hydrolysis in aqueous solution during several hours at room temperature. (Some hydrolysis on long standing was indicated for all halides by the development of an odour of dimethylamine during storage). ^{31}P n.m.r. spectroscopy confirmed the tetracoordinate phosphonium structure for all three compounds in solution, the chemical shifts (δ_P ca. 60 ppm) being independent of the halogen present. In solvents such as $CDCl_3$ they may be expected to exist as ion-pairs.[63,64] Thermal decomposition in deuterochloroform was negligibly slow at room temperature but occurred at 100 °C to give neopentyl halides without rearrangement of the neopentyl group, indicating S_N2-type cleavage of the alkyl-oxygen bond:



($R = Me_3CCH_2$)

The early work of Michaelis indicated the formation of diethylammonium iodide in addition to methylphosphonic bisdiethylamide during decomposition of bisdiethylamino(methyl)ethyloxyphosphonium iodide in ether[62] but in the present studies no evidence was found for the formation of dialkylammonium salts when water was rigorously excluded.

$$(Et_2N)_2P(OEt)MeI \longrightarrow (Et_2N)_2P(O)Me \quad + \quad EtI \quad + \quad Et_2NH_2I$$

An n.m.r. peak assignable to the dimethylammonium cation (δ_H 2.66 ppm) appeared in certain circumstances, however, during thermal decomposition in deuterochloroform and was shown to be enhanced if water was deliberately added. Under these conditions, hydrolysis of the bromide led to the formation of small but identifiable amounts of dimethylammonium bromide and the dimethylammonium neopentyl methanephosphonate and bisdimethylammonium methanephosphonate:

$$(Me_2N)_2\overset{+}{P}(OR)Me\ X^- \xrightarrow{2H_2O} Me_2\overset{+}{N}H_2\ {}^-OP(O)(OR)Me \quad + \quad Me_2NH_2X$$

$$(Me_2N)_2\overset{+}{P}(OR)Me\ X^- \xrightarrow{3H_2O} (Me_2\overset{+}{N}H_2)_2\ {}^{=}O_2P(O)Me + ROH + HX$$

$(R = Me_3CCH_2)$

The ^1H n.m.r. and ^{31}P n.m.r. data for bisdimethylamino(methyl)neopentyloxyphosphonium halides and their decomposition products and starting materials are in Table XVII.

The relative importance of inductive and mesomeric effects of attached ligands in the stabilisation of alkoxyphosphonium salts has been discussed previously. For alkoxy and phenoxy ligands the inductive effect of oxygen was considered to be more important.[64] In the examples of alkoxyphosphonium salts carrying nitrogen ligands, as in the compounds referred to here, the mesomeric (electron-donating) influence of nitrogen appears to be more important in view of the stabilising effect of the dialkylamino groups. This conclusion is supported by recent X-ray diffraction studies of the bisdimethylamino(methyl)neopentyloxyphosphonium iodide which have shown the nitrogen atoms to be planar, with phosphorus-nitrogen bond lengths corresponding to significant double bond character.[65] The P....I distance of 4.987 Å confirms the phosphonium structure for the compound. Bond angles at phosphorus also demonstrate the tetrahedral structure.

Bond lengths (Å)

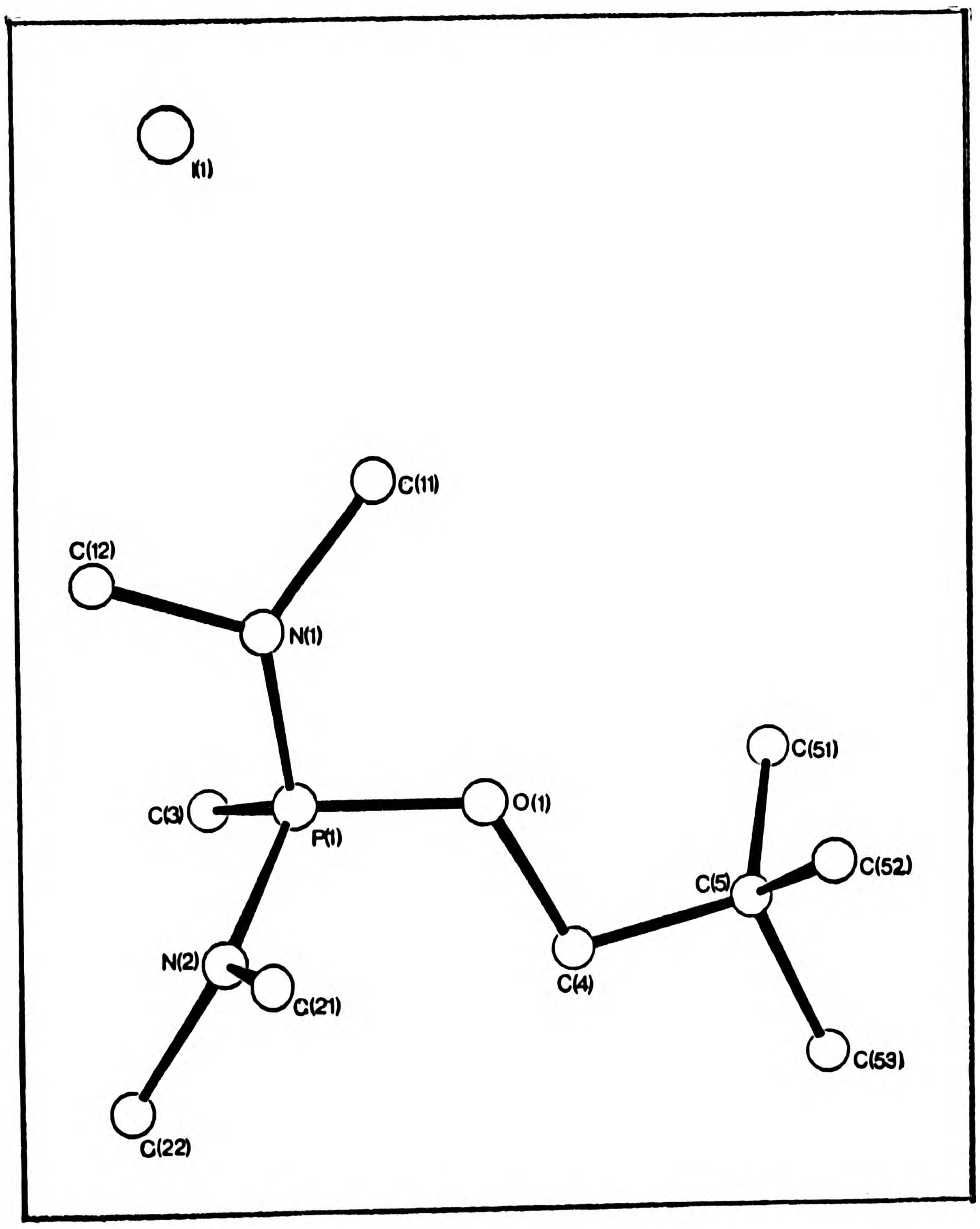
P(1) - O(1)	1.546(7)	P(1) - N(1)	1.581(10)
P(1) - N(2)	1.609(11)	P(1) - C(3)	1.768(14)
N(1) - C(12)	1.506(21)	N(1) - C(11)	1.408(25)
N(2) - C(22)	1.440(14)	N(2) - C(21)	1.467(18)

Bond Angles (°)

N(1) - P(1) - O(1)	114.1(4)	N(2) - P(1) - O(1)	100.3(5)
N(2) - P(1) - N(1)	109.2(6)	C(3) - P(1) - O(1)	109.4(5)
C(3) - P(1) - N(1)	108.6(6)	C(3) - P(1) - N(2)	115.3(6)
C(12)- N(1) - P(1)	119(1)	C(11)- N(1) - P(1)	125(1)
C(21)- N(2) - P(1)	121.6(8)	C(12)- N(1) - C(11)	114(1)
C(22)- N(2) - C(21)	112(1)	C(22)- N(2) - P(1)	119(1)

Fig. 21

X-ray crystal structure of $(Me_2N)_2\overset{+}{P}(OR)Me\ I^-$
(R = neopentyl)



NMR data ($CDCl_3$) for bisdimethylamino(methyl)neopentyloxyphosphonium halides, products and starting materials (Table XVII)

Structure	^1H							
	^{31}P	CH_2OP CH_2		Me_2		P-Me		Me-C
	δ (ppm)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)	J (Hz)	δ (ppm)
$(Me_2N)_2P(OR)MeCl^-$	60.34	3.86(d)	5.0	2.89(d)	10.2	2.37(d)	14.7	1.00
$(Me_2N)_2P(OR)MeBr^-$	60.18	3.93(d)	4.8	2.92(d)	9.9	2.47(d)	15.6	1.01
$(Me_2N)_2P(OR)MeI^-$	59.60	3.91(d)	4.2	2.89(d)	9.6	2.35(d)	13.8	1.01
$(Me_2N)_2P(O)Me$	36.84	-		2.61(d)	10.2	1.41(d)	15.0	-
$Me_2N^+H_2\,^-OP(O)(OR)Me$	24.00*	3.45(d)	5.1	2.53(s)	-	1.24(d)	15.9	0.91
$(Me_2N^+H_2)_2\,^-O_2P(O)Me$	23.52	-		2.66(s)	-	1.30(d)	16.0	-
$ROPCl_2$	178.31	3.88(d)	8.4	-		-		0.95
$ROPBr_2$	200.44	3.83(d)	8.4	-		-		0.96
$ROP(NMe_2)_2$	137.23	3.19(d)	6.3	2.51(d)	8.6	-		0.90
$ROPClNMe_2$	178.44	3.55(d)	7.2	2.66(d)	12.6	-		0.94
$ROPBrNMe_2$	198.29	3.65(d)	7.2	2.64(d)	13.8	-		0.96
Me_2NH_2Cl	-	-		2.70(s)	-	-		-
$(CH_3)_3\cdot CCH_2\ OH$	-	3.27(s)	-	-		-		0.90
$(CH_3)_3\cdot CCH_2Br$	-	3.27(s)	-	-		-		1.02

* quartet of triplets

SUMMARY

Preparation and properties of quasiphosphonium intermediates

During this work 18 crystalline solid quasiphosphonium intermediates have been isolated. All were prepared in dry conditions by nucleophilic attack of a phosphorus (III) ester on alkyl halide and with the use of a range of different temperatures (from below 0 °C to 290 °C) and reactions times (between 2 and 190 hours). Some were prepared without solvents, while others were prepared in solvents, such as acetone and chloroform. None of the phosphonium intermediates was soluble in ether, and it is for this reason that the intermediates were generally precipitated from reaction mixtures by the addition of sodium-dried ether.

All were washed with dry ether, dried under high vacuum and analysed by ^1H and ^{31}P n.m.r. spectroscopy. Where possible they were also assayed quantitatively for C, H, P, and halogen.

Stabilities

The alkyloxyphosphonium intermediates are more resistant to hydrolysis than the aryloxyphosphonium intermediates; they are, however, less thermally stable than the latter. A factor influencing the stability of the phosphonium intermediates is the relative number of RO and R' groups attached to phosphorus. Thus in the structure: $(RO)_nP^+R'_{4-n}\ X^-$ (R=Ph or neopentyl;

R'=Me or Ph; n=0 to 3), the stability of the intermediate is found to increase as n decreases. That is, the replacement of electron-attracting (-I) alkoxy or aryloxy groups by electron-releasing (+I) alkyl or aryl groups causes an increase in stability. The attachment of nitrogen ligands to phosphorus also causes a considerable increase in stability, possibly associated with electron donation from nitrogen to phosphorus (+M) by $P_{\pi}-d_{\pi}$ interaction. Steric factors, as in the neopentyl group, are also important in providing stabilisation. The possibility of isolating reaction intermediates, whose properties and reactions can then be studied under controlled conditions, make possible a much clearer and more precise understanding of reaction mechanisms than was possible before.

CHAPTER III EXPERIMENTAL

III.1 METHYLTRIARYLOXYPHOSPHONIUM HALIDES AND THEIR DECOMPOSITION PRODUCTS

STARTING MATERIALS

Alcohols

Neopentyl alcohol (2,2-Dimethyl-propan-1-ol)	Aldrich Chem.Co., Ltd.

Amines

N,*N*-Dimethylaniline G.P.R. (Dried barium oxide, redistilled 66 °C at 6 mmHg)	Hopkin & Williams Ltd.
N,N-Dimethylamine	" "
Pyridine (kept over potassium hydroxide)	" "

Halides

Methyl bromide Fine Chemicals	" "
Methyl chloride cylinder	B.D.H.Chemicals Ltd.
Methyl iodide G.P.R (Dried over sodium sulphate, redistilled b.p. 43 °C)	Hopkin & Williams Ltd.
α-Bromoacetophenone	Aldrich Chem.Co., Ltd.
α-Chloroacetophenone	" "
o-Cresol (redistilled 67 °C at 6 mmHg)	Hopkin & Williams Ltd.

Phosphorus compounds

Triphenyl phosphite (redistilled 172 °C at 0.5 mmHg)	Aldrich Chem.Co., Ltd.
Phosphorus trichloride G.P.R. (redistilled b.p. 73-74 °C)	Hopkin & Williams Ltd.
Phosphorus tribromide G.P.R	" "

Chlorodiphenylphosphine (redistilled 120 °C at 1.0 mmHg)	Aldrich Chem.Co., Ltd.
Dichlorophenylphosphine	" "

Solvents

AnalaR Acetone (refluxed with potassium permanganate, distilled b.p. 56 °C)	Hopkin & Williams Ltd.
Anhydrous ether (kept over sodium wire)	" "
Chloroform AnalaR (distilled from phosphorus pentoxide b.p. 61 °C)	" "
Petroleum spirit b.p. 30-40 °C (kept over sodium wire)	" "

Analytical Techniques and Instrumentation

Carbon-Hydrogen-Nitrogen Analysis

These elements were determined in the Microanalytical Laboratory of the Department using a Perkin-Elmer 240 Elemental Analyser. The samples were submitted in a small desiccator to protect them from moisture.

Halogens

Chlorine, bromine, iodine were determined by Vohlard's method.

A sample of halogen - containing compound (ca. 0.5 g) was weighed out in a sample tube, and was added to a stoppered conical flask containing 2.0 g potassium hydroxide in 100 ml H_2O. Then the sample tube was reweighed. As soon as the sample was dissolved, 2M nitric acid (25 ml) and an excess of 0.1M silver nitrate solution were added. The sample was then back titrated against 0.1M ammonium thiocyanate solution with ferric alum as indicator.

Phosphorus

The sample (0.2-0.5 g) was heated with concentrated sulphuric acid (ca. 10 ml) for 10 to 20 h in a Kjeldahl flask until clear. In some cases selenium (Kjeldahl catalyst) tablets were added. The contents were then cooled and concentrated nitric acid (ca. 10 ml) was added and the mixture was heated again until nitrous fumes were no longer evolved. The contents of the flask were then cooled, washed into a beaker and neutralized with 0.88 ammonia to methyl red indicator, and just acidified. Magnesia mixture (25 ml) was added, then phosphorus was precipitated as magnesium ammonium phosphate hexahydrate by adding 0.88 ammonia solution according to the method described by Vogel.[51] After 24 h the precipitate was filtered on a No. 4 sintered glass crucible and washed with dilute ammonia solution. The precipitate was redissolved in hot 10% hydrochloric acid and reprecipitated with magnesia mixture (2 ml) and 0.88 ammonia. After 24 h the final precipitate was washed with dilute ammonia, rectified spirit and anhydrous ether, dried in a desiccator and weighed as $MgNH_4PO_4.6H_2O$.

Nuclear Magnetic Resonance Spectra

^1H n.m.r. spectra were recorded on a Perkin-Elmer R12B spectrometer operating at 60 MHz with tetramethylsilane (TMS) as an internal standard.

^{31}P n.m.r. spectra were obtained on a Bruker WP80 spectrometer at 32.395 MHz, with 85% phosphoric acid as an external standard.

^{13}C n.m.r. spectra were obtained on the Bruker WP80 spectrometer at 20.12 MHz, with TMS as internal standard.

Infrared Spectroscopy

Spectra were recorded using neat liquids on a Perkin-Elmer 137 KBr infracord spectrometer. The KBr disc method was also used.

Refractive Indices

These were measured on a Bellingham and Stanley Ltd. Refractometer, thermostatted at 20 °C.

Gas Liquid Chromatography

A Perkin-Elmer 11 apparatus with flame-ionization detector and nitrogen as a carrier gas was used. The glass column was 1cm x 5m with 10% PEGA on Celite (60-80 mesh). The inlet pressure was 17 p.s.i. and the nitrogen flow-rate 20 ml/min at 115 °C.

Mass Spectroscopy

Spectra were obtained on an A.E.I. MS9 instrument operating at an electron-impact energy of 70 e.V. and with a source temperature of 180-200 °C.

X-Ray Crystallography

Determinations were performed by Dr. K. Henrick (PNL), on a Phillips PW1100 computer-controlled single crystal X-ray diffractometer. The sample (0.5 mm cube) was sealed into a glass tube and was loaded to the diffractometer centre automatically.

III.1 METHYLTRIARYLOXYPHOSPHONIUM HALIDES AND THEIR DECOMPOSITION PRODUCTS

Preparation of Methyltriphenoxyphosphonium Bromide[15]

Triphenyl phosphite (21.6 g, 1.0 mol. equiv.) was placed in a thick-walled glass tube with a constriction for sealing and corked. The tube was cooled to -80 °C in a mixture of acetone and dry ice. An ampoule with methyl bromide was cooled first to 0 °C in an ice-bath and then to -80 °C in the acetone-dry ice mixture. It was then carefully opened and liquid methyl bromide (approx. 5.6 ml, 9.69 g, 1.46 mol. equiv.) was added to the triphenyl phosphite.

The tube was sealed, brought to room temperature and the contents thoroughly mixed. It was then heated in a thermostatted oil bath at 100 °C for 50 h, after which time the mixture became white and crystalline.

The tube was then gradually cooled to -80 °C and opened, and the volatile materials (unreacted methyl bromide, δ_H 2.61 ppm in $CDCl_3$) were removed under water pump pressure and collected in a cold trap. The crude solid product was transferred into a sintered-glass funnel with a cap, washed several times with dry ether, and dried under high vacuum to yield methyltriphenoxyphosphonium bromide (25.7 g, 90%), m.p. 155-158 °C (sealed tube) (Found: Br, 19.6. Calc. for $C_{19}H_{18}BrO_3P$: Br, 19.7%), δ_H ($CDCl_3$) 3.24 (Me, d, J_{PCH} 17.4 Hz), 7.35 (phenoxy protons, s), δ_P ($CDCl_3$) 41.8 (quartet), δ_C ($CDCl_3$) 10.1 (CH_3, d, J_{PC} 127.0 Hz), 120.4 (d, J 4.3 Hz), 128.4 (d, J 1.2 Hz), 131.3 (d, J 1.2 Hz), 148.8 (d, J_{POC} 10.4 Hz) (Ar).

Preparation of Methyltriphenoxyphosphonium Iodide[15]

Redistilled triphenyl phosphite (16.7 g, 1 mol. equiv.) and methyl iodide (11.3 g, 1.48 mol. equiv.) were placed in a round-bottomed flask fitted with a double-surface reflux condenser and a calcium chloride tube. The mixture was refluxed gently at 86-90 °C on an oil bath for a total of 16 h, after which the mixture became viscous and reddish-brown in colour. After cooling for one hour the mixture started to solidify, and in two hours time the crude product (25.3 g, 104%) m.p. 70 °C (sealed tube) was obtained. It was then ether washed and vacuum dried to give the purified product as white needle-like crystals, m.p. 115 °C (sealed tube), δ_H ($CDCl_3$) 3.12 (Me, d, J_{PCH} 16.8 Hz), 7.44 (phenoxy protons, s). The only difference between the ^1H n.m.r. spectra of the crude and purified products was that the former had a peak at δ 2.12 assumed to be due to unreacted MeI, whereas in the latter this was missing. (Before heating the peak due to MeI in the reaction mixture lies at δ 1.84).

Recrystallisation of the crude product (3.8 g) by dissolving in acetone and adding ether as described[15] gave creamy crystals of methyltriphenoxyphosphonium iodide (2.2 g, 57.9%), m.p. 115 °C (sealed tube) (Found: I, 28.0. Calc. for $C_{19}H_{18}IO_3P$: I, 28.1%), δ_P ($CDCl_3$) 40.9 (quartet), δ_C ($CDCl_3$) 10.9 (CH_3, d, J_{PC} 127.5 Hz), 120.2 (d, J 4.1 Hz), 128.1 (d, J 1.4 Hz), 131.2 (s), 148.5 (d, J_{POC} 10.2 Hz) (Ar).

It was later discovered that dry chloroform was preferable to acetone for use in recrystallisation. Also sunlight was best excluded as this caused the crystals to decompose very quickly and to turn red in colour.

Preparation of Diphenyl Methanephosphonate[15]

Crude methyltriphenoxyphosphonium iodide (21.5 g) was treated with 2 M KOH (20 ml) with shaking and cooling. When all the solid had dissolved, the brownish colour disappeared and the mixture was then transferred to a separating funnel. The oily product was washed further with 2 M KOH (20 ml) and with H_2O, and dried over sodium sulphate to yield the crude phosphonate (8.8 g, 77.5%) as an oily liquid.

The product was distilled to give diphenyl methanephosphonate (6.0 g, 52.8%), b.p. 146-148 °C at 0.3 mmHg, n_D^{20} 1.5520, m.p. 35.0 °C (sealed tube) (after solidification on standing) (lit.[2] b.p. 190-195 °C at 11 mmHg, m.p. 36-37 °C), δ_H ($CDCl_3$) 1.65 (Me, d, J_{PCH} 17.7 Hz), 7.17 (phenoxy protons, s), δ_P ($CDCl_3$) 23.8 (quartet), δ_C ($CDCl_3$) 11.4 (CH_3, d, J_{PC} 144.6 Hz), 120.6 (d, J 4.4 Hz), 125.3 (d, J 1.1 Hz), 129.9 (d, J 1.1 Hz), 150.4 (d, J_{POC} 8.2 Hz) (Ar).

Attempted Deoxygenation of Diphenyl Methanephosphonate by Triphenyl Phosphite

Diphenyl methanephosphonate (0.16 g, 1.0 mol. equiv.) and triphenyl phosphite (0.20 g, 1.0 mol. equiv.) were sealed in a ^1H n.m.r. tube. The ^1H n.m.r. spectrum of the mixture showed a singlet for phenoxy protons in the aromatic region and a doublet (J_{PCH} 17.7 Hz) for the methyl protons. The difference in chemical shift of the two was 5.48 ppm. Then the tube was heated in an oil bath, starting at 80 °C, and gradually increasing the temperature in steps to 150 °C. After 15 h no noticeable reaction had occurred. Finally the tube was heated continuously in a thermostatted bath for 305.5 h (175 °C) and 30.5 h (220 °C) but there was still no change in the ^1H n.m.r. spectrum. After the addition of TMS the chemical shifts were shown to be exactly the same as those of the freshly prepared unheated reaction mixture: δ 1.52 (Me, d, J_{PCH} 17.7 Hz), 7.09 (phenoxy protons, s). The chemical shift difference remained the same at 5.43 ppm, δ_P ($CDCl_3$) 128.1 (s), 23.7 (quartet) and traces at -17.1

To make sure that deoxygenation had not occurred in the above experiment methyl iodide (0.18 g, 2 mol. equiv.) was added, the tube was resealed and the mixture heated for 16 h at 100 °C. The ^1H n.m.r. spectrum ($CDCl_3$) then showed only the presence of unreacted phosphonate, δ 1.69 (Me, d, J_{PCH} 17.7 Hz) and 7.18 (phenoxy protons, s), an excess of unreacted methyl iodide, δ 2.02 (s), and methyltriphenoxyphosphonium iodide, δ 3.09 (Me, d, J_{PCH} 16.8 Hz) and 7.40 (phenoxy protons, s).

Preparation of Tri-o-tolyl Phosphite

o-Cresol (38.3 g, 3 mol. equiv.), petroleum (15 ml, b.p. 30-40 °C) and pyridine (28.0 g, 3 mol. equiv.) were placed in a three-necked flask, fitted with mechanical stirrer, thermometer and dropping funnel. Phosphorus trichloride (16.2 g, 1 mol. equiv.) in petroleum (25 ml), was added slowly to the reaction mixture with cooling at 0 °C, and stirring. After the phosphorus trichloride was added another portion of petroleum (10 ml) was added and the mixture stirred for 20 minutes at room temperature. Ether (100 ml) was then added and pyridinium chloride removed by filtration. The filtrate was washed twice with distilled water (50 ml) and the etherate solution was dried with sodium sulphate, concentrated under high vacuum and distilled to give a main fraction (24.3 g, 58.4%), b.p. 160-162 °C at 0.01 mmHg, (Found: C, 72.2, H, 6.3, P, 8.5. Calc. for $C_{21}H_{21}O_3P$: C, 71.6, H, 6.0, P, 8.8%), n_D^{20} 1.5780, δ_H ($CDCl_3$) 2.17 (CH_3, s), 7.03 (phenoxy protons, m), δ_P ($CDCl_3$) 130.7 (s), δ_C ($CDCl_3$) 16.6 (CH_3, s), 120.5 (d, J 11.0 Hz), 124.1 (d, J 1.1 Hz), 126.9 (s), 129.9 (d, J 2.8 Hz), 131.4 (s), 150.4 (d, J_{POC} 2.2 Hz) (Ar).

Preparation of Methyltri-o-tolyloxyphosphonium Bromide

Tri-o-tolyl phosphite (15.35 g, 1 mol. equiv.) was placed in a thick-walled tube and cooled to -80 °C. Methyl bromide (8.06 g, 1.95 mol. equiv.), also at -80 °C, was slowly added to the ester. Then the tube was sealed and heated in thermostatted oil bath at 100 °C for 31.75 h after which time the mixture became a white solid. The tube was then cooled to -80 °C, opened, and volatile materials were removed at 15 mmHg.

The product was transferred to a sintered glass funnel, washed with dry ether and dried under high vacuum to give white crystals of methyltri-o-tolyloxyphosphonium bromide (13.5 g, 69.3%), m.p. 184-187 °C (sealed tube) (Found: C, 60.0, H, 6.6, Br, 17.8, P, 6.4. $C_{22}H_{24}BrO_3P$ requires: C, 59.1, H, 5.4, Br, 17.9, P, 6.9%), δ_H ($CDCl_3$) 2.19 ($\underline{CH_3}C_6H_4$, s), 3.26 (CH_3P, d, J_{PCH} 15.8 Hz), 7.33 (Ar, s), δ_P ($CDCl_3$) 42.1 (quartet), δ_C ($CDCl_3$) 10.9 (CH_3P, d, J_{PC} 125.4 Hz), 16.2 ($\underline{CH_3}C_6H_4$, s), 119.6 (d, J 2.7 Hz), 128.3-129.3 (m), 133.1 (s), 147.9 (d, J_{POC} 10.2 Hz) (Ar).

Preparation of Methyltri-o-tolyloxyphosphonium Iodide

Tri-o-tolyl phosphite (5.2 g, 1 mol. equiv.) and methyl iodide (3.17 g, 1.51 mol. equiv.) were sealed in a test tube, which was then heated in a thermostatted oil bath for 19.5 h at 100 °C. The content of the tube became a dark liquid, which solidified after cooling to room temperature. The tube was cooled, opened and volatile materials were removed under high vacuum. The product was transferred to a sinterred-glass funnel with a cap, washed with dry ether and dried under high vacuum to yield yellow crystals of methyltri-o-tolyloxyphosphonium iodide (5.0 g, 68.5%), m.p. 140-148 °C (sealed tube).

Recrystallisation of the product (5 g) by dissolving in a mixture of acetone and chloroform (1:1) then adding ether gave white crystals (3.5 g, 50%) m.p. 155-157 °C (sealed tube)

(Found: C, 52.5, H, 5.0, I, 25.6, P, 5.7. $C_{22}H_{24}IO_3P$ requires: C, 53.5, H, 4.9, I, 25.7, P, 6.3%), δ_H ($CDCl_3$) 2.20 ($\underline{CH_3}C_6H_4$, s), 3.16 (CH_3P, d, J_{PCH} 15.9 Hz), 7.32 (Ar, s), δ_P ($CDCl_3$) 41.3 (quartet), δ_C ($CDCl_3$) 11.9 (CH_3P, d, J_{PC} 127.0 Hz), 16.3 ($\underline{CH_3}C_6H_4$, s), 119.5 (d, J 3.1 Hz), 128.3-129.2 (m), 133.1 (s), 147.7 (d, J_{POC} 10.4 Hz) (Ar).

Thermal Decomposition of Methyltriphenoxyphosphonium Bromide in the absence of solvent

Methyltriphenoxyphosphonium bromide (approx. 0.8 g) was sealed in a ^{1}H n.m.r. tube. The tube was heated in a thermostatted bath at 175 °C for a total time of 86.5 h, after which the solid became a liquid that even after cooling remained as a clear viscous fluid. The ^{1}H n.m.r. spectrum showed signals for phenoxy protons centred at δ 7.26, phosphonium protons at δ 3.70 (Me, d, J_{PCH} 16.8 Hz), 41.6%, unidentified protons (X_1) at δ 3.20 (doublet, J 15.0 Hz), 28.3%, and phosphonate protons at δ 1.76 (Me, d, J_{PCH} 17.4 Hz), 30.0%, on the basis of signal height. The tube was then heated at 175 °C for another 40.5 h and at 200 °C for 12 h after which the ^{1}H n.m.r. spectrum showed new signals at δ 2.90 (doublet, J 14.4 Hz), 5.0% for other unidentified protons (X_2), phosphonium signals at δ 3.70 (Me, d), which had decreased from 41.6% to 9.5%, signals (X_1) at δ 3.20 (doublet) which had decreased from 28.3% to 28.1% and phosphonate signals at δ 1.76 (Me, d) which had increased from 30.0% to 57.3%. The tube was heated again at 200 °C for 52 h. Then the ^{1}H n.m.r. spectrum showed that the phosphonium protons at δ 3.70 (Me, d) had completely disappeared, and that protons (X_1) had decreased from 28.1% to 22.2%, protons (X_2) had increased from 5.0% to 9.0% and that the phosphonate protons had increased from 57.3% to 68.8%. The heating was prolonged at 200 °C (at intervals) for 262 h, and because decomposition was slow, for a further 78 h at 225 °C. Then the ^{1}H n.m.r. spectrum showed the appearance of more new signals for unidentified protons (X_3), which steadily grew at δ 1.66 (doublet, J 14.4 Hz), 16.0%, in the phosphonate area. After further heating for 55 h at 225 °C the ^{1}H n.m.r. spectrum again showed the appearance of new signals (X_4) at δ 2.22 (doublet, J 15.0 Hz), 1.2%, and the presence of the following signals: (X_1), (X_2), (X_3) and phosphonate.

The heating was further prolonged at 225 °C at intervals, for 26 h, and for 32 h at 250 °C, at which stage the ^{1}H n.m.r. spectrum showed that the signals at δ 3.11 (d) due to the protons (X_1) had disappeared. The heating was continued for another 30 h at 250 °C, after which the ^{1}H n.m.r. spectrum showed the following composition based on heights of the signals: δ 2.74 (doublet) (X_2) 9.7%, δ 2.22 (doublet) (X_4) 5.9% and δ 1.66 (doublet) (X_3) 17.5%. The phosphonate signals at 1.76 (doublet) however remained stable at 66.9%. Further heating was discontinued.

^{31}P n.m.r. ($CDCl_3$) showed δ -17.0 (s) due to $(PhO)_3P{=}O$, δ 23.7 (quartet) due to $(PhO)_2P(O)Me$, δ 52.9, 71.9, 22.5 (small signal) unidentified.

Identification of the Products of Thermal Decomposition of Methyltriphenoxyphosphonium Bromide in the absence of solvent

In a number of further experiments the products were identified by a combination of ^{1}H n.m.r., and ^{31}P n.m.r. as in the following table.

^{1}H N.M.R. and ^{31}P N.M.R. DATA OF THERMAL DECOMPOSITION OF $(PhO)_3P^+MeBr^-$ (Table I)

Time h	Temp. °C	Ar centred	$(PhO)_3P^+MeBr^-$			$(PhO)_2P^+Me_2Br^-$			$PhOP^+Me_3Br^-$			$(PhO)_2P(O)Me$		
			Height of signals	Compound %	δ_H Hz	Height of signals	Compound %	δ_H Hz	Height of signals	Compound %	δ_H Hz	Height of signals	Compound %	δ_H Hz
48	175	7.25 7.45	29.0	67.8	3.26 17.4	13.7	16.0	2.95 15.6	-	-	-	6.9	16.1	1.76 17.7
72	175	7.26 7.42	33.5	60.0	3.22 17.4	23.5	21.0	2.91 15.0	-	-	-	10.6	19.0	1.75 17.7
96	175	7.20 7.47	23.1	52.3	3.21 17.4	19.7	22.3	2.90 15.0	-	-	-	11.2	25.4	1.75 17.7
97	175	7.21 7.40	28.0	50.5	3.21 17.4	25.0	22.5	2.90 15.0	-	-	-	15.0	27.0	1.75 17.7
120	175	7.22 7.40	25.4	44.8	3.21 17.4	28.6	25.2	2.91 15.0	2.2	1.2	2.62 14.4	16.3	28.8	1.75 17.7
144	175	7.22 7.40	21.8	37.8	3.22 17.4	30.3	26.3	2.91 15.0	3.4	2.1	2.64 14.4	19.5	33.8	1.75 17.7
192	175	7.23 7.41	16.2	28.4	3.20 17.2	33.1	29.0 max.	2.88 15.0	4.4	2.6	2.59 14.4	22.8	40.0	1.73 17.7

Table I (continued)

Time h	Temp. ^{o} C	$(PhO)_3P^+MeBr^-$			$(PhO)_2P^+Me_2Br^-$			$PhOP^+Me_3Br^-$			$(PhO)_2P(O)Me$			Phosphate
		%	δ_H Hz	δ_P	%	δ_H Hz	δ_P	%	δ_H Hz	δ_P	%	δ_H Hz	δ_P	δ_P
98	175	45.6	3.74 16.8	41.8 quart.	20.9	3.23 15.6	96.2 sept.	-	-	-	33.5	1.76 17.4	24.0 quart.	-17.6 (s) *
168	175	32.5	3.22 17.4	42.0 quart.	28.3	2.90 15.0	96.2 sept.	2.2	2.63 14.4	-	37.0	1.75 17.7	23.7 quart.	-17.3 (s)
240	175	14.6	3.74 17.4	-	20.5	3.25 15.0	-	3.6	2.88 15.0	-	61.2	1.75 17.7	-	- *
120 24	175 200	6.9	3.56 16.8	-	17.3	3.14 15.6	-	3.4	2.86 14.7	-	72.3	1.76 17.7	-	- *
24 96	175 200	-	-	-	21.7	2.87 15.0	-	6.3	2.56 14.4	-	72.0	1.72 17.7	-	-
120 68	175 200	-	-	-	16.6	3.22 15.4	96.3 sept.	4.9	2.86 14.7	102.4 (m)	78.4	1.76 17.7	23.9 quart.	-17.6 (s) *

* ^{1}H n.m.r. without solvent

Table I (continued)

Time	Temp.	$(PhO)_2P^+Me_2Br^-$			$PhOP^+Me_3Br^-$			$(PhO)_2P(O)Me$			$PhOP(O)Me_2$			Phos-phate
h	° C	%	δ_H Hz	δ_P	%	δ_H Hz	δ_P	%	δ_H Hz	δ_P	%	δ_H Hz	δ_P	δ_P
120	210	11.5	2.89 14.7	-	7.7	2.56 14.1	-	76.9	1.74 17.7	-	3.8	1.63 14.4	-	-
120 107 81	175 200 225	2.9	3.18 15.0	96.0 sept.	10.3 max.	2.85 14.7	102.2 (m)	77.7	1.76 17.7	23.9 quart	8.1	1.64 14.7	(a) -	* -17.6 (s)
120 68 86 6	175 200 225 250	1.7	2.78 15.0	96.2 sept.	9.2	2.42 14.5	102.0 decet	78.1	1.62 17.4	23.8 quart	9.4	1.48 14.4	(aa) 54.5 sept.	(b) -17.6 (s)
3 3 16 11 3	190 220 230 240 260	1.3	2.78 15.0	96.5	6.7	2.42 14.5	102.5 (m)	85.0	1.62 17.7	23.6 quart	6.0	1.48 14.4	(aa) 55.0 (m)	(c) (d) -17.7 (s)

* ^1H n.m.r. without solvent. New unidentified signals: (a), δ_H (*) 2.36 (d, J 14.4 Hz), 0.9%, (aa), δ_H ($CDCl_3$) 1.98 (d, J 14.7 Hz), 1.4%, δ_P 22.8, 10.6 (small signals). (b), δ_C ($CDCl_3$) 10.8 (CH_3, d, J_{PC} 144.0 Hz) due to $(PhO)_2P(O)Me$, 14.7 (CH_3, d, J_{PC} 95.2 Hz) due to $PhOP(O)Me_2$, 12.3 (CH_3, d, J_{PC} 64.1 Hz) due to $PhOP^+Me_3Br^-$, 115.2 - 130.9 (m), 149.6 - 150.1 (m) Ar. (c), δ_P 127.8 (s) due to $(PhO)_3P$. (d), δ_H 7.2 (centred) Ar.

Thermal Decomposition of Methyltriphenoxyphosphonium Iodide in the absence of solvent

Methyltriphenoxyphosphonium iodide (approx. 0.8 g) was sealed in a ^{1}H n.m.r. tube. The tube was heated in a thermostatted bath at 150 °C for a total time of 71 h, after which the solid became a dark viscous fluid. The ^{1}H n.m.r. spectrum (without solvent) showed signals for phenoxy protons at δ 6.0-8.0 (m), phosphonium protons at δ 2.5-4.0 (broad signal), and phosphonate protons at δ 1.2-1.7 (d). The tube was opened, $CDCl_3$ with TMS was added and the tube was resealed.

The ^{1}H n.m.r. spectrum ($CDCl_3$) showed signals at δ 1.80 (Me, d, J_{PCH} 18.0 Hz) $(PhO)_2P(O)Me$ 11.0%, δ 3.23 (Me, d, J_{PCH} 16.3 Hz) $(PhO)_3P^+MeI^-$ 87.5%, new signals at δ 2.6 (Me, d, J_{PCH} 15.0 Hz) due to $(PhO)_2P^+Me_2I^-$ 1.5% and δ 7.45 (centred) phenoxy protons.

Identification of the Products of Thermal Decomposition of Methyltriphenoxyphosphonium Iodide in the absence of solvent

In a number of further experiments the products were identified by a combination of ^{1}H n.m.r., and ^{31}P n.m.r. as in the following table.

^{1}H N.M.R. and ^{31}P N.M.R. DATA OF THERMAL DECOMPOSITION OF $(PhO)_3P^+MeI^-$ (Table II)

Time h	Temp °C	Ar centred	$(PhO)_3P^+MeI^-$			$(PhO)_2P^+Me_2I^-$			$CH_3 - P^+ - O - P$			$(PhO)_2P(O)Me$		
			Height of signals	Compound %	δ_H Hz	Height of signals	Compound %	δ_H Hz	Height of signals	Compound %	dd** δ_H Hz	Height of signals	Compound %	δ_H Hz
½	175	7.48	tall	-	3.18 16.8	small	-	2.80 over-lapped	small	-	2.22 15.0	small	-	1.80 17.7
24	175	7.48	8.5	75.6	3.05 17.4	2.7	12.0	2.83 15.0	0.4	3.6	2.15 15.6	1.0	8.8	1.77 17.7
48	175	7.46	27.5	63.4	3.03 17.4	16.4	18.9	2.83 15.0	1.8	4.1	2.15 15.6	5.9	13.6	1.77 17.7
72	175	7.44	25.1	57.4	3.02 16.8	16.9	19.4	2.82 15.0	1.4	3.2	2.14 15.6	8.8	20.1	1.76 17.7
120	175	7.44	24.0	43.0	3.02 16.8	28.2	25.3	2.86 15.0	1.8	3.2	2.13 15.6	15.9	28.5	1.80 17.7
144	175	7.28 7.45	20.4	39.2	3.01 16.8	28.0	26.9	2.79 14.4	1.8	3.5	2.12 15.0	15.9	30.4	1.75 17.7
192	175	7.25 7.40	5.8	24.7	2.97 16.8	16.6	35.3	2.77 15.0	traces			8.3	35.3	1.73* 17.7

* New signals at δ 2.62 (d, J_{PCH} 14.0 Hz) $PhOP^+Me_3I^-$ (4.7%) ** δ_H J_{PCH}

Table II (continued)

Time h	Temp. ^{o}C	Ar cent-red	$(PhO)_3P^+MeI^-$			$(PhO)_2P^+Me_2I^-$			$PhOP^+Me_3I^-$			$(PhO)_2P(O)Me$		
			Height of sig-nals	Com-pound %	δ_H Hz	Height of sig-nals	Com-pound %	δ_H Hz	Height of sig-nals	Com-pound %	δ_H Hz	Height of sig-nals	Com-pound %	δ_H Hz
48	210	7.18	1.1	3.9	2.86 16.8	6.4	11.3	2.62 14.4	12.6	14.8	2.35 14.0	19.8	70.0	1.66 a 17.7
3 3 16	190 220 230	7.22	-	-	- -	7.0	4.4	2.50 14.0	22.0	9.3	2.21 13.8	68.0	86.3	1.65 bc 17.7

a δ_P $(CDCl_3)$ -17.0 (s) $(PhO)_3PO$, 23.9 (quartet) $(PhO)_2P(O)Me$, 40.8 (small) $(PhO)_3P^+MeI^-$, 94.1 (septet) $(PhO)_2P^+Me_2I^-$, 100.7 (decet) $PhOP^+Me_3I^-$, 124.4 (s) due to $(PhO)_3P$.

b δ_P $(CDCl_3)$ -17.5 (s), 24.0 (quartet) $(PhO)_2P(O)Me$, 23.2 (small) $Me_4P^+I^-$, 94.5 (m) $(PhO)_2P^+Me_2I^-$, 100.9 (m) due to $PhOP^+Me_3I^-$.

c δ_C $(CDCl_3)$ 11.43 $(CH_3$, d, J_{PC} 143.4 Hz) $(PhO)_2P(O)Me$,
12.11 $(CH_3$, d, J_{PC} 87.9 Hz) $(PhO)_2P^+Me_2I^-$
13.25 $(CH_3$, d, J_{PC} 63.5 Hz) due to $PhOP^+Me_3I^-$.

^{1}H N.M.R. DATA OF THERMAL DECOMPOSITION OF METHYLTRI-o-TOLYLOXYPHOSPHONIUM BROMIDE IN ABSENCE OF SOLVENT AT 200 °C. (Table III)

Phosphonium crystals (approx. 0.2 g) were sealed in each of 4 tubes, which after heating were opened and resealed with added $CDCl_3$.

Tube	Time	AROMATIC PROTONS		$(\underline{CH_3}C_6H_4O)_3P^+\underline{Me}Br^-$		$(\underline{CH_3}C_6H_4O)_2P(O)\underline{Me}$		$\underline{CH_3}C_6H_4Br$
		δ 7.25 (s)	δ 7.09 (s)	δ 2.15 (s)	δ 3.23 J 15.6 Hz	δ 2.23 (s)	δ 1.80 J 17.4 Hz	δ 2.34 (s)
No.	(h)	Height %	Height %	Height %	(mole %)	Height %	(mole %)	Height %
1	2	82.2	17.8	75.0	73.9	17.5	26.1	7.5
2	7	41.7	58.3	27.1	25.9	46.4	74.1	26.5
3	12	-	(m)	12.6	traces	54.6	ca. 92	32.8
4	21	-	(m)	8.6	-	58.5	ca. 95	32.9

A similar ^{1}H n.m.r. tube containing methyltri-o-tolyloxyphosphonium bromide was heated at 200 °C for 38.5 h to give $(CH_3C_6H_4O)_2P(O)Me$ δ_P ($CDCl_3$) 23.5 (quartet). Afterwards the tube was opened to the atmosphere for two days, then the ^{1}H n.m.r. spectrum ($CDCl_3$) showed $(CH_3C_6H_4O)_2P(O)Me$ at δ 1.75 (Me, d, J_{PCH} 17.8 Hz), 2.23 ($CH_3C_6H_4$, s), δ_P 23.9. δ_C 11.77 (CH_3P, d, J_{PC} 145.2 Hz), 16.4 ($CH_3C_6H_4$, s), o-$CH_3C_6H_4Br$ δ_H 2.31 (s), δ_C 22.8 (s), o-$CH_3C_6H_4OH$ δ_H 2.15 (s), δ_C 16.04 (s), small peaks of $CH_3C_6H_4OP(O)Me_2$ δ_P 55.8 and $P(O)Me_3$ δ_P 74.3.

^{1}H N.M.R. ($CDCl_3$) DATA OF THERMAL DECOMPOSITION OF METHYLTRI-o-TOLYLOXYPHOSPHONIUM IODIDE IN THE ABSENCE OF SOLVENT AT 200 °C. (Table IV)

Phosphonium iodide crystals (approx. 0.1 g) were sealed in each of two tubes, which after heating were opened and $CDCl_3$ was added.

Tube	Time	AROMATIC PROTONS	$(\underline{CH_3}C_6H_4O)_3P^+\underline{Me}I^-$		$(\underline{CH_3}C_6H_4O)_2P(O)\underline{Me}$		$\underline{CH_3}C_6H_4I$	Tolyl-POP
			δ 2.20 (s)	δ 3.17 J 15.9 Hz	δ 2.25 (s)	δ 1.81 J 18.0 Hz	δ 2.41 (s)	δ 2.00 (s)
No.	(h)		Height %	(mole %)	Height %	(mole %)	Height %	(mole %)
before heating		δ 7.32 (s)	100	100	-	-	-	-
1	3.00	(m) centred δ 7.32	50.6	41.3 δ 3.11	36.2	58.7	13.2	2.6
2	6.33	(m) centred δ 7.28 δ 7.19	30.7	20.4 δ 3.03	50.7	79.6	16.4	2.1

Isolation of Dimethyldiphenoxyphosphonium Bromide

Methyltriphenoxyphosphonium bromide crystals (4.3 g, 10.6 mmol) were sealed in a glass tube and heated for 7 days at 175 °C in a thermostatted oil bath. After heating the tube the contents became liquid, and on standing for several days started again to crystallise. After 8 weeks of standing the tube was cooled to -80 °C, volatile materials were removed at 0.5 mmHg, collected in a cold trap at -80 °C, and shown to be mainly bromobenzene, δ_H (multiplet) 7.1 to 7.6 ppm. The solid residue was washed with ether and vacuum dried to give a mixture (1.9 g) of $(PhO)_3P^+MeBr^-$ and $(PhO)_2PMe_2Br^-$. The filtrate, after concentration, showed the presence of phosphonate. Recrystallisation of the solid mixture (1.9 g) was carried out by dissolving it in a mixture of 20% acetone (ethanol free) and 80% chloroform (by volume) and adding dry ether to give a product (1.0 g), m. p. (sealed capillary) 145 °C for fast heating, and 145-180 °C for slow heating, which was mainly $(PhO)_2P^+Me_2Br^-$, δ_H ($CDCl_3$) 2.95 (Me, d, J_{PCH} 15.0 Hz), 7.45 (Ar, s). Small signals assigned to the impurities $(PhO)_3P^+MeBr^-$ and $(PhO)P^+Me_3Br^-$ were also present. The solid crystals were washed with cold acetone and then with hot acetone (40-45 °C) and were recrystallised from chloroform/ether, washed with dry ether, and dried under high vacuum to give pure dimethyldiphenoxyphosphonium bromide (0.6 g, 1.83 mmol, 34%), m. p. (sealed capillary) 200-210 °C, (Found: C, 50.3, H, 4.9. Calc. for $C_{14}H_{16}BrO_2P$: C, 51.4, H, 4.9%), δ_H ($CDCl_3$) 2.95 (Me, d, 6H,

J_{PCH} 14.7 Hz), 7.41 (Ar, s, 10H), δ_P ($CDCl_3$) 96.6 (septet), δ_C ($CDCl_3$) 12.4 (CH_3, d, J_{PC} 87.4 Hz), 120.9 (d, 4.4 Hz), 127.9 (d, J 1.6 Hz), 131.2 (d, J 1.1 Hz), 149.3 (d, J_{POC} 11.0 Hz) (Ar).

Hydrolysis of Dimethyldiphenoxyphosphonium Bromide

The nmr tube containing the above product was opened to the atmosphere and hydrolysis slowly took place (50% in 20 days) to give phenyl dimethylphosphinate $PhOP(O)Me_2$, δ_H ($CDCl_3$) 1.63 (Me, d, J_{PCH} 14.6 Hz), 7.19 (Ar, m), δ_P ($CDCl_3$) 60.7, δ_C ($CDCl_3$) 15.7 (CH_3, d, J_{PC} 95.2 Hz), 115.6-130.2 (m) (Ar). A singlet at 8.0 ppm in the ^1H n.m.r. spectrum due to OH of the phenol formed was also observed. Pure crystals of the phosphonium bromide left in a sample bottle over night, became liquid. The ^1H n.m.r. spectrum in deuterochloroform then showed the same signals for $PhOP(O)Me_2$.

Thermal Disproportionation of Dimethyldiphenoxyphosphonium Bromide

Dimethyldiphenoxyphosphonium bromide which was isolated and purified as above was sealed (in small amount) in two ^1H n.m.r. tubes which were placed in thermostatted oil bath. The solid did not melt at temperatures up to 200 °C but began to melt slowly at 210 °C and the heating was then continued for 7.5 days (190 hours). After this time one of the tubes was cooled and opened in a nitrogen atmosphere, and then deuterochloroform was added to dissolve the substance (approx. 12-15% concentration) and the tube was resealed. The ^1H n.m.r. spectrum showed signals at δ 2.89 (Me, d, J_{PCH} 15.0 Hz) due to $(PhO)_2P^+Me_2Br^-$ (36.5 mole %), at δ 2.59 (Me, d, J_{PCH} 14.4 Hz) due to $PhOP^+Me_3Br^-$ (35.3 mole %), and at δ 1.75 (Me, d, J_{PCH} 17.8 Hz) due to $(PhO)_2P(O)Me$ (28.2 mole %). In the aromatic region were three multiplets centred at 7.23, 7.35, 7.44 ppm, and a small singlet at 8.8 ppm. The ^{31}P n.m.r. spectrum confirmed the assignments for $(PhO)_2P^+Me_2Br^-$, δ 96.0 (septet), for $PhOP^+Me_3Br^-$, δ 102.2 (decet), and for $(PhO)_2P(O)Me$, δ 23.9 (quartet), and also showed the presence of $(PhO)_3P(O)$, δ -17.7 (singlet). A small signal at δ 125.1 was probably due to $(PhO)_3P$.

The second tube was heated at 210 °C for a total of 10-12 days after which time some drops of liquid condensed on the walls of the tube. The drops were separated from the solid mass by turning the tube upside down and the tube was left in a fridge for several weeks. The liquid product and the solid product were separated by cutting the tube in two and were separately dissolved in deuterochloroform in a N_2 atmosphere. The ^1H n.m.r. spectrum of the liquid product showed it to consist of diphenyl methylphosphonate δ 1.77 (Me, d, J_{PCH} 17.7 Hz) (86.8 mole %) and of phenyl dimethylphosphinate δ 1.70 (Me, d, J_{PCH} 14.4 Hz) (13.2 mole %); aromatic protons appeared as a wide multiplet centred at 7.24 ppm. The solid product contained dimethyldiphenoxyphosphonium bromide δ 2.92 (Me, d, J_{PCH} 14.7 Hz) (28.1 mole %), trimethylphenoxyphosphonium bromide δ 2.64 (Me, d, J_{PCH} 14.0 Hz) and then deuterochloroform was added to dissolve the substance (approx. 12-15% concentration) and the tube was resealed. The ^{1}H n.m.r. spectrum showed signals at δ 2.89 (Me, d, J_{PCH} 15.0 Hz) due to $(PhO)_2P^+Me_2Br^-$ (36.5 mole %), at δ 2.59 (Me, d, J_{PCH} 14.4 Hz) due to $PhOP^+Me_3Br^-$ (35.3 mole %), and at δ 1.75 (Me, d, J_{PCH} 17.8 Hz) due to $(PhO)_2P(O)Me$ (28.2 mole %). In the aromatic region were three multiplets centred at 7.23, 7.35, 7.44 ppm, and a small singlet at 8.8 ppm. The ^{31}P n.m.r. spectrum confirmed the assignments for $(PhO)_2P^+Me_2Br^-$, δ 96.0 (septet), for $PhOP^+Me_3Br^-$, δ 102.2 (decet), and for $(PhO)_2P(O)Me$, δ 23.9 (quartet), and also showed the presence of $(PhO)_3P(O)$, δ -17.7 (singlet). A small signal at δ 125.1 was probably due to $(PhO)_3P$.

The second tube was heated at 210 °C for a total of 10-12 days after which time some drops of liquid condensed on the walls of the tube. The drops were separated from the solid mass by turning the tube upside down and the tube was left in a fridge for several weeks. The liquid product and the solid product were separated by cutting the tube in two and were separately dissolved in deuterochloroform in a N_2 atmosphere. The ^{1}H n.m.r. spectrum of the liquid product showed it to consist of diphenyl methylphosphonate δ 1.77 (Me, d, J_{PCH} 17.7 Hz) (86.8 mole %) and of phenyl dimethylphosphinate δ 1.70 (Me, d, J_{PCH} 14.4 Hz) (13.2 mole %); aromatic protons appeared as a wide multiplet centred at 7.24 ppm. The solid product contained dimethyldiphenoxyphosphonium bromide δ 2.92 (Me, d, J_{PCH} 14.7 Hz) (28.1 mole %), trimethylphenoxyphosphonium bromide δ 2.64 (Me, d, J_{PCH} 14.0 Hz)

(54.2 mole %), and diphenyl methylphosphonate δ 1.77 (Me, d, J_{PCH} 17.7 Hz) (12.5 mole %). A signal at δ 2.19 (Me, d, J_{PCH} 14.0 Hz) was assigned to trimethylphosphine oxide (5.3 mole %). Aromatic protons appeared as multiplets centred at 7.25, 7.35 and 7.45 ppm.

Isolation of Trimethylphenoxyphosphonium Bromide containing some Dimethyldiphenoxyphosphonium Bromide

The contents of the above ^{1}H n.m.r. tube (solid product) were treated with dry ether. The liquid became cloudy and was placed in fridge over night when a very fine powder was precipitated. Then the liquid was decanted and the solid powder was washed with dry ether in a nitrogen atmosphere and dried under high vacuum to give a mixture of trimethylphenoxyphosphonium bromide δ_H ($CDCl_3$) 2.66 (Me, d, J_{PCH} 14.0 Hz) (64.0 mole %) and dimethyldiphenoxyphosphonium bromide δ 2.95 (Me, d, J_{PCH} 15.0 Hz) (36.0 mole %). Aromatic protons appeared as a multiplet centred at 7.48 ppm.

Hydrolysis of Trimethylphenoxyphosphonium Bromide and Dimethyldiphenoxyphosphonium Bromide

An nmr tube containing $(PhO)_2PMe_2Br$ (36.5 mole %), $PhOPMe_3Br$ (35.3 mole %), $(PhO)_2P(O)Me$ (28.2 mole %) and some triphenyl phosphate, in deuterochloroform was opened to the atmosphere for 4 weeks, after which it contained $Me_3P(O)$, δ_H 1.81 (Me, d, J_{PCH} 14.1 Hz), δ_P 76.8 (multiplet), $PhOP(O)Me_2$, δ_H 1.62 (Me, d, J_{PCH} 14.4 Hz), δ_P 58.0 (septet),

$(PhO)_2P(O)Me$, δ_H 1.75 (Me, d, J_{PCH} 17.7 Hz), δ_P 24.4 (quartet), and $(PhO)_3P(O)$, δ_P -17.7 (small singlet). Aromatic multiplet signals centred at 7.17 ppm, and a tall singlet at 8.63 ppm, were also observed.

In a similar experiment a mixture of $PhOPMe_3Br$ (64.0 mole %) and $(PhO)_2PMe_2Br$ (36.0 mole %) in $CDCl_3$ was allowed to undergo slow hydrolysis in a loosely sealed nmr tube. The composition at various time intervals was measured on the basis of the methyl doublets (recorded above) as follows:

Table V

Days	$(PhO)_2\overset{+}{P}Me_2\overset{-}{Br}$		$Ph O\overset{+}{P}Me_3Br^-$		$Me_3P(O)$		$PhOP(O)Me_2$	
	δ_H 2.84 Height	mole %	δ_H 2.59 Height	mole %	δ_H 2.10 Height	mole %	δ_H 2.04 Height	mole %
-	81	36.4	212	63.6	-	-	-	-
6	16	22.4	33	30.8	50	46.7	traces	-
8	16	21.9	20	18.4	65	59.6	traces	-[a]
12	8	17.4	6	8.7	42	60.9	6	13.0
18	11	15.8	traces	-	103	63.8	22	20.4
23 *	-	-	-	-	59	64.2	22	35.8[b]

a Small signal singlet at 8.10 ppm.
* The tube was fully opened to the atmosphere.
b Tall signal (s) at 5.25 ppm, probably due to (OH). Aromatic protons remained multiplet centred at 7.28 ppm.

Isolation of Mixture of Tetramethylphosphonium Bromide containing Trimethylphosphine Oxide

Dimethyldiphenoxyphosphonium bromide previously isolated, was sealed (in small amount) in a ^{1}H n.m.r. tube, which was heated in oil bath for 3 h at 190-220 °C, 25.5 h to 240 °C, 14.5 h to 260 °C and about 3 h at 290 °C. After cooling and opening the tube, $CDCl_3$ was added and the tube was resealed. The ^{1}H n.m.r. spectrum showed multiplet centred δ 7.27 (tall signal) (Ar), and presence of trimethylphenoxyphosphonium bromide, δ 2.53 (Me, d, J_{PCH} 14.0 Hz) (24.0 mole %), δ_P 101.9 (m), δ_C 13.3 (CH_3, d, J_{PC} 64.6 Hz), of diphenyl methanephosphonate, δ_H 1.74 (Me, d, J_{PCH} 17.7 Hz) (48.5 mole %), δ_P 23.9 (quartet), δ_C 11.5 (CH_3, d, J_{PC} 144.7 Hz), of phenyl dimethylphosphinate, δ_H 1.78 (Me, d, J_{PCH} 14.4 Hz) (14.9 mole %), δ_P 60.3 (m), δ_C (not shown), and a further product tetramethylphosphonium bromide $(CH_3)_4P^+Br^-$, δ_H 2.12 (Me, d, J_{PCH} 14.7 Hz) (12.5 mole %), δ_P 22.6 (small signal), δ_C 10.6 (CH_3, d, J_{PC} 55.5 Hz); also δ_P -17.7 due to $(PhO)_3P(O)$.

Then the tube was opened to the atmosphere, for 8 days, after which time the hydrolysis was nearly complete. The ^{1}H n.m.r. ($CDCl_3$) spectrum showed multiplet centred δ 7.25 (tall) (Ar) and presence of $(CH_3)_4P^+Br^-$ (not hydrolysed), δ 1.99 (Me, d, J_{PCH} 14.7 Hz) (9.5 mole %), δ_P 23.4 (small signal), δ_C 10.4 (CH_3, d, J_{PC} 55.5 Hz), of trimethylphosphine oxide $(CH_3)_3P(O)$, δ_H 1.9 (Me, d, J_{PCH} 13.5 Hz) (20.8 mole %), δ_P 70.5 (m), δ_C 15.3 (CH_3, d, J_{PC} 68.4 Hz), of $PhOP(O)Me_2$, δ_H 1.63 (Me, d, J_{PCH} 14.4 Hz) (15.9 mole %), δ_P 56.5 (m), δ_C 15.4 (CH_3, d, J_{PC} 95.2 Hz), and $(PhO)_2P(O)Me$, δ_H 1.75

(Me, d, J_{PCH} 17.4 Hz) (53.8 mole %), δ_P 24.2 (quartet), δ_C 11.4 (CH_3; d, J_{PC} 144.7 Hz); also δ_P -17.7 (s) due to $(PhO)_3P(O)$.

Then the solvent ($CDCl_3$) was removed at 12 mmHg, and the contents were extracted with D_2O, which was separated with a pipette into a ^1H n.m.r. tube, for which the ^1H n.m.r. spectrum (no reference) showed Me (doublet) for $(Me)_4P^+Br^-$, and Me (doublet) for $(CH_3)_3P(O)$.

The residue δ_H ($CDCl_3$) showed only 1.76 (Me, d, J_{PCH} 17.7 Hz) (90.3 mole %) due to $(PhO)_2P(O)Me$ and 1.59 (Me, d, J_{PCH} 14.4 Hz) (9.7 mole %) due to $PhOP(O)Me_2$, also 7.22 ppm centred tall signal (Ar). Then the D_2O solution was concentrated under high vacuum and DMSO was added for which the ^1H n.m.r. spectrum showed $(CH_3)_4P^+Br^-$ at δ 1.87 (CH_3, d, J_{PCH} 15.0 Hz) (31.4 mole %), δ_P 25.1 (small signal) (lit.[41] δ_P 25.2, solvent DMSO); δ_C (DMSO) 8.93 (CH_3, d, J_{PC} 55.5 Hz), and $(CH_3)_3P(O)$ at δ 1.55 (Me, d, J_{PCH} 13.2 Hz) (68.6 mole %) (lit.[42] δ_H 1.39, J_{H-P} 13.2), δ_P 53.7 (small signal), 51.1 due to $PhOP(O)Me_2$ (impurities), δ_C (DMSO) 16.3 (CH_3, d, J_{PC} 68.4 Hz).

Isolation of Trimethylphosphine Oxide

Methyltriphenoxyphosphonium bromide (5.0 g) was sealed in a test tube, then the tube was heated in an oil bath for a total time of 38.5 h at 190 to 260 °C. After cooling it became a mixture of solid and liquid. Then the tube was opened, and after removing volatile materials, small portion of ether was added and the crystals were filtered and washed with ether giving product of $(PhO)_2P^+Me_2Br^-$ (approx. 0.2 g, weight was not recorded), m.p. (sealed tube) softened at 160 °C, and melted at 180-195 °C. The ^1H n.m.r. ($CDCl_3$) spectrum confirmed the product at δ 2.96 (Me, d, J_{PCH} 14.7 Hz), 7.47 (s) (Ar).

The ethereal extract after concentration and adding ether gave a second product of grey solid approx. (0.4 g), (m. p. not recorded, very sensitive to moisture). The product was dissolved in $CDCl_3$ and was sealed in a ^1H n.m.r. tube. The ^1H n.m.r. spectrum showed δ 7.29, 7.37, 7.47 (Ar) and a mixture of three products: δ 2.88 (Me, d, J_{PCH} 15.0 Hz) (23.6 mole %), δ_P 96.5 (m), δ_C 12.2 (CH_3, d, J_{PC} 87.3 Hz) due to $(PhO)_2P^+Me_2Br^-$, δ_H 2.60 (Me, d, J_{PCH} 14.0 Hz) (52.3 mole %), δ_P 102.1 (m), δ_C 13.5 (CH_3, d, J_{PC} 64.7 Hz) due to $PhOP^+Me_3Br^-$, and δ_H 2.19 (Me, d, J_{PCH} 14.0 Hz) (24.0 mole %), δ_C 14.9 (CH_3, d, J_{PC} 67.7 Hz) due to $Me_3P(O)$ the hydrolysis product. Traces of $(PhO)_2P(O)Me$, δ_P 24.2, and (probably) $Me_4P^+Br^-$, δ_P 22.9 were also detected.

The tube was opened and the contents were hydrolysed with a few drops of H_2O (in dilute $CDCl_3$ hydrolysis by atmosphere was complete after 14 days). The ^1H n.m.r. spectrum ($CDCl_3$) then showed δ 8.56 (s) tall signal, and multiplet at 6.5-7.8 ppm (Ar), δ 3.4 (s) for H_2O, $Me_3P(O)$ at δ 1.92 (Me, d, J_{PCH} 14.0 Hz) (74.1 mole %), δ_P 74.4 (m), δ_C 15.0 (CH_3, d, J_{PC} 68.4 Hz), and $PhOP(O)Me_2$ at δ_H 1.69 (Me, d, J_{PCH} 14.0 Hz) (25.9 mole %), δ_P 58.7 (m), δ_C 15.2 (CH_3, d, J_{PC} 94.6 Hz), and small signals for $(CH_3)_4P^+Br^-$, δ_H 2.22 (CH_3, d, J_{PCH} 13.8 Hz) (3.1 mole %), δ_P 21.9. The solvent ($CDCl_3$) was then removed at 12 mmHg and the residue was extracted with D_2O, which was separated with a pipette to give a solution containing trimethylphosphine oxide $Me_3P(O)$, δ_H (D_2O) 1.57 (Me, d, J_{PCH} 13.2 Hz) (99%), δ_C (D_2O) 18.7 (CH_3, d, J_{PC} 70.2 Hz), (J_{C-H} 128.8 Hz) coupling constant in D_2O, (lit.[43] C^{13}-H coupling constant 129 in D_2O), δ_P(D_2O) 53.6 (at pH 4), 53.0 (at pH 7) (decet), m.p. 130 °C (sealed tube), m/z(%) 92 ($M^{+\cdot}$, 100), 77 (Me_2PO^+, 100).

Isolation of Dimethyldiphenoxyphosphonium Iodide

Methyltriphenoxyphosphonium iodide crystals (16.0 g, 35.4 mmol) were sealed in a glass tube and then heated for 120 h at 175 °C in a thermostatted bath. After cooling the tube, the contents became a dark viscous fluid. Then the tube was opened, volatile materials were removed at 12 mmHg, by collecting in a cold trap at -80 °C, and shown to be iodobenzene δ_H ($CDCl_3$) 6.7-7.8 ppm (m) (Ar), and 2.12 ppm due to (unreacted) methyl iodide. The residue showed signals at δ_H ($CDCl_3$) 1.73 (Me, d, J_{PCH} 17.7 Hz) due to $(PhO)_2P(O)Me$ (47.8 mole %), 2.12 (Me, dd) due to CH_3P^+-O-P intermediate (traces), 2.64 (Me, d, J_{PCH} 14.4 Hz) due to $(PhO)_2P^+Me_2I^-$ (18.4 mole %), and 2.83 (Me, d, J_{PCH} 16.8 Hz) due to $(PhO)_3P^+MeI^-$ (33.8 mole %).

Then dry ether was added to the residue, which precipitated dark crystals a mixture of $(PhO)_2P^+Me_2I^-$ and $(PhO)_3P^+MeI^-$ (approx. 6 g). The filtrate after concentration, showed the presence of phosphonate. The solid mixture was recrystallised from acetone/ether several times, and finally from acetonitrile/ether, washed with dry ether, and dried under high vacuum to give pure white needles of dimethyldiphenoxyphosphonium iodide (1.0 g, 2.67 mmol, 15.2%), m. p. 152-155 °C (sealed tube) (Found: C, 43.3, H, 4.3, I, 33.9. $C_{14}H_{16}IO_2P$ requires: C, 44.9, H, 4.3, I, 33.9%), δ_H ($CDCl_3$) 2.91 (Me, d, J_{PCH} 14.4 Hz), 7.45 (Ar, s), δ_P ($CDCl_3$) 94.8 (septet), δ_C 13.2 (CH_3, d, J_{PC} 87.9 Hz), 120.5 (d, J 4.3 Hz), 121.2 (s), 128.0 (s), 131.3 (s), 149.1 (d, J_{POC} 11.0 Hz) (Ar).

Hydrolysis of Dimethyldiphenoxyphosphonium Iodide

The ^1H n.m.r. tube containing the above product was opened to the atmosphere and hydrolysis slowly took place (in 11 days) to give phenyl dimethylphosphinate $PhOP(O)Me_2$, δ_H 1.78 (Me, d, J_{PCH} 14.2 Hz), 6.7-7.5 (m), and 8.22 (Ar, s), δ_P 63.4 (m), δ_C 15.2 (CH_3, d, J_{PC} 95.6 Hz), 115.6-130.3 (m), 149.7 (d, J_{POC} 9.5 Hz) (Ar). Pure crystals of dimethyldiphenoxyphosphonium iodide in a desiccator became red in 24 h. The same crystals left in a sample bottle over 2 days, became red liquid; the ^1H n.m.r. spectrum ($CDCl_3$) then showed the same signals for $PhOP(O)Me_2$.

Thermal Decomposition of Dimethyldiphenoxyphosphonium Iodide

Dimethyldiphenoxyphosphonium iodide isolated and purified was sealed (in small amount) in a ^1H n.m.r. tube, which then was heated in an oil bath for total time of 28.5 h at

190-240 °C. After cooling the tube was opened, $CDCl_3$ added and the tube was resealed. The ^1H n.m.r. spectrum showed δ 7.26, 7.40, 7.49 multiplet (Ar), δ 2.80 (Me, d, J_{PCH} 14.4 Hz), δ_P 93.7 (m), δ_C 12.9 (CH_3, d, J_{PC} 87.9 Hz) due to $(PhO)_2P^+Me_2I^-$ (26.0 mole %), which had not decomposed, δ_H 2.60 (Me, d, J_{PCH} 13.8 Hz), δ_P 100.4 (m), δ_C 14.1 (CH_3, d, J_{PC} 64.5 Hz) due to $PhOP^+Me_3I^-$ (36.2 mole %), and δ_H 1.75 (Me, d, J_{PCH} 17.8 Hz), δ_P 24.0 (m), δ_C 11.6 (CH_3, d, J_{PC} 144.0) due to $(PhO)_2P(O)Me$ (37.8 mole %). Also δ_P 40.4 (small signal) probably due to $(PhO)_3P^+MeI^-$.

Then the tube was opened to the atmosphere, when hydrolysis was very slow (approx. 15-20 days), after which δ_H ($CDCl_3$) showed multiplet lines centred at δ 7.15, 7.20 (Ar), and overlapped signals at δ 1.70 (Me, d, J_{PCH} 13.8 Hz), δ_P 65.7 (m), δ_C 16.2 (Me, d, J_{PC} 69.6 Hz) due to $Me_3P(O)$, δ_H 1.6 (Me, d, J_{PCH} 14.0 Hz), δ_P 59.1 (m), δ_C 15.7 (Me, d, J_{PC} 92.2 Hz) due to $PhOP(O)Me_2$, and δ_H 1.75 (Me, d, J_{PCH} 17.8 Hz), δ_P 25.5 (m), δ_C 11.6 (Me, d, J_{PC} 144.0 Hz) due to $(PhO)_2P(O)Me$.

Isolation of Trimethylphenoxyphosphonium Iodide containing traces of Tetramethylphosphonium Iodide

A ^1H n.m.r. tube, approximately ¾ filled with methyltriphenoxyphosphonium iodide, was sealed. The tube was heated in a thermostatted bath at 210 °C for approx. 120 h. Then the tube was opened and dry ether was added, which precipitated dark crystals; these were recrystallised from acetone/ether, washed with dry ether, and high vacuum dried to give trimethylphenoxyphosphonium iodide, m.p. 139-142 °C (sealed tube), δ_H ($CDCl_3$) 2.65 (Me, d, J_{PCH} 13.5 Hz), 7.42 (Ar, s), δ_P ($CDCl_3$) 101.3 (decet), and traces of tetramethylphosphonium iodide, δ_H ($CDCl_3$) 2.25 (Me, d, J_{PCH} 13.5 Hz), δ_P ($CDCl_3$) 23.3 (small signal).

The washings, on standing gave a second very small crop of long needles, δ_H 1.89 (d, J_{PCH} 12.2 Hz) (unidentified).

Isolation of Trimethylphosphine Oxide from the Thermal Decomposition of $(PhO)_3P^+MeI^-$

Methyltriphenoxyphosphonium iodide (7.7 g, 17.0 mmol) was sealed in a test tube and then heated in an oil bath for a total of 21.5 h at 190-240 °C. After the tube was opened, and volatile materials removed, ether was added to precipitate dark crystals, which were filtered, washed with ether and vacuum dried to give 1 g of a mixture, m. p. (sealed tube) softened 80-85 °C, melted about 115 °C, δ_H ($CDCl_3$) 7.43 (m), 7.49 (s) (Ar), 2.76 (Me, d, J_{PCH} 14.0 Hz), δ_P 93.2 (septet). δ_C 13.2 (CH_3, d, J_{PC} 87.9 Hz) due to $(PhO)_2P^+Me_2I^-$ (45.8 mole %), and δ_H 2.54 (Me, d, J_{PCH} 13.5 Hz), δ_P 100.1 (decet), δ_C 14.4 (CH_3, d, J_{PC} 64.7 Hz) due to $PhOP^+Me_3I^-$ (54.2 mole %). The ethereal washings after concentration gave $(PhO)_2P(O)Me$ (6 g, 13.3 mmol) .

Then the contents of the ^1H n.m.r. tube were hydrolysed with a few drops of H_2O, and the ^1H n.m.r. spectrum ($CDCl_3$) showed δ 6.6 to 7.4 (Ar, m), 1.70 (Me, d, J_{PCH} 13.8 Hz), δ_P 57.6 (septet), δ_C 15.6 (CH_3, d, J_{PC} 95.8 Hz) due to

PhOP(O)Me_2 (50.2 mole %), δ_H 1.79 (Me, d, J_{PCH} 13.2 Hz), δ_P 64.6 (decet), δ_C 16.4 (CH_3, d, J_{PC} 69.6 Hz) due to $Me_3P(O)$ (49.8 mole %).

The solvent ($CDCl_3$) was removed at 15 mmHg, and the residue was extracted with H_2O (0.5 ml), which was separated and concentrated under high vacuum, to give trimethylphosphine oxide, δ_H (DMSO-d_6) 1.50 (Me, d, J_{PCH} 13.2 Hz)^a, δ_P (DMSO-d_6) 46.4 (m), δ_C (DMSO-d_6) 16.7 (CH_3, d, J_{PC} 68.4 Hz).

(a) (lit.^{42} δ_H 1.39, J_{H-P} 13.2 in DMSO).

A similar ^1H n.m.r. tube containing the mixture of PhOP(O)Me_2 and P(O)Me_3 was additionally hydrolysed with drops of KOH solution and extracted with ether. Then the ethereal extract was washed with H_2O, dried (Na_2SO_4), and concentrated to give δ_H ($CDCl_3$) 6.5-7.5 (Ar, m) 1.62 (Me, d, J_{PCH} 13.8 Hz), δ_P ($CDCl_3$) 55.2 due to PhOP(O)Me_2. The aqueous layer was evaporated to dryness under reduced pressure to give a residue δ_H ($CDCl_3$) 1.47 (Me, d, J_{PCH} 13.5 Hz), δ_P ($CDCl_3$) 40.0 of purified $Me_3P(O)$, δ_P ($CDCl_3$) 57.3 (at pH 4).

Hydrolysis of Methyltriphenoxyphosphonium Bromide in Deuterochloroform

Methyltriphenoxyphosphonium bromide, approx. 4% solution in deuterochloroform, was transferred to an unsealed ^{1}H n.m.r. tube. Half an hour after preparation, the ^{1}H n.m.r. spectrum showed signals at δ 7.38 (Ar, s), δ 3.12 (Me, d, J_{PCH} 17.1 Hz) (phosphonium salt, 77 mole %), and δ 1.75 (Me, d, J_{PCH} 17.7 Hz) (phosphonate, 23 mole %). As time progressed the phosphonium peaks decreased in size, and moved from δ 3.12 to δ 2.93, while the phosphonate peaks at δ 1.75 grew at a constant chemical shift. A second peak also appeared in the phenoxy protons region at δ 7.18 corresponding to the phosphonate product and grew steadily, while the original phenoxy proton signal at δ 7.38 (for the phosphonium salt) decreased in size and slowly shifted to δ 7.28. After 48 h exposure to air both peaks were equal in height. Finally a peak for the OH group of phenol appeared at δ 6.12, and moved slowly to δ 4.85. (Confirmed by adding a drop of phenol when a single OH peak was obtained at δ 5.96). Hydrolysis of the phosphonium salt to the phosphonate was 90% complete after 70 h, and 100% complete after 11 days.

In a second experiment methyltriphenoxyphosphonium bromide, approx. 12% solution in deuterochloroform, was placed in an unsealed ^{1}H n.m.r. tube and the ^{1}H n.m.r. spectrum was monitored at ambient temperature over a period of 18.5 days. The results were as follows (t/h, phosphonium salt/mole %, phosphonate/mole %): 0, 100, 0; 14, 98.58, 1.42; 22, 97.40, 2.60; 48, 92.31, 7.69; 89, 80.72, 19.28; 171, 62.29, 37.71; 218, 52.22, 47.78; 262.5, 49.40, 50.60; 357.5, 37.43, 62.57; 446, 27.55, 72.45.

Hydrolysis of Methyltriphenoxyphosphonium Iodide in Deuterochloroform

Methyltriphenoxyphosphonium iodide, approx. 12% solution in $CDCl_3$, was transferred to a loosely capped ^1H n.m.r. tube, δ_H 3.08 (Me, d, J_{PCH} 16.5 Hz), 7.43 (Ar, s). After 20 h at room temperature phosphonate signals appeared at δ_H 1.80 (Me, d, J_{PCH} 17.7 Hz) (13 mole %), in addition to the phosphonium signals (87.0 mole %) as above. The change of phosphonium compound to phosphonate was observed for 13 days by ^1H n.m.r. spectroscopy. The results were as follows (t/h, phosphonium salt/mole %, phosphonate/mole %): 20, 86.6, 13.4; 39.5, 73.3, 26.7; 64.75, 57.5, 42.5; 90, 48.0, 52; 137.5, 32.2, 67.8; 162.5, 23.8, 76.2; 186.5, 18.5, 81.5; 217.5, 12.2, 87.8; 240, 10.0, 90.0; 13 days - 100%.

Hydrolysis of Methyltri-o-tolyloxyphosphonium Bromide in Deuterochloroform

Methyltri-o-tolyloxyphosphonium bromide, approx. 8% solution in deuterochloroform, was transferred to an unsealed ^{1}H n.m.r. tube. After 20 h the ^{1}H n.m.r. spectrum showed signals at δ 7.26, 7.10 (Ar, m), δ 2.16 (CH_3, s), 3.24 (Me, d, J_{PCH} 15.6 Hz) (phosphonium salt, 74.2 mole %) and δ 2.24 (CH_3, s), 1.81 (Me, d, J_{PCH} 17.4 Hz) (phosphonate, 25.8 mole %). As time progressed the phosphonium peaks decreased in size, while the phosphonate peaks at δ 2.24 and δ 1.81 grew at constant chemical shift. The results were as follows (t/h, phosphonium salt/mole %, phosphonate/mole %): 20, 74.2, 25.8; 39.5, 69.9, 30.1; 48.33, 65.1, 34.9; 63.5, 58.4, 41.6; 13 days, -, 100. A peak for the OH group of phenol appeared at δ 5.27 and moved slowly to δ 5.8; a peak for CH_3 of cresol was recorded at δ 2.21 (s).

Hydrolysis in air

Crystals of $(CH_3C_6H_4O)_3P^+MeBr^-$ were placed and stoppered in a sample tube; they became liquid over-night at room temperature. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed that hydrolysis was complete.

Hydrolysis of Methyltri-o-tolyloxyphosphonium Iodide in Deuterochloroform

Methyltri-o-tolyloxyphosphonium iodide, approx. 8% solution in deuterochloroform, was transferred to a loosely-capped ^{1}H n.m.r. tube, δ_H 3.15 (Me, d, J_{PCH} 16.2 Hz), 2.18 (CH_3, s) and 7.31 (Ar, s). After 25 h phosphonate signals appeared at δ_H 2.24 (CH_3, s), 1.80 (Me, d, J_{PCH} 17.4 Hz) (55.5 mole %), in addition to the phosphonium signals (44.5 mole %) as above. The change of phosphonium compound to phosphonate was observed for 65 h by ^{1}H n.m.r. spectroscopy. The results were as follows (t/h, phosphonium salt/mole %, phosphonate/mole %): 25.0, 44.5, 55.5; 29.5, 36.4, 63.6; 44.5, 32.8, 67.2; 53.5, 31.5, 68.5; 65.0, 28.1, 71.9; 9 days, - , 100. A peak for the OH group of phenol appeared at δ 5.10 and moved slowly to δ 6.20.

Thermal Decomposition of Methyltriphenoxyphosphonium Bromide in Deuterochloroform in a Sealed ^{1}H n.m.r. Tube

Methyltriphenoxyphosphonium bromide, approx. 8% solution in deuterochloroform, was prepared in a sealed ^{1}H n.m.r. tube. The ^{1}H n.m.r. spectrum, δ 7.39 (phenoxy protons, s), 3.22 (Me, d, J_{PCH} 17.4 Hz) did not change after 90 h at room temperature, followed by 64 h at 55 °C, 14 h at 95 °C, and 51.5 h at 100 °C in a thermostatted oil bath. The temperature was increased to 125 °C and new, unexpected peaks appeared centered at δ 2.15 (apparently two closely spaced doublets, each with J_{PCH} 14.4 Hz but subsequently shown to be a doublet of doublets due to the structure P-O-P-Me), about 24.7% in height relative to the phosphonium doublet (δ 3.07) after 15.5 h, and 38.8% in height after 60 h. Then the temperature was increased to 150 °C for 37.5 h during which time signals due to diphenyl methanephosphonate, δ 1.75 (Me, d, J_{PCH} 17.7 Hz), appeared.

After a further 46.5 h at 175 °C a new phenoxy signal δ 7.22 (singlet) grew steadily, together with peaks due to dimethyldiphenoxyphosphonium bromide, δ 2.74 (J_{PCH} 14.4 Hz). Heating was continued at 175 °C for another 230 h, when the phosphonium peaks at δ 7.33 and at 2.98 (Me doublet) disappeared along with the doublet of doublets at δ 2.15. The phosphonate signals δ 7.21 (singlet), 1.75 (Me doublet, J_{PCH} 17.7 Hz), and those due to $(PhO)_2PMe_2Br$, remained. ^{31}P n.m.r. (sealed tube) confirmed the presence of

$(PhO)_3P(O)$ δ -18.0 (16.4%), $(PhO)_2P(O)Me$ δ +23.64 (50.5%), $(PhO)_3P^+MeBr^-$ δ 43.2 (traces), $(PhO)_2P^+Me_2Br^-$ δ 95.8 (18.6%), and showed peak for unidentified compound at 33.7 (14.5%), based on integration of the broad-band decoupled spectrum.

The course of this experiment was followed by ^1H n.m.r. and the results are shown in the following table.

Thermal decomposition of $(PhO)_3P^+MeBr^-$ in $CDCl_3$ at 55-175 °C. (Table VI)

Spectrum Nos	Temperature °C	Heating time (hours)	Total heating (hours)	Phenyl protons δ 7.39 Height %	Phenyl protons δ 7.21 Height %	P^+MeBr^- δ 3.22 Height %	$P^+Me_2Br^-$ δ 2.74 Height %	MeP-O-P δ 2.15 Height %	P(O)Me δ 1.75 Height %
1	room	after	sealing	100	-	100	-	-	-
3	room	after	90 hours	100	-	100	-	-	-
4	55	64	64	100	-	100	-	-	-
5	95	14	78	100	-	100	-	-	-
6	100	51.5	129.5	100	-	100	-	-	-
7	125	15.5	145	98	- (m)	75.3	-	24.7	-
9	125	21.5	166.5		-	66.3	-	33.7	-
10	125	23	189.5		-	61.2	-	38.8	-
11	150	18.5	208		-	72.9	-	23.5	3.6
12	150	19	227		-	71.4	-	23.5	5.0
13	175	46.5	273.5	48.7	51.2	30.5	20.8	31.6	17.0
14	175	20	293.5	43.4	56.6	25.1	26.0	26.8	22.1
15	175	23	316.5	35.0	65.0	20.0	26.8	21.6	31.5
16	175	18.5	335	25.2	74.8	17.3	27.3	18.9	36.5
17	175	70	405	17.3	82.7	10.3	26.9	12.0	50.8
18	175	24.5	429.5	17.4	82.6	5.2	30.8	traces	63.9
20	175	74.5	504	10.8	89.2	traces	26.8	-	73.2

Thermal Decomposition of Methyl-Triaryloxyphosphonium Halides in $CDCl_3$ under various conditions

$MeP^+(OPh)_3Br^-$, $MeP^+(OPh)_3I^-$, $MeP^+(OC_6H_4\text{-}\underline{o})_3Br^-$, and $MeP^+(OC_6H_4\text{-}\underline{o})_3I^-$ were each dissolved in $CDCl_3$ and heated in sealed ^1H n.m.r. tubes. The product compositions were monitored by following the ^1H n.m.r. signals for the Me-P protons as described in the previous experiment. Results are shown in the following tables (pp. 128-138). In each case the components are given as mole %.

Thermal Decomposition of Methyltriphenoxyphosphonium Bromide (4.5% in $CDCl_3$) at 125 °C

Total heating time (h)	P^+MeBr^-	$P^+Me_2Br^-$	MeP-O-P	P(O)Me
-	91.5	-	-	8.5
8.0	80.4	-	6.7	12.9
24.5	66.8	-	19.4	13.8
29.0	61.2	-	24.4	14.4
32.0	52.8	-	28.2	19.0
48.5	45.7	-	36.9	17.4
68.5	44.2	-	38.5	17.3
95.0*	38.5[a]	-	41.8[b]	19.7[c]

*) During 8 weeks at room temperature changed to 40.9, 44.7, 14.4 resp.,

a) δ_P 42.2 (quartet),

b) δ_P 34.04 (d, J_{POP} 30.0 Hz), 77.40 (dq, J_{POP} 30.0 Hz, J_{PCH} 14.7 Hz),

c) δ_P 23.89 (quartet).

Thermal Decomposition of Methyltriphenoxyphosphonium Bromide (8.0% in CDCl$_3$) at 125 °C

Total heating time (h)	P^+MeBr^-	$P^+Me_2Br^-$	MeP-O-P	P(O)Me
-	96.2	-	-	3.8
6.0	90.7	-	4.9	4.4
9.0	88.0	-	6.7	5.2
12.0	83.5	-	8.7	7.8
17.0	81.2	-	12.1	6.7
32.0	71.0	-	21.8	7.2
41.0	72.2	-	21.0	6.8
48.0	73.0	-	21.3	5.6
61.0	72.1	-	22.9	5.0
81.0	65.0	-	28.2	6.8
98.0	62.6	-	31.0	6.4
		(30% in CDCl$_3$) at 125 °C		
-	100%	-	-	-
5.0	99.0	-	traces	-
10.0	94.3	-	5.7	-
12.5	91.0	-	9.0	-
17.5	88.5	-	11.5	-
33.5	83.8	-	16.2	-
38.5	83.0	-	17.0	-
53.5	82.4	-	17.6	-
68.5	83.3	-	16.7	-
112.5*	80.0	-	20.0	-
133.5**	82.7	traces	17.2	-

*) Heated 44 h at 118 °C

**) Heated 21 h at 140 °C

Thermal Decomposition of Methyltriphenoxyphosphonium Bromide (4.5% in $CDCl_3$) at 175 °C

Total heating time (h)	P^+MeBr^-	$P^+Me_2Br^-$	MeP-O-P	P(O)Me
-	92.7	-	-	7.3
3.0	51.0	-	36.2	12.8
6.0	47.0	-	38.0	14.9
8.5	47.9	-	34.7*	17.3
10.5	45.9	-	36.1	18.0
14.0	22.6	2.6	49.2	25.6
16.0	21.5	3.3	45.4	29.8
21.0	33.3	4.0	31.0	31.7
24.0	28.9	4.5	36.6	30.0
30.0	37.4	6.5	27.4	28.7
36.0	38.6	7.9	26.0	27.5
50.0	17.6	7.4	37.5	37.5
57.0	27.3	7.9	27.3	37.5
65.0	26.3	10.1	19.7	43.9
77.0	24.7	9.3	24.7	41.3
129.0	traces	(m)	traces	tall
201.0	-	(m)	-	tall
302.0	-	9.9	-	90.1

363.0 Including 44 h at 200 °C; the contents became brown.

δ_P ($CDCl_3$) 23.74 due to $(PhO)_2P(O)Me$ (89.5%), also $(PhO)_3P(O)$ δ_P -17.78 ppm (10.5%), and $(PhO)_2PMe_2Br^-$ δ_P 95.75 (traces).

*) ^1H n.m.r. after 4 days at room temperature.

Thermal Decomposition of Methyltriphenoxyphosphonium Bromide (8.0% in CDCl$_3$) at 175 °C

Total heating time (h)		P^+MeBr^-	$P^+Me_2Br^-$	MeP-O-P	P(O)Me
-		95.8	-	-	4.2
3.0	(a)	47.6	-	45.1	7.2
5.5		44.2	traces	45.2	10.6
		(30.0% in CDCl$_3$) at 200 °C			
-		100%	-	-	-
0.75		72.0	-	25.2	2.8
1.5		67.3	traces	28.2	4.5
2.5	(b)	65.7	1.4	27.2	5.7
3.0		63.3	2.4	27.2	7.1

(a) and (b) joined together gave δ_P (CDCl$_3$ concentrated solution) 33.96 (d, J_{POP} 40.36 Hz) (19.6%), δ_P 76.83 (dq, J_{POP} 40.36 Hz, J_{PCH} 14.7 Hz) (22.7%), δ_P 23.86 (quartet) (2.0%), 41.75 (quartet) (51.8%), 96.06 (m) (1.6%) and 33.85 (s) unidentified (2.3%).

(*ca*. 40.0% in CDCl$_3$) at 175 °C

Total heating time (h)	P^+MeBr^-	$P^+Me_2Br^-$	MeP-O-P	P(O)Me
6.0	76.6	1.5	19.4	2.5

δ_P (CDCl$_3$) 41.0 (quartet) due to $(PhO)_3P^+MeBr^-$ (62.9%), δ_P 33.5 (d, J_{POP} 42.65 Hz) (16.8%), δ_P 76.1 (dq, J_{POP} 42.65 Hz, J_{PCH} 14.7 Hz) (20.2%), δ_C (CDCl$_3$) 8.43 (CH_3P, d, J_{PC} 127.0 Hz) due to $(PhO)_3P^+MeBr^-$, δ_C 13.2 (CH_3-POP, dd, J_{PC} 106.2 Hz, J_{POPC} 4.3 Hz).

Thermal Decomposition of Methyltriphenoxyphosphonium Bromide (10.0% in $CHCl_3$) at 125 °C

Total heating time (h)	P^+MeBr^-	$P^+Me_2Br^-$	MeP-O-P	P(O)Me
-	100%	-	-	-
6.0	97.0	-	3.0	traces
11.5	88.5	-	8.5	3.0
37.5	75.1	-	21.3	3.6
60.5	73.6	-	20.9	5.5
84.5	76.0	-	19.0	4.7
114.0	78.6	-	16.8	4.5
155.0*	79.6	traces	14.5	6.4

*) Heated 41 h at 150 °C

NB $CHCl_3$, not $CDCl_3$, used in this experiment.

Thermal Decomposition of Methyltriphenoxyphosphonium Bromide (10.0% in CDCl$_3$)

a) in the presence of Triphenyl phosphate (1.2 mol. equiv.)

Temperature in °C	Total heating time (h)	P^+MeBr^-	$P^+Me_2Br^-$	MeP-O-P	P(O)Me
room	-	100%	-	-	-
125	3.0	100	-	-	-
150	4.5	100	-	-	-
160	8.5	55.2	-	44.8	traces
175	10.5	44.7	-	51.1	4.2
175	15.5	55.2	-	40.5	4.3
175	23.5	44.8	-	46.5	8.7
180	31.0	54.4	3.5	31.6	10.5
170	38.0	33.3	3.0	52.2	11.5
170	66.0	21.0	8.8	42.1	28.1
170	87.0	23.5	16.2	30.9	29.4

b) in the presence of Triphenyl phosphate (1.5 mol. equiv.)

room	-	100%	-	-	-
160	4.0	57.5	-	36.8	5.7
175	6.0	53.9	-	41.7	4.4
175	11.0	56.2	-	35.5	8.3
180	19.0	48.1	-	38.9	13.0
160	26.5	50.0	2.5	37.2	10.3
170	33.5	43.2	3.4	37.5	15.9
170	61.5	29.8	6.4	31.9	31.9
170	82.5	30.2	13.7	20.5	35.6

c) in the presence of Triphenyl phosphite (1 mol. equiv.)

room	-	100%	-	-	-
160	4.0	71.0	-	6.9	22.1
180	14.0	66.3	-	10.5	23.2
170	28.5	52.8	1.9	13.9	31.4
170	56.5	50.9	1.8	10.5	36.8

Thermal Decomposition of Methyltriphenoxyphosphonium Iodide (8.0% in $CDCl_3$)

at 125 °C

Total heating time (h)	P^+MeBr^-	$P^+Me_2Br^-$	MeP-O-P	P(O)Me
room	88.7	-	-	11.3
room*	79.6	-	-	20.4
12.0	70.7	-	9.1	20.2
21.0	64.5	-	16.6	18.9
33.0	62.3	-	20.9	16.8
42.0	47.0	-	22.5	30.5
64.0	49.5	-	19.1	31.4
76.0	57.8	-	18.4	23.8
103.0	39.9	-	20.8	39.3

*) On standing for one year in sealed tube

at 125 °C

room	100%	-	-	-
15.0	81.5	-	18.5	-
22.5	82.7	-	17.3	-
38.0	77.8	traces	22.2	-
62.5	79.3	traces	17.5	3.2

at 175 °C

room	100%	-	-	-
0.5	72.2	1.7	22.7	3.4

Thermal Decomposition of Methyltri-o-tolyloxyphosphonium Bromide
(ca 8.0% in $CDCl_3$) at 125 °C

Total heating time (h)	Aromatic protons		$(Tol\text{-}O)_3P^+\underline{Me}Br^-$ *	$\underline{Me}P\text{-}O\text{-}P$ **	$(Tol\text{-}O)_2P(O)\underline{Me}$ ***
	δ 7.31	δ 7.17	δ 3.27, 15.6 Hz	δ 2.38 13.0 Hz	δ 1.80 17.4 Hz
	Height %	Height %	mole %	mole %	mole %
-	(m)	(m)	90.0	-	10.0
12.0 a	(m)	(m)	88.0	-	12.0
21.0 a	75.0	25.0	83.4	traces	16.6
42.0 a	56.8	43.2	58.3	16.7	25.0
54.0 a	47.0	53.0	54.5	19.5	26.0
64.0 a	44.3	55.7	47.3	27.3	25.5
76.0 b	42.6	57.4	47.6	23.8	28.6
85.0 b	38.6	61.4	39.5	25.9	34.6
103.0 b	34.5	65.5	43.1	23.8	33.8

(a) deep blue colour when hot, changing to green on cooling and then becoming colourless,
(b) brown colour; also were recorded signals of * $(\underline{CH_3}C_6H_4O)_3P^+MeBr^-$ at δ 2.16 (s),
** $(\underline{CH_3}C_6H_4O)_3P\text{-}O\text{-}P$ at δ 2.00 (s), *** $(\underline{CH_3}C_6H_4O)_2P(O)Me$ at δ 2.25 (s).

Thermal Decomposition of Methyltri-o-tolyloxyphosphonium Bromide
(*ca* 10.0% in $CDCl_3$) at 200 °C

Total heating time (h)	Aromatic protons δ 7.31 Height %	Aromatic protons δ 7.19 Height %	$(Tol\text{-}O)_3P^+\underline{Me}Br^-$ * δ 3.27, 15.8 Hz mole %	$\underline{Me}P\text{-}O\text{-}P$ ** δ 2.38 13.0 Hz mole %	$(Tol\text{-}O)_2P(O)\underline{Me}$ *** δ 1.77 17.4 Hz mole %
-	100	-	100	-	-
0.5	69.3	30.7	90.3	9.7	-
1.0 a	57.1	42.9	82.0	18.0	-
1.5 a	52.8	48.8	80.0	20.0	traces
2.25a	45.6	54.4	68.4	23.7	7.9
3.75	43.3	56.7	51.1	31.9	17.0
8.75b	41.9	58.1	29.3	36.6	34.1
13.75	41.8	58.2	15.6	53.1c	31.2
21.75	44.6	55.4	9.1	54.5c	36.4
44.0	-	(m)	-	- d	ca 99.0

(a) deep blue colour when hot, changing to green on cooling and then becoming colourless, (b) brown colour, (c) possible overlap with a new signal (d); also were recorded signals of * $(\underline{CH_3}C_6H_4O)_3P^+MeBr^-$ at δ 2.16 (s), ** $(\underline{CH_3}C_6H_4O)_3P\text{-}O\text{-}P$ at δ 2.00 (s), and δ 2.10 (s), *** $(\underline{CH_3}C_6H_4O)_2P(O)Me$ at δ 2.25 (s), and (d) $\underline{CH_3}C_6H_4Br$ at δ 2.36.

THERMAL DECOMPOSITION OF METHYLTRI-o-TOLYLOXYPHOSPHONIUM BROMIDE (<u>ca</u>. 10.0% in $CDCl_3$) AT 150 °C. (Table VII)
(Dark-blue colour appears on heating. On standing at 33 °C changes to green and aromatic signals change in height)

Spectrum	Time	AROMATIC PROTONS		$(CH_3C_6H_4)_3P^+MeBr^-$	MeP-O-P δ 2.28	$(CH_3C_6H_4O)_2P(O)Me$	Remarks
		δ 7.33 (s)	δ 7.12 (s)	δ 3.27 J 15.6 Hz	J 14.0 Hz	δ 1.80 J 17.4 Hz	Colours
No.	(h)	Height %	Height %	(mole %)	(mole %)	(mole %)	-
0	-	100	-	100	-	-	Colourless
1	20 [a]	29.7	70.3	54.4	42.1	3.5	blue
3	0.17	29.8	70.2				green-blue
4	0.33	32.4	67.6				
5	0.50	34.5	65.5				
6	0.67	35.5	64.5	Change in aromatic signals observed at 33 °C over 1.25 h. No change in other n.m.r. signals			green
7	0.78	36.5	63.5				
9	0.92	37.8	62.2				
11	1.08	38.0	62.0				brown-green
13	1.17	38.7	61.3				
15	1.25 [b]	42.5	57.5				

<u>a</u> Shifting of signals on heating: δ 7.33 moved to 7.23, δ 3.27 moved to 3.13. Also were recorded signals at δ 1.99 (s), 2.09 (s) due to <u>Tol</u>-POPMe, 2.14 (s) due to $(\underline{CH_3}C_6H_4O)_3P^+MeBr^-$, and 22.2 (s) due to $(\underline{CH_3}C_6H_4)_2P(O)Me$.

<u>b</u> δ_P ($CDCl_3$) 32.0 (d, J 35.5 Hz), 76.8 (d, J 35.5 Hz) due to MePOP (43.8 mole %), 42.0 due to $(CH_3C_6H_4O)_3P^+MeBr^-$ (54.9 mole %), and 23.6 due to $(CH_3C_6H_4O)_2P(O)Me$ (1.3 mole %). Then further heating for 14 h increased the height of phosphonate signals. The blue colour disappeared, while green colour remained, when the tube was hot.

THERMAL DECOMPOSITION OF METHYLTRI-o-TOLYLOXYPHOSPHONIUM IODIDE (ca 8.0% in $CDCl_3$). (Table VIII)

Spect-rum	Time	Tempe-rature	AROMATIC PROTONS		$(CH_3C_6H_4O)_3P^+\underline{Me}I^-$	P-O-P$\underline{Me}$	$(CH_3C_6H_4O)_2P(O)\underline{Me}$
			δ 7.32 (s)	δ 7.20 (s)	δ 3.17 J 15.9 Hz	o 2.28 J 14.0 Hz	δ 1.81 J 18.0 Hz
No.	h	°C	height %	height %	(mole %)	(mole %)	(mole %)
1	-	No heating	100	-	100	-	-
2	26.5	120	-	-	No change		
1	-	No heating	100	-	100	-	-
2	0.5	200	72.9	27.1	71.3	17.2	11.5
3	1.0	200	63.0	37.0	61.6	26.1	12.3
4	1.5	200	55.9 [a]	44.1 [a]	52.1	34.9	13.0
5	2.0	200	51.2 [a]	48.8 [a]	35.7	47.2	17.6
6 [b]	4.0	200	54.0 [c]	46.0	24.1	51.7	24.1
7 [d]	6.0	200	51.7	48.3	15.2	54.5	30.3

(a) Change in aromatic signals at room temperature from 55.9 to 65.1 and from 44.1 to 34.9; and from 51.2 to 54.8, and from 48.8 to 45.2 in height. (b) The tube became deep red in colour. (c) Appearance of additional signal at 7.25 ppm (Ar). (d) The tube became brown with a tarry deposit in it, and tolyl signals were detected at δ 2.00 (s) due to tolyl-POPMe (31.6%), 2.17 (s) due to $(\underline{CH_3}C_6H_4O)_3P^+MeI^-$ (51.3%), 2.24 (s) due to $(\underline{CH_3}C_6H_4O)_2P(O)Me$ (17.1%) in height.

Hydrolysis of P-O-P Intermediate obtained from Methyltriphenoxyphosphonium Bromide in Deuterochloroform

The product obtained by heating a concentrated solution of $(PhO)_3P^+MeBr^-$ in $CDCl_3$ for 98 h at 125-140 °C was divided and used for two further experiments: (a) for hydrolysis by atmosphere, and (b) for attempted isolation of the P-O-P compound.

(a) The tube was sealed with parafilm and observed by ^1H n.m.r. spectroscopy. After 7 days no change had occurred but after 14 days the ^1H n.m.r. spectrum showed the first stage of hydrolysis (See Table IX a).

(b) The solution was treated with dry ether to precipitate a small amount of white crystals which were removed by filtration under nitrogen. The ^1H n.m.r. spectrum ($CDCl_3$) for the crystals showed the same signals as for the solution, before separation of the crystals, viz. δ 2.16 (MeP-O-P, dd, J_{PCH} 14.5 Hz) (9.5 mole %), 3.1 (Me, d, J_{PCH} 16.8 Hz) due to $(PhO)_3P^+MeBr^-$ (79.0 mole %), and 1.75 (Me, d, J_{PCH} 17.7 Hz) due to $(PhO)_2P(O)Me$ (11.5 mole %). The contents of the ^1H n.m.r. tube were transferred into a small flask, parafilm sealed, and stored in desiccator ($CaCl_2$) for 13 days after which time the ^1H n.m.r. spectrum showed the same signals as above for the first stage of hydrolysis (See Table IXa). After two more weeks at room temperature the second stage of hydrolysis took place (See Table IX b).

In a further similar experiment the product from the second stage of hydrolysis in $CDCl_3$ (after 6 weeks) showed ^1H n.m.r. signals at δ 1.86 (d, J 15.0 Hz), unidentified (X_1) 11.1%, 2.82 (d, J 18.0 Hz), unidentified (X_3) 3.4%, 3.17 (d, J 18.0 Hz), unidentified (X_4) 3.4%, and 1.72 (Me, d, J_{PCH} 17.7 Hz) due to $(PhO)_2P(O)Me$, 82.1%, in the aromatic region multiplet appeared at 6.5 to 7.8 ppm. The ^{31}P n.m.r. ($CDCl_3$) spectrum showed a strong signal at δ 24.8 (MeP, q, J_{PCH} 17.6 Hz) due to $(PhO)_2P(O)Me$ (63%) and two smaller signals of approx. equal intensity (18-19% each by integration) at 46.7 and 12.0 ppm, appearing as doublets (J <u>ca</u>. 4 Hz) in the broad-band proton-decoupled spectrum and assigned to the P-O-P structure. In the fully coupled spectrum the signal at 46.7 consisted of six lines (interpreted as two overlapping quartets) (J_{PCH} 16.0 Hz) and that at 12.0 appeared as a triplet (J 20.3 Hz).

^{1}H n.m.r. data for hydrolysis of P-O-P intermediate and products after thermal decomposition of $(PhO)_3\overset{+}{P}MeBr^-$ in deuterochloroform at 125-140 °C (Table IXa,b)

Exp.	Time (days)	$(PhO)_3\overset{+}{P}MeBr^-$		X_5		X_4		X_3		X_2		P-O-P intermediate		X_1		$(PhO)_2P(O)Me$	
		ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%	ppm	%
(a)	0	3.20 (d) J 16.8 Hz	83.0%									2.18 (dd) J 14.4 Hz	14.5%			1.77 (d) J 17.7 Hz	2.5%
	7	3.15 (d) J 16.8 Hz	79.0%									2.17 (dd) J 14.4 Hz	13.9%			1.77 (d) J 17.7 Hz	7.0%
	14	2.93 (d) J 16.8 Hz	35.0%	(*) traces		traces overlapped				(*) 2.79 (d) J 14.7 Hz	13.0%	-		1.91 (d) J 15.0 Hz	6.2%	1.77 (d) J 17.7 Hz	45.6%
(b)	13	2.90 (d) J 16.8 Hz	32.0%	small 3 signals at 4.51,4.85, 5.19(ppm)		traces overlapped				2.77 (d) J 15.0 Hz	18.6%	-		1.92 (d) J 15.0 Hz	11.9%	1.77 (d) J 17.7 Hz	37.5%
	28	-		-		(**) 3.27 (d) J 18.0 Hz	4.0%	(**) 2.92 (d) J 18.0 Hz	4.0%	-		-		(**) 1.91 (d) J 15.0 Hz	16.5%	1.77 (d) J 17.7 Hz	75.5%

* First stage of hydrolysis
** Second stage of hydrolysis

Thermal Decomposition of Methyltriphenoxyphosphonium Iodide and simultaneous distillation of products

Pure crystals of methyltriphenoxyphosphonium iodide (13.0 g, 10.6 mmol) were used for simple vacuum distillation. The apparatus (before use) was flushed with nitrogen. Then the compound was heated for 6.5 h under 0.2-0.4 mmHg pressure (bath at 200 °C). The crystals melted to give a very dark liquid, which after cooling remained dark and viscous. A cold trap collected iodobenzene (few drops), δ 6.7-7.9 (m), an unidentified component, δ 5.2 (s) and a trace of (probably) MeI, δ 2.08 (s). The receiver (cooled in ice) also collected a few drops of iodobenzene, δ 6.2-7.7 (m).

The ^{1}H n.m.r. spectrum ($CDCl_3$) of the residue showed the presence of phosphonate (18.0 mole %), δ 1.77 (Me, d, J_{PCH} 17.7 Hz), and of undecomposed phosphonium salt (82.0 mole %), δ 3.11 (Me, d, J_{PCH} 16.8 Hz). Signals for phenoxy protons appeared at δ 7.48 (tall singlet) with a small multiplet of lines at δ 6.98-7.5 ppm.

Distillation was continued for a further 6 h under 0.2-0.4 mmHg pressure, at a bath temperature of 230-240 °C. Two cold traps collected iodobenzene, δ 6.7-8.1 (m), containing a very small amount of impurity, δ 3.12, whilst the receiver collected a mixture (approx. 1 g) of liquid and a small amount of red solid. The liquid contained mainly the phosphonate, $(PhO)_2P(O)Me$, δ_H ($CDCl_3$) 1.67 (Me, d, J_{PCH} 17.7 Hz), δ_P ($CDCl_3$) 25.0 (quartet).

The ^{1}H n.m.r. spectrum ($CDCl_3$) of the distillation residue showed signals at δ 1.75 (Me, d, J_{PCH} 17.7 Hz) due to phosphonate (61.1% in height), δ 2.12 (MePOP, dd, J_{PCH} 14.4 Hz) due to the P-O-P intermediate (10.3% in height), δ 2.79 (Me, d, J_{PCH} 14.4 Hz) due to $(PhO)_2P^+Me_2I^-$ (9.5% in height) and δ 3.0 (Me, d, J_{PCH} 16.8 Hz) due to undecomposed $(PhO)_3P^+MeI^-$ (19.1% in height). Phenoxy protons appeared at 6.7-7.8 (m). ^{31}P n.m.r. ($CDCl_3$) confirmed the assignments for $(PhO)_2P(O)Me$ (38.9 mole %), δ 23.6 (quartet), $(PhO)_3P^+MeI^-$ (17.8 mole %), δ 40.4 (quartet), $(PhO)_2P^+Me_2I^-$ (5.0 mole %), δ 93.9 (septet), and for the P-O-P intermediate (29.4 mole %), δ 33.6 (d, J_{POP} 45.3 Hz), 75.7 (m, J_{POP} 45.3 Hz), and also showed the presence of $(PhO)_3P{=}O$ (2.7 mole %), δ -18.1 (s), and of $(PhO)_3P$ (6.2 mole %), δ 127.7 (s).

Then the residue was washed with dry ether. The oily mass did not crystallise, but the concentration of phosphonate was reduced (signals 36.6% in height). Attempted crystallisation from dry chloroform, by adding dry ether gave only an oily mass. The ^{1}H n.m.r. spectrum showed signals for the phosphonate (13.8% in height), the P-O-P compound (24.6% in height), $(PhO)_2P^+Me_2I^-$ (21.4% in height), and $(PhO)_3P^+MeI^-$ (not decomposed) (40.1% in height). No further separation could be achieved.

Hydrolysis of the P-O-P Intermediate Formed during Thermal Decomposition of Methyltriphenoxyphosphonium Iodide in the absence of Solvent

The distillation residue after volatile products had been removed was washed with ether and then recrystallised (a) from $CHCl_3$, (b) from acetone, the latter causing some hydrolysis to occur. Two stages of hydrolysis were observed for solutions of the distillation residue in $CDCl_3$ in unsealed n.m.r. tubes. ^{1}H n.m.r. data are given in Table X. ^{31}P n.m.r. data ($CDCl_3$) were as follows:

First stage of hydrolysis

δ 24.1 (quartet) due to $(PhO)_2P(O)Me$, 40.6 (quartet) due to $(PhO)_3P^+MeI^-$, 93.7 (m) due to $(PhO)_2P^+Me_2I^-$, 76.0 (d, J_{POP} 43.3 Hz) and 33.4 (d, J_{POP} 40.0 Hz) due to unchanged POP intermediate (v. small), -17 (s) due to $(PhO)_3PO$, -25 (s) assigned to $(PhO)_4P^+I^-$, and unidentified peaks at 4.98 (t, J *ca.* 20 Hz), 84.4 (m), 96.8 (m), and -11.9 (s).

Second stage of hydrolysis

δ 25.0 (quartet) due to $(PhO)_2P(O)Me$, 91.9 (m) due to $(PhO)_2P^+Me_2I^-$ (small), unidentified peaks at 11.7 (triplet, J 23.3 Hz), and 47.7 (m, possibly two overlapping quartets) (cf. hydrolysis of corresponding bromide, p.140), and very small signals at -5 (s), and -12 (s).

^{1}H n.m.r. data for products of $(PhO)_3P^+MeI^-$ thermally decomposed and their hydrolysis. (Table X)

	P^+MeI^-	$P^+Me_2I^-$	X_5	X_4	X_3	X_2	MeP-O-P	X_1	P(O)Me
	ppm J	ppm J	ppm J	ppm J	ppm J	ppm J	ppm J	ppm J	ppm J
Residue after distill.	19.1% 3.0 (d) 16.8 Hz	9.5% 2.79 (d) 14.4 Hz					10.3% 2.12 (dd) 14.4 Hz		61.0% 1.75 (d) 17.7 Hz
Res.after ether wash	28.0% 3.0 (d) 16.8 Hz	17.3% 2.82 (d) 14.4 Hz					18.1% 2.14 (dd) 15.0 Hz		36.6% 1.76 (d) 17.7 Hz
Residue $CHCl_3$ recryst.	40.1% 3.01 (d) 16.8 Hz	21.4% 2.82 (d) 14.4 Hz					24.6% 2.14 (dd) 15.0 Hz		13.9% 1.75 (d) 17.7 Hz
Residue acetone recryst.	38.0% 2.90 (d) 16.8 Hz	24.5% 2.72 (d) 14.4 Hz	11.5% 4.41 ppm 4.75 ppm 5.09 ppm			25.9% 2.82 (d) 14.4 Hz			
First stage of hydrolysis	31.1% 2.93 (d) 16.8 Hz	19.2% 2.74 (d) 14.4 Hz	12.4% as above			23.1% 2.85 (d) 14.4 Hz	6.3% 2.10 (dd) 14.4 Hz		14.2% 1.76 (d) 17.7 Hz
Isolated first stage of hydrolysis	28.2% 2.90 (d) 16.8 Hz	21.9% 2.72 (d) 14.4 Hz	13.7% 4.58 (d) 20 Hz 4.92 (d) 20 Hz			27.2% 2.82 (d) 14.4 Hz			8.9% 1.76 (d) 17.7 Hz
Second stage of hydrolysis		8.7% 2.45 (d) 14.4 Hz		8.5% 3.25 (d) 17.0 Hz	7.7% 2.89 (d) 17.0 Hz			27.0% 1.88 (d) 15.0 Hz	48.1% 1.75 (d) 17.7 Hz

Thermal Decomposition of Solid Methyltri-o-tolyloxyphosphonium Bromide and Distillation under High Vacuum

Pure crystals of methyltri-o-tolyloxyphosphonium bromide (3.0 g, 0.007 mol) were placed in a small flask protected from moisture with a calcium chloride tube and heated in an oil bath (200 °C) for 2 h at 0.1 mmHg. A cold trap (-80 °C) collected a few drops of liquid which were shown to contain o-bromotoluene (79.6%) δ_H ($CDCl_3$) 2.35 (CH_3, s) and o-cresol (20.4%) δ_H 2.20 (CH_3, s), 4.29 (OH, s). Aromatic protons were recorded in the region 6.6 - 7.6 ppm (m). During a further 3 h a clear liquid distillate (1.8 g), b.pt. 160-180 °C at 0.1-0.05 mmHg was slowly collected in a second cold trap (-80 °C). N.m.r. spectroscopy ($CDCl_3$) showed the distillate to consist of di-o-tolyl methanephosphonate (52.4%) δ_H 1.78 ($\underline{Me}$P, d, J_{PCH} 17.4 Hz), 2.21 (o-CH_3, s), δ_P 23.85 (quartet), o-bromotoluene (18.2%) δ_H 2.34 (CH_3, s) and o-cresol (29.4%) δ_H 2.17 (CH_3, s), based on height of the tolyl CH_3 signals. Aromatic protons appeared at δ 7.10 (m). The ^{31}P n.m.r. spectrum also showed small unidentified signals, δ_P 13.3, 10.9, -8.4, and -11.5 ppm.

G.L.C. analysis of the contents of both cold traps was carried out on a 1 cm x 5 m glass column with 10% PEGA on Celite (60-80 mesh), at 115 °C and 17 psi N_2 pressure. In each case o-cresol (t_R 5 min 35 sec) and o-bromotoluene (t_R 38 min 50 sec) were positively identified. No m- or p-bromotoluene (t_R 42 min 10 sec for both) were detectable.

Isolation of MeP-O-P Intermediate after Thermal Decomposition of Solid Methyltri-o-tolyloxyphosphonium Bromide and Distillation of Volatile Products

The ^{1}H n.m.r. spectrum in deuterochloroform of the dark-brown hard solid residue (0.5 g) from the above experiment showed signals at δ 2.00 ($\underline{CH}_3C_6H_4$, s) (unidentified, 47.8% in height), 2.15 ($\underline{CH}_3C_6H_4$, s) (unidentified, 33.1% in height), 2.24 ($\underline{CH}_3C_6H_4$, s) for di-o-tolyl methanephosphonate (18.9% in height) and 7.17 ppm (Ar, s). A small doublet centred at δ 2.45 ppm corresponded to one region of the Me-P-O-P signal (J_{POPCH} 1.9 Hz), the other half being hidden beneath the tolyl phosphonate signal at δ 2.24. After 6 weeks (tube unsealed) the appearance of three small singlets at 4.88, 5.20, and 5.53 ppm, indicated the products of hydrolysis of a P-O-P complex. Similar signals were found after hydrolysis of the Me-P-O-P intermediate from methyltriphenyloxyphosphonium bromide. See p. 141.

The total residue was then dissolved in chloroform and treated with dry ether, which precipitated a small amount of white solid and also an oily mass. The solid was decanted with ether, separated, washed with ether, and dried under high vacuum to give white crystals which became dark in colour on standing, δ_H ($CDCl_3$) 2.02 ($\underline{CH}_3C_6H_4$, d, J_{POCCCH} 0.9 Hz, 9 H), 2.18 ($\underline{CH}_3C_6H_4$, d, J_{POCCCH} 0.9 Hz, 6 H), 2.38 ($\underline{Me}$-P-O-P, J_{PCH} 13.9 Hz, J_{POPCH} 1.9 Hz, 3 H), 7.20 (Ar, s, 20 H), δ_P ($CDCl_3$) 32.3 (MePO$\underline{P}$, d, J_{POP} 32.4 Hz), 77.0 (Me$\underline{P}$OP, dq, J_{POP} 32.4 Hz, J_{PCH} 16.0 Hz).

III.2.1 OBSERVATION OF THE COURSE OF THE REACTIONS BETWEEN PHENACYL HALIDES AND PHOSPHORUS (III) ESTERS IN DEUTEROCHLOROFORM BY ^{1}H N.M.R. SPECTROSCOPY

(a) Trineopentyl Phosphite and Phenacyl Bromide

Concentrated solutions (ca. 25%) in deuterochloroform of trineopentyl phosphite (0.155 g, 1.0 mol. equiv.) and of phenacyl bromide (0.105 g, 1.0 mol. equiv.) were separately prepared and were mixed together in a ^{1}H n.m.r. tube. The ^{1}H n.m.r. spectrum 15 min after preparation showed signals for the following:

Starting materials (57.2 mole %): phosphite, δ 0.91 (Me_3C, s), 3.44 (CH_2OP, d, J_{POCH} 6.3 Hz); phenacyl bromide, 4.39 (CH_2, s).

Arbuzov intermediate (10.6 mole %), δ 1.02 (Me_3C, s), 4.34 (CH_2OP^+, d, J_{POCH} 4.8 Hz), 5.74 (CH_2P^+, d, J_{PCH} 18.3 Hz).

Arbuzov product (18.4 mole %), δ 0.86 (Me_3C, s), 3.72 (CH_2OP, d, J_{POCH} 4.8 Hz), 3.65 (CH_2P, d, J_{PCH} 22.8 Hz).

Perkow product (13.7 mole %), δ 0.93 (Me_3C, s), 3.78 (CH_2OP, d, J_{POCH} 5.1 Hz), 5.3 ($CH_2{=}C$, m).

Neopentyl bromide (ca. 30 mole %), δ 1.03 (Me_3C, s), 3.27 (CH_2, s).

Aromatic protons appeared as a multiplet (7.3-8.4 ppm). The ^1H n.m.r. spectrum was re-examined at intervals and recorded (table No. XI). After 23.5 h only traces of starting materials remained together with the Arbuzov intermediate (4.6 mole %), the Arbuzov product (49.3 mole %) and the Perkow product (46.0 mole %).

Results of reaction between trineopentyl phosphite and α-bromoacetophenone (1:1 molar ratio) in deuterochloroform at 36 °C. Product compositions in mole %. (Table XI)

Time (h)	$(RO)_3P$	$(RO)_3P^+CH_2COPh$	$(RO)_2P(O)CH_2COPh$	Total Arbuzov reaction	$(RO)_2P(O)OC(:CH_2)Ph$
0.25	57.5	10.6	18.4	29.0	13.7
0.42	49.5	11.9	19.3	31.2	19.3
0.66	38.5	14.8	20.0	34.8	26.7
0.91	30.4	14.9	22.5	37.4	31.2
1.08	28.6	14.7	25.0	39.7	31.7
1.58	21.7	14.2	28.2	42.4	35.8
1.83	17.2	13.1	32.4	45.5	37.3
4.50	11.4	10.4	34.2	45.6	44.0
23.50	-	4.6	49.3	53.9	46.0

(b) Dineopentyl Phenylphosphonite and Phenacyl Bromide

Dineopentyl phenylphosphonite (0.17 g, 1.0 mol. equiv.) and phenacyl bromide (0.12 g, 1.0 mol. equiv.) were dissolved separately in deuterochloroform (ca. 25-30%) and the solutions were mixed and transferred into a ^{1}H n.m.r. tube. The ^{1}H n.m.r. spectrum immediately after preparation showed several signals due to:

Arbuzov intermediate (41 mole %), δ 1.07 (Me_3C, s), 4.34 (CH_2OP^+, m), 5.99 (CH_2P^+, d, J_{PCH} 15.6 Hz).

Perkow product (57 mole %), δ 0.89 (Me_3C, s), 3.75 (CH_2OP, d, J_{POCH} 5.1 Hz), 5.18 (POC=CH, d, J_{POCCH} 2.5 Hz).

Neopentyl bromide (ca. 55 mole %), (product of decomposition), δ 1.00 (Me_3C, s), 3.22 (CH_2, s).

Unreacted starting materials (approx. 2 mole %), δ 4.45 (CH_2, s) for phenacyl bromide and δ 0.92 (Me_3C, s), 3.4 (CH_2OP, m) for the ester (traces only).

The Arbuzov product and Perkow intermediate were not detected. No further change was observed after 3 days.

(c) Neopentyl Diphenylphosphinite and Phenacyl Bromide

Neopentyl diphenylphosphinite (0.203 g, 1.0 mol. equiv.) and phenacyl bromide (0.1484 g, 1.0 mol. equiv.) were dissolved separately in deuterochloroform (ca.20-30%) and the solutions were mixed and transferred into a ^{1}H n.m.r. tube. The ^{1}H n.m.r. spectrum of the mixture 15 min after preparation showed signals for:

Arbuzov intermediate (68 mole %), δ 0.99 (Me_3C, s), 4.15 ($POCH_2$, d, J_{POCH} 4.2 Hz), 6.25 (CH_2P, d, J_{PCH} 12.6 Hz).

Perkow intermediate (10 mole %), δ 0.95 (Me_3C, s), 4.04 (CH_2OP, d, J_{POCH} 5.4 Hz), 5.48 ($CH_2{=}C$, m, 5.41-5.54).

Perkow product (13 mole %), δ 5.10 (CH_2C, m, 5.0-5.2).

Neopentyl bromide (ca. 13 mole %), δ 3.21 (CH_2, s).

Unreacted ester (8 mole %), δ 3.4 (CH_2OP, m) and phenacyl bromide, δ 4.8 (CH_2, s).

Aromatic protons gave a multiplet between 7.2-8.35 ppm. After 3 h the vinyloxyphosphonium (Perkow) intermediate was already decomposed, but the ketophosphonium (Arbuzov) intermediate, which seemed to be stable, did not show decomposition after 28 hours.

(d) Trineopentyl Phosphite and Phenacyl Chloride

Concentrated solutions (ca. 25-30%) in deuterochloroform of trineopentyl phosphite (0.155 g, 1.0 mol. equiv.) and of phenacyl chloride (0.082 g, 1.0 mol. equiv.) were separately prepared and were mixed together in a ^1H n.m.r. tube. The ^1H n.m.r. spectrum, 10 min after preparation showed signals for the following:

Perkow product (35.3 mole %), δ 0.95 (Me_3C, s), 3.78 (CH_2OP, d, J_{POCH} 4.8 Hz), 5.24 ($CH_2{=}C$, m, 5.14-5.34).

Neopentyl chloride (ca. 35 mole %), δ 0.96 (Me_3C, s), 3.29 (CH_2, s).

Starting materials: trineopentyl phosphite (64.6 mole %), δ 0.91 (Me_3C, s), 3.44 (CH_2OP, d, J_{POCH} 6.30 Hz); phenacyl chloride, δ 4.68 (CH_2, s).

Aromatic protons appeared as a multiplet between 7.2-8.10 ppm. The reaction was followed by ^1H n.m.r. (see table) and was shown to be fast; no signals for a phosphonium intermediate were observed.

After 2.58 h the reaction was 93.2% complete.

Results of reaction between trineopentyl phosphite and α-chloroacetophenone (1:1 molar ratio) in deuterochloroform at 36 °C. Product compositions in mole %.

Time (h)	$(RO)_3P$	$(RO)_2P(O)OC(:CH_2)Ph$
0.17	64.7	35.3
0.50	35.6	64.4
0.67	31.3	68.7
0.83	24.4	75.6
1.33	16.7	83.3
1.50	15.4	84.6
1.75	12.2	87.8
2.58	6.8	93.2
24.42	-	100.0
48.00	-	100.0

(e) Dineopentyl Phenylphosphonite and Phenacyl Chloride

Dineopentyl phenylphosphonite (0.30 g, 1.0 mol. equiv.) and phenacyl chloride (0.16 g, 1.0 mol. equiv.) were dissolved in deuterochloroform (ca. 0.6 ml). The ^1H n.m.r. spectrum immediately after preparation showed that the reaction had already taken place, to give the following:

1-Phenylvinyl neopentyl phenylphosphonate (Perkow product), δ 0.89 (Me_3C, s), 3.77 (CH_2OP, d, J_{POCH} 5.1 Hz), 5.19 ($CH_2{=}C$, d, J_{PCH} 2.5 Hz), 7.15-8.10 ppm (Ar, m).

Neopentyl chloride, δ 0.96 (Me_3C, s), 3.22 (CH_2, s).

A small signal remained for unreacted phenacyl chloride, δ 4.6 (CH_2, s). The ^1H n.m.r. spectrum was re-examined after 22 h, but showed no change.

(f) Neopentyl Diphenylphosphinite and Phenacyl Chloride

Phenacyl chloride (0.1231 g, 1 mol. equiv.), dissolved in deuterochloroform (ca. 0.5 ml), was added in a nitrogen atmosphere to neopentyl diphenylphosphinite (0.2168 g, 1.0 mol. equiv.), and the solution was transferred to a ^1H n.m.r. tube and sealed. The ^1H n.m.r. spectrum 10 min after preparation showed signals for:

Starting materials: ester (20 mole %), δ 0.93 (Me_3C, s), 3.45 (CH_2OP, d, J_{POCH} 6.3 Hz), and phenacyl chloride, δ 4.86 (CH_2, s).

Perkow intermediate (35 mole %), δ 0.98 (Me_3C, s), 4.10 (CH_2OP^+, d, J_{POCH} 4.8 Hz), 5.55 ($P^+OC{=}CH_2$, m, 5.49-5.61).

Perkow product (vinyl diphenylphosphinate) (45 mole %), δ 5.15 ($CH_2{=}C$, m, 5.06-5.24).

Neopentyl chloride, δ 0.96 (Me_3C, s), 3.26 (CH_2, s).

Aromatic signals appeared between 7.10-8.2 ppm. The ^1H n.m.r. spectrum after 20, and 30 min showed decreasing amounts of the phosphonium intermediate; after 1 hour traces only remained.

III.2.2 PREPARATION AND ISOLATION OF PHOSPHONIUM INTERMEDIATES

The Arbuzov intermediates

Preparation of Trineopentyloxy(phenacyl)phosphonium Bromide

Solutions of trineopentyl phosphite (3.0 g, 1.0 mol. equiv.) in acetone (2 ml) and α-bromoacetophenone (2.5 g, 1.22 mol. equiv.) in acetone (6 ml) were mixed at room temperature. After 1.5 h the acetone was removed under reduced pressure and anhydrous ether was added. The white crystalline product that was precipitated was filtered off, washed with ether, and dried under high vacuum to give trineopentyloxy(phenacyl)phosphonium bromide (0.6 g, 12%) (Found: C, 56.8, H, 8.1. $C_{23}H_{40}BrO_4P$ requires: C, 56.2, H, 8.2%), m.p. 85 - 86 °C (sealed tube), δ_H ($CDCl_3$) 1.02 (Me_3C, s), 4.35 (CH_2OP, d, J_{POCH} 4.8 Hz), 5.74 (CH_2P, d, J_{PCH} 18.3 Hz), 7.3 - 8.4 (Ar, m), δ_P ($CDCl_3$) 41.0 ppm.
In a similar preparation, trineopentyl phosphite (3.3 g, 1.0 mol. equiv.) and α-bromoacetophenone (2.5 g, 1.11 mol. equiv.) were allowed to interact for 3 h. After removal of acetone and the addition of ether, the mixture was first cooled to 0 °C and then maintained at 16 °C overnight to yield crystals of the same intermediate (1.1 g, 20%) (Found: Br, 16.2. Calc. for $C_{23}H_{40}BrO_4P$: Br, 16.3%), m.p. 83 - 84 °C (sealed tube).

Preparation of Dineopentyloxy(phenacyl)phenylphosphonium Bromide

(a) Preparation in ether

α-Bromoacetophenone (2.6 g, 1.0 mol. equiv.) in dry ether (approx. 25 ml) was added from a dropping funnel, with stirring and cooling (16 °C) to dineopentyl phenylphosphonite (3.75 g, 1.0 mol. equiv.) which was diluted with 1.0 ml of dry ether. After 10 min the product started to precipitate, and after 1.5 h crystals were filtered off, washed with ether and dried under high vacuum; yield 0.7 g, m.p. 122 °C (sealed tube). After standing overnight (approx. 18 h) the ethereal residue yielded a second crop of crystals (1.3 g), m.p. 122 °C (sealed tube). The total yield of dineopentyloxy(phenacyl)phenylphosphonium bromide was 2.0 g (31.5%) (Found: C, 59.5, H, 7.1, Br, 16.4, P, 5.9. $C_{24}H_{34}BrO_3P$ requires: C, 59.9, H, 7.1, Br, 16.6, P, 6.4%), δ_H ($CDCl_3$) 1.07 (Me_3C, s), 4.34 [CH_2OP, d AB, $\delta(H_A)$ 4.42, $\delta(H_B)$ 4.26, J_{AB} 8.0, $J_{POCH(A)}$ 4.0, $J_{POCH(B)}$ 4.1 Hz], 5.99 (CH_2P, d, J_{PCH} 15.6 Hz), 7.2 - 8.4 (Ar, m), δ_P ($CDCl_3$) 67.1.

(b) Preparation in chloroform

α-Bromoacetophenone (2.1 g, 1.0 mol. equiv.) was dissolved in dry chloroform (5 ml), and added slowly with shaking and cooling (16 °C) to dineopentyl phenylphosphonite (3.0 g, 1.0 mol. equiv.), which was diluted in 1.0 ml of dry chloroform. After 2.5 h, dry ether (40 ml) was added to the reaction mixture. After a further 0.5 h white crystals which appeared were filtered off, washed with ether and dried under high vacuum to give the phosphonium bromide (1.5 g, 29.4%), m.p. 118 °C (sealed tube), with the same ^{1}H n.m.r. spectrum as in the previous experiment.

Preparation of Neopentyloxy(phenacyl)-diphenylphosphonium Bromide

(a) Preparation in acetone

α-Bromoacetophenone (1.5 g, 1.0 mol. equiv.) was dissolved in the smallest possible quantity of dry acetone (approx. 4-5 ml), and was added dropwise to neopentyl diphenylphosphinite (2.0 g, 1.0 mol. equiv.) with shaking and cooling (in a water bath at room temperature) since the reaction is strongly exothermic. Within 15 min the reaction mixture became cloudy and a precipitate appeared. The crystals were filtered off, washed several times with dry ether and then dried under high vacuum to yield the first crop of product (1.36 g, 39.0%) m.p. 146 - 148 °C (sealed tube). After a further 4 h a second crop (0.23 g, 6.8%) was isolated. The total yield of neopentyloxy(phenacyl)diphenylphosphonium bromide 1.58 g (45.8%) (Found: C, 63.1, H, 6.0, Br, 16.0, P, 6.5. $C_{25}H_{28}BrO_2P$ requires: C, 63.7, H, 6.0, Br, 17.0, P, 6.6%), δ_H ($CDCl_3$) 0.99 (Me_3C, s), 4.15 (CH_2OP, d, J_{POCH} 4.2 Hz), 6.25 (CH_2P, d, J_{PCH} 12.6 Hz), 7.20 - 8.35 ppm (Ar, m), δ_P ($CDCl_3$) 68.3.

(b) Preparation in chloroform

α-Bromoacetophenone (1.42 g, 1.0 mol. equiv.) was dissolved in the minimum of dry chloroform (4.5 ml) and was added slowly to neopentyl diphenylphosphinite (1.95 g, 1.0 mol. equiv.) also in dry chloroform (1 ml), with shaking and cooling in ice-water. After 10 min the reaction mixture became cloudy and crystals started to separate. After 3 h the precipitate was filtered off, washed with dry ether and dried under high vacuum to yield the product (2.47 g), m.p. 135 - 136 °C (sealed tube) (Found: C, 53.1, H, 5.1, Br, 29.0%), δ_P ($CDCl_3$) 68.3 ppm. The product was recrystallised by dissolving it in dry chloroform and adding dry ether, followed by filtration and drying under high vacuum to give white crystals (stable when stored under $CHCl_3$), m.p. 143 °C (sealed tube), of the phosphonium bromide containing one bound $CHCl_3$ molecule of crystallisation i. e. $Ph_2(RO)P^+CH_2COPhBr^-,CHCl_3$, (Found: C, 53.1, H, 5.2. $C_{26}H_{29}BrCl_3O_2P$ requires: C, 53.0, H, 5.0%), δ_H ($CDCl_3$) 0.99 (Me_3C, s, 9H), 4.15 (CH_2OP, d, J_{POCH} 4.2 Hz, 2H), 5.25 (CH_2P, d, J_{PCH} 12.6 Hz, 2H), 7.2 - 8.3 (Ar, m, 16H) including $CHCl_3$ peak at δ 7.25 (s, 1H).

(c) Preparation in ether

α-Bromoacetophenone (2.3 g, 1.0 mol. equiv.), dissolved in dry ether (60 ml), was slowly added from a dropping funnel to neopentyl diphenylphosphinite (3.0 g, 1.0 mol. equiv.) with stirring at room temperature. An oily liquid began to appear but did not produce crystals after 3 h at room temperature or after 24 h at 8 °C. Then the ether was evaporated off, the oily mixture remaining was dissolved in dry chloroform and the product was precipitated with ether, washed with ether, and dried under high vacuum to give the product as a white crystalline powder containing one molecule of $CHCl_3$ of crystallisation, m.p. 140 - 144 °C (sealed tube) (Found: C, 54.3, H, 6.0%). The ^1H n.m.r.

spectrum ($CDCl_3$) showed the same signals as the products prepared above.

The Perkow intermediate

Preparation of Neopentyloxydiphenyl-1-phenylvinyloxyphosphonium Chloride

α-Chloroacetophenone (1.13 g, 1.0 mol. equiv.), dissolved in the minimum of dry chloroform (approx. 2.5 ml), was cooled to between -5 and 0 °C and then slowly added with shaking and cooling to neopentyl diphenylphosphinite (1.99 g, 1.0 mol. equiv.). The reaction mixture was concentrated under H_2O pump pressure and then high vacuum and dry ether (10-15 ml) was added to give a cloudy, oily liquid, which was washed by decantation with a small portion of ether at low temperature in a nitrogen atmosphere. The oily mass solidified when stored under ether at -6 °C for two days, after which it was washed with ether at low temperature and dried under nitrogen to give white crystals of neopentyloxydiphenyl-1-phenylvinyloxyphosphonium chloride (Found: C, 62.95, H, 6.1. $C_{25}H_{28}ClO_2P$ with 0.5 mol $CHCl_3$ requires: C, 62.9, H, 6.1%), δ_H ($CDCl_3$) 0.98 (Me_3C, s), 4.04 (CH_2OP, d, J_{POCH} 4.8 Hz), 5.48 (CH_2=C, 5.41 - 5.54, m), 7.20 - 8.20 (Ar, m). Products of decomposition, i.e. neopentyl chloride δ 3.1 (CH_2, s), and vinyl diphenylphosphinate δ 5.15 (CH_2=C, m, 5.05 - 5.25 ppm) and traces of unreacted phenacyl chloride δ 4.72 ppm were also present, δ_P ($CDCl_3$) 55.9. The crystals kept under ether at room temperature were decomposed after one week.

III.2.3 OBSERVATION OF THE COURSES OF THE DECOMPOSITION OF ISOLATED PHOSPHONIUM INTERMEDIATES IN DRY $CDCl_3$ BY ^1H n.m.r. SPECTROSCOPY

Decomposition of Arbuzov intermediates

Decomposition of Trineopentyloxy(phenacyl)-phosphonium Bromide in Deuterochloroform

The phosphonium bromide (0.1 g) was dissolved in deuterochloroform (ca. 2.5%) in an unsealed ^1H n.m.r. tube. After 10 min signals were observed for trineopentyloxy(phenacyl)-phosphonium bromide (87 mole %), δ 1.02 (Me_3C, s), 4.35 (CH_2OP, d, J_{POCH} 4.8 Hz), 5.74 (CH_2P, d, J_{PCH} 18.3 Hz), 7.3 - 8.4 ppm (Ar, m), and the decomposition products dineopentyl phenacylphosphonate (13 mole %), δ 0.86 (Me_3C, s), 3.72 (CH_2OP, d, J_{POCH} 4.8 Hz), 3.65 (CH_2P, d, J_{PCH} 22.8 Hz), 7.2 - 8.1 ppm (Ar, m) and neopentyl bromide (13 mole %), δ 1.03 (Me_3C, s), 3.27 ppm (CH_2, s). Decomposition increased to 30.6% after 25 min at 33 °C, to 86.0% after a further 15 h at room temperature, and was complete after 3 days.

Thermal Decomposition of Dineopentyloxy(phenacyl)-phenylphosphonium Bromide in Deuterochloroform

The phosphonium bromide was dissolved in deuterochloroform (ca. 3.0%) and the solution was sealed in a ^1H n.m.r. tube. Signals for the ketophosphonium intermediate only were observed at δ 1.07 (Me_3C, s), 4.34 (CH_2OP, m), 5.99 (CH_2P, d, J_{PCH} 15.6 Hz), 7.2 - 8.4 ppm (Ar, m). No change occurred in 3 days at room temperature. The tube was then heated at 100 °C (oil bath) for 0.5 h after which the phosphonium intermediate had decomposed completely to two products: neopentyl phenacyl(phenyl)phosphinate δ 0.81 (Me_3C, s), 3.3 - 4.0 (CH_2OP and CH_2P, overlapping signals, m), 7.26 - 8.3 (Ar, m), and neopentyl bromide δ 1.02 (Me_3C, s), 3.22 (CH_2C, s). The tube was then opened and a few drops of D_2O were added. After shaking and standing 24 h the ^1H n.m.r. spectrum showed that the signal at 3.77 ppm (PCH_2, dd) had disappeared because of exchange with D. The signal at 3.52 ppm ($POCH_2$, m) which had previously overlapped with the PCH_2 signals, however remained.

Thermal Decomposition of Neopentyloxy(phenacyl)-diphenylphosphonium Bromide in Deuterochloroform

The phosphonium bromide was dissolved in deuterochloroform (*ca*. 3%) and sealed in a ^1H n.m.r. tube. The ^1H n.m.r. spectrum showed signals for the phosphonium intermediate only at δ 0.99 (Me_3C, s), 4.15 (CH_2OP, d, J_{POCH} 4.2 Hz), 6.25 (CH_2P, d, J_{PCH} 12.6 Hz), 7.2 - 8.3 ppm (Ar, m). No change occurred in 5 days at room temperature. The tube was heated for 0.5 h at 100 °C in an oil bath, after which time the phosphonium bromide had decomposed completely to phenacyl(diphenyl)phosphine oxide[44] δ 4.14 (CH_2P, d, J_{PCH} 15.6 Hz) and neopentyl bromide, δ 1.02 (Me_3C, s), 3.25 (CH_2C, s), 7.3 - 8.5 ppm (Ar, m).

In another experiment solution of the phosphonium bromide was heated in a sealed ^{1}H n.m.r. tube at 80 °C (40 min) (decomposition at this temperature was very slow) and then at 90 °C for 20 min. The decomposition was below 50% under these conditions.

Decomposition of the Perkow intermediate

Decomposition of Neopentyloxy(diphenyl)-1-phenylvinyloxyphosphonium Chloride in Deuterochloroform

Isolated crystals of the Perkow intermediate were placed in a ^{1}H n.m.r. tube and dissolved in deuterochloroform (ca. 4%). The ^{1}H n.m.r. spectrum immediately after preparation showed signals for the vinyloxyphosphonium intermediate (45.7 mole %) δ 4.04 (Me_3CCH_2, d), 5.48 ppm (CH_2=C, m), the vinyl phosphinate (54.3 mole %) δ 5.10 (CH_2=C, m), and neopentyl chloride δ 3.3 (CH_2, s), and some minor impurities, mainly phenacyl chloride, δ 4.72 ppm.

The tube was kept at 33 °C and as the decomposition proceeded the signals of the vinyloxyphosphonium compound, δ 4.04 (d), 5.48 (m) decreased and the signals for the decomposition products, δ 3.33 (s), and 5.15 (m) increased. The decomposition is summarized in the table below.

Time after preparation (min)	phosphonium (%)	phosphinate (%)
0	45.7	54.3
15	34.8	65.2
35	24.7	75.3
60	16.6	83.4

The half-life of the decomposition at 33 °C was ca. 40 min.

III.2.4 PREPARATION AND ISOLATION OF ARBUZOV AND PERKOW PRODUCTS

Preparation and Isolation of the following Arbuzov Products formed on the Decomposition of the Corresponding isolated Arbuzov Intermediates

Preparation and Isolation of Neopentyl Phenacyl(phenyl)phosphinate

Dineopentyloxy(phenacyl)phenylphosphonium bromide (1.2 g, 2.5 mmol) was dissolved in deuterochloroform (4 ml) and sealed in three ^{1}H n.m.r. tubes. The tubes were heated for 40 min at 100-105 °C in an oil bath, after which the ^{1}H n.m.r. spectrum confirmed that the phosphonium salt had decomposed completely. The contents of the tubes were then combined and concentrated under high vacuum to give a hard white solid (0.7 g) (85.4% calculated as the ketophosphinate), m.p. 71-77 °C (sealed tube). The product was recrystallised from ether/petroleum (b.p. 40-60 °C), washed well with petroleum, and dried under high vacuum to give neopentyl phenacyl(phenyl)phosphinate (0.48 g, 58.5%), m.p. 82-83 °C (sealed tube) (Found: C, 68.8, H, 7.1. $C_{19}H_{23}O_3P$ requires: C, 69.1, H, 7.0%), δ_H ($CDCl_3$) 0.81 (Me_3C, s, 9H), 3.52 [CH_2OP, d AB, $\delta(H_A)$ 3.67, $\delta(H_B)$ 3.37, J_{AB} 8.9, $J_{POCH(A)}$ 5.1, $J_{POCH(B)}$ 4.8 Hz], overlapping with 3.77 [CH_2P, dd AB, $\delta(H_A)$ 3.79, $\delta(H_B)$ 3.74, J_{AB} 0, $J_{POCH(A)}$ 18.4, $J_{POCH(B)}$ 17.5 Hz] (4H total), 7.3-8.3 (Ar, m, 10H),

δ_P ($CDCl_3$) 32.1, m/z 330 (10%, M^+), 261 (100%), IR (KBr disc) $v_{C=O}$ 1667, $v_{P=O}$ 1219, v_{POC} 1031 cm^{-1}. The filtrate gave a second crop of crystals (0.15 g, 18.3%), m.p. 74-79 °C (sealed tube). Total yield was 76.8%.

Preparation of Phenacyl(diphenyl)phosphine Oxide

Neopentyloxy(phenacyl)diphenylphosphonium bromide (0.66 g, 1.4 mmol) was dissolved in deuterochloroform (4.5 ml) and the solution was sealed in three ^1H n.m.r. tubes. The tubes were heated at 100-105 °C in an oil bath for 40 min, after which the ^1H n.m.r. spectrum showed that the phosphonium bromide had decomposed completely. The combined solutions were concentrated under high vacuum to give a hard white crystalline product (0.4 g, 89.0% calculated as the phosphine oxide), m.p. 126-134 °C. Recrystallisation from dry chloroform/ether gave long thin crystals which were washed with ether and dried under high vacuum to give phenacyl(diphenyl)phosphine oxide, m.p. 138-140 °C (sealed tube) (lit.[44] m.p. 140-140.5 °) (Found: C, 75.5, H, 5.5. Calc. for $C_{20}H_{17}O_2P$: C, 75.0, H, 5.4%), δ_H ($CDCl_3$) 4.14 (CH_2P, d, J_{PCH} 15.6 Hz 2H), 7.3-8.5 (Ar, m, 15H), δ_P ($CDCl_3$) 28.2, m/z 320 (27%, M^+), 201 (100%), IR (KBr disc) $v_{C=O}$ 1680, $v_{P=O}$ 1184 (lit.[44] 1190) cm^{-1}.

Preparation and Isolation of the following Perkow Products

Preparation of Neopentyl 1-Phenylvinyl Phenylphosphonate

Phenacyl chloride (5.56 g, 1 mol. equiv.) in dry chloroform (15 ml) was added slowly, stirring well, to dineopentyl phenylphosphonite (10.5 g, 1 mol. equiv.) also in dry chloroform (8.0 ml) at 0 to 5 °C. The temperature was then gradually increased to 25 °C and the mixture was stirred for another hour before being stoppered and kept in dry conditions for 2 days. The mixture was then concentrated under reduced pressure giving 11.5 g (94%) of crude product. Distillation of the product gave a first fraction (4.0 g), b.p. 123-144 °C at 0.1 mmHg, consisting of a mixture of vinyl phosphinate and phenacyl chloride, a second fraction (5.0 g), b.p. 170-184 °C at 0.1 mmHg, which was mainly vinyl phosphinate with traces of phenacyl chloride, and a third fraction consisting of pure neopentyl 1-phenylvinyl phenylphosphonate (2.0 g, 17%) b.p. 184-190 °C at 0.1 mmHg, n_D^{20} 1.5420, (Found: C, 69.1, H, 7.0. $C_{19}H_{23}O_3P$ requires: C, 69.1, H, 7.0%), δ_H ($CDCl_3$) 0.89 (Me_3C, s, 9H), 3.77 (CH_2OP, d, 2H, J_{POCH} 5.1 Hz), 5.19 ($CH_2=C$, d, 2H, $J_{PC=CH}$ 2.5 Hz), 7.2-8.1 (Ar, m, 10H), δ_P ($CDCl_3$) 15.0, m/z 330 (9%, M^+), 105 (100%), IR $v_{C=C}$ 1622, $v_{P=O}$ 1260, v_{POC} 990-1040(br.)cm^{-1}. The total yield in the second and third fractions was 7.0 g, (58.0%).

Preparation of 1-Phenylvinyl Diphenylphosphinate

α-Chloroacetophenone (2.25 g, 1 mol. equiv.) was dissolved in dry chloroform (4 ml) and was added from a dropping funnel to neopentyl diphenylphosphinite (4.0 g, 1 mol. equiv.) with stirring and cooling at -25 °C; the reaction is exothermic. Dry ether (10 ml) was added to the viscous mass and the mixture was kept at room temperature for 24 hours. Solvent was removed under reduced pressure to leave a viscous residue which solidified on standing (12 h). The residue was then distilled to give a first fraction (0.2 g), b.p. 60-120 °C at 0.1 mmHg, which solidified in the receiver, a second fraction (1.2 g) b.p. 160-190 °C at 0.1 mmHg which also solidified on standing, and the third main fraction consisting of 1-phenylvinyl diphenylphosphinate[45] (1.4 g, 29.8%) b.p. 190-194 °C at 0.1 mmHg as a very viscous liquid which solidified after 2 hours, m.p. 77-78 °C (sealed tube) (Found: C, 75.3, H, 5.4. Calc. for $C_{20}H_{17}O_2P$: C, 75.0, H, 5.4%), δ_H ($CDCl_3$) 5.15 (CH_2=C, m, 2H), 7.2-8.2 (Ar, m, 15H), δ_P ($CDCl_3$) 29.7, m/z 320 (27%, M^+), 201 (100%), IR (KBr disc) $\nu_{C=C}$ 1622, $\nu_{P=O}$ 1225, ν_{POC} 1029, 1005, 990 cm^{-1}.

III.3 PREPARATION AND THERMAL DECOMPOSITION OF THE INTERMEDIATES FORMED BY REACTION OF NEOPENTYL *N*,*N*,*N'*,*N'*-TETRAMETHYLPHOSPHORODIAMIDITE WITH HALOGENOMETHANES

Preparation of Neopentyl Phosphorodichloridite[46,47]

Neopentyl alcohol (30.0 g, 1.0 mol. equiv.) in dry ether (60 ml) was added dropwise (1.5 h) with stirring to phosphorus trichloride (50.0 g, 1.07 mol. equiv.) in dry ether (45 ml), cooling to -15 °C (in an ice salt bath). The clear liquid mixture was brought to room temperature, stored for 15 h in dry conditions, and concentrated under reduced pressure. Distillation gave two fractions: 41.0 g, (63.7%), b.p. 64 - 66 °C at 20 mmHg, n_D^{22} 1.4620 (lit.[46] b.p. 47.5 - 48 °C at 10 mmHg), δ_H ($CDCl_3$) 0.95 (Me_3C, s, 9H), 3.88 (CH_2OP, d, J_{POCH} 8.4 Hz, 2H), δ_P ($CDCl_3$) 178.3, and 5.0 g, (7.8%), b.p. 66 - 67 °C at 20 mmHg, n_D^{22} 1.4590; total yield 46.0 g (71.5%).

Preparation of Neopentyl *N*,*N*,*N'*,*N'*-Tetramethylphosphorodiamidite[48]

Neopentyl phosphorodichloridite (23.2 g, 1.0 mol. equiv.) in sodium dried petroleum ether (80 ml, b.p. 30-40 °C) was added in small portions (1 h) to dimethylamine (23.0 g, 4.0 mol. equiv.) also in dry petroleum ether at -20 to -10 °C, stirring well. Vigorous reaction occurred producing white fumes. The mixture was then slowly brought to room

temperature, stored over night in dry conditions, filtered under nitrogen, and the filtrate was concentrated under reduced pressure to give a liquid residue (21.6 g, 85.4%). Distillation gave the pure product (17.8 g, 70.3%), b.p. 86-87 °C at 15 mmHg, n_D^{22} 1.4430, δ_H ($CDCl_3$) 0.90 (Me_3C, s, 9H), 2.5 (Me_2N, d, J_{PNCH} 8.6 Hz, 6H), 3.19 (CH_2O, d, J_{POCH} 6.3 Hz, 2H), δ_P ($CDCl_3$) 137.2.

Preparation of Neopentyl Phosphorodibromidite[47]

Neopentyl alcohol (30.0 g, 1.0 mol. equiv.) in dry ether (60 ml) was added dropwise (1.5 h) to phosphorus tribromide (94.7 g, 1.0 mol. equiv.) in dry ether (30 ml), cooled to -15 to -20 °C and stirred well. The the reaction mixture was brought to room temperature, stored over night in dry conditions, concentrated under reduced pressure and distilled twice to give the pure product (46.4 g, 49.1%), b.p. 45-50 °C at 0.1 mmHg, δ_H ($CDCl_3$) 0.96 (Me_3C, s, 9H), 3.83 (CH_2O, d, J_{POCH} 8.4 Hz, 2H), δ_P ($CDCl_3$) 200.4 ppm.

Preparation of Neopentyl N,N-Dimethylphosphoramidochloridite

Dimethylamine (6.3 g, 2.0 mol. equiv.) in petroleum ether (b.p. 30-40 °C) (23 ml) was cooled to -20 °C and added dropwise with stirring (15 min) to neopentyl phosphorodichloridite (13.2 g, 1.0 mol. equiv.) also in light petroleum (47 ml) at -20 °C. The mixture was filtered at room temperature and the filtrate was distilled after removal of solvent to give neopentyl N,N-dimethylphosphoramidochloridite (7.2 g, 52.3%), b.p. 44-48 °C at

0.1 mmHg, n_D^{23} 1.4581 (Found: Cl, 17.8. $C_7H_{17}ClNOP$ requires: Cl, 17.9%), δ_H ($CDCl_3$) 0.94 (Me_3C, s, 9H), 2.66 (Me_2N, d, J_{PNCH} 12.6 Hz, 6H), 3.55 (CH_2O, d, J_{POCH} 7.2 Hz, 2H), δ_P ($CDCl_3$) 178.4.

Preparation of Neopentyl N,N-Dimethylphosphoramidobromidite

Dimethylamine (7.1 g, 2.0 mol. equiv.) in petroleum ether (b.p. 30-40 °C) (30 ml) was cooled to -20 °C and added dropwise (20 min) to neopentyl phosphorodibromidite (21.0 g, 1.0 mol. equiv.), also in light petroleum (60 ml) at -20 °C. Diethyl ether (50 ml) was added at room temperature, the mixture was filtered, and the filtrate was concentrated and distilled to give a main fraction (10.7 g), b.p. 55-63 °C at 0.1 mmHg. Redistillation afforded pure neopentyl N,N-dimethylphosphoramidobromidite (2.8 g, 15.3%), b.p. 81-82 °C at 0.3 mmHg (Found: Br, 31.6. $C_7H_{17}BrNOP$ requires: Br, 33.0%), δ_H ($CDCl_3$) 0.96 (Me_3C, s, 9H), 2.64 (Me_2N, d, J_{PNCH} 13.8 Hz, 6H), 3.65 (CH_2O, d, J_{POCH} 7.2 Hz, 2H), δ_P ($CDCl_3$) 198.3.

Preparation of Bisdimethylamino(methyl)neopentyloxyphosphonium Chloride

Neopentyl N,N,N',N'-tetramethylphosphorodiamidite (4.0 g, 1.0 mol. equiv.) and chloromethane (2.4 g, 2.48 mol. equiv.) were mixed at -80 °C, sealed in a glass tube, and allowed to stand at room temperature. After 24 h a little solid separated and a second liquid layer formed which became solid in 6 days. Excess of chloromethane was then removed to leave a white solid (5.0 g) which gave a cloudy solution in $CDCl_3$. Filtration under N_2 afforded tetramethylammonium chloride (0.22 g, 10.4%), sublm. > 360 °C, which was identified by infrared (KBr disc).[49] Addition of dry ether to the filtrate gave an oily layer which remained as a liquid residue (4.3 g) after drying under high vacuum and which contained the phosphonium chloride, δ_H ($CDCl_3$) 1.00 (Me_3C, s), 2.42 (MeP, d, J_{PCH} 14.4 Hz), 2.90 (Me_2N, d, J_{PNCH} 10.8 Hz), 3.90 (CH_2O, d, J_{POCH} 4.8 Hz), δ_P ($CDCl_3$) 59.8 and the phosphoramidochloridite, δ_H 0.95 (Me_3C, s), 2.66 (Me_2N, d, J_{PNCH} 9.6 Hz), 3.55 (CH_2O, d) (mol ratio _ca._ 83 : 17), δ_P 179.2. The product crystallised in 10 weeks at 0 °C and was then washed with anhydrous ether (0 °C) and dried under high vacuum to give _bisdimethylamino(methyl)neopentyloxyphosphonium chloride_ (1.5 g, 30.1%), m.p. 55-60 °C (sealed tube) (Found: C, 45.8, H, 10.2, Cl, 13.5, N, 11.3, P, 11.3. $C_{10}H_{26}ClN_2OP$ requires: C, 46.8, H, 10.2, Cl, 13.8, N, 10.9, P, 12.1%), δ_H ($CDCl_3$) 1.0 (Me_3C, s, 9H), 2.37 (MeP, d, J_{PCH} 14.7 Hz, 3H), 2.89 (Me_2N, d, J_{PNCH} 10.2 Hz, 6H), 3.86 (CH_2O, d, J_{POCH} 5.0 Hz, 2H), δ_P ($CDCl_3$) 60.3.

Preparation of Bisdimethylamino(methyl)neopentyloxyphosphonium Bromide

Neopentyl _N_,_N_,_N'_,_N'_-tetramethylphosphorodiamidite (1.7 g, 1.0 mol. equiv.) was added to bromomethane (2.0 g, 2.5 mol. equiv.) at -80 °C and the mixture was allowed to stand at room temperature (22 h). After removal of the excess of bromomethane the solid residue (2.8 g) was dissolved in the minimum of $CDCl_3$ (some cloudiness remained) and shown to contain the phosphonium bromide, δ_H 1.01 (Me_3C, s), 2.44 (MeP, d, J_{PCH} 15.3 Hz), 2.93 (Me_2N, d, J_{PNCH} 10.2 Hz), 3.93 (CH_2O, d, J_{POCH} 4.8 Hz), δ_P 60.2, and the phosphoramidohalidite, δ_H 3.65 (CH_2O, d, J_{POCH} 7.2 Hz) (mol ratio <u>ca</u>. 86 : 14), δ_P 199.1. Solid which separated was washed with chloroform and ether and identified (infrared, KBr disc)[49] as tetramethylammonium bromide (0.05 g, 3.9%), m.p. > 300 °C. Concentration of the filtrate followed by addition of dry ether gave white, crystalline <u>bisdimethylamino(methyl)neopentyloxyphosphonium bromide</u> (2.2 g, 88.6%), (Found: C, 38.3, H, 8.4, Br, 26.5, N, 9.5, P, 10.0. $C_{10}H_{26}BrN_2OP$ requires: C, 39.9, H, 8.6, Br, 26.6, N, 9.3, P, 10.3%), m.p. 122 °C, δ_H ($CDCl_3$) 1.01 (Me_3C, s, 9H), 2.47 (CH_3P, d, J_{PCH} 15.6 Hz, 3H), 2.92 (Me_2N, d, J_{PNCH} 9.9 Hz, 6H), 3.93 (CH_2O, d, J_{POCH} 4.8 Hz, 2H), δ_P ($CDCl_3$) 60.2.

<u>Preparation of Bisdimethylamino(methyl)neopentyloxyphosphonium Iodide</u>[48]

Neopentyl <u>N</u>,<u>N</u>,<u>N</u>',<u>N</u>'-tetramethylphosphorodiamidite (1.0 g, 1.0 mol. equiv.) in $CDCl_3$ was placed in a ^{31}P n.m.r. tube and cooled in an ice-bath. Iodomethane (1.5 g, 2.18 mol. equiv.) was added slowly, when a vigorous exothermic reaction occurred. Immediately after the addition the ^{31}P n.m.r. spectrum showed a signal due to the phosphonium iodide, δ_P 59.7 ppm. No other products were detectable. Then the deuterochloroform solution was treated with dry ether, which precipitated white crystals of the phosphonium salt.

Investigation of the Action of Halogenomethanes on N,N-Dimethylphosphoramidohalidites

(a) Chloromethane

The phosphoramidochloridite (2.5 g, 1.0 mol. equiv.) and chloromethane (1.7 g, 2.66 mol. equiv.) were mixed at -80 °C and sealed in a glass tube. After 28 h at room temperature the tube was cooled and opened and chloromethane was allowed to escape. The residue (2.8 g) contained only the unreacted chloridite, δ_H ($CDCl_3$) 0.95 (Me_3C, s), 2.66 (Me_2N, d, J_{PNCH} 12.6 Hz), 3.56 (CH_2O, d, J_{POCH} 7.2 Hz) and a little chloromethane δ_H 2.99(s). Signals assignable to the dichloridite, $ROPCl_2$, δ_P ($CDCl_3$) 178.4 were absent.

(b) Bromomethane

By a similar procedure the phosphoramidobromidite (1.7 g, 1.0 mol. equiv.) and bromomethane (2.0 g, 3.0 mol. equiv.), after 4 days at room temperature, gave a residue (2.1 g) containing the unreacted bromidite, δ_H ($CDCl_3$) 0.97 (Me_3C, s), 2.63 (Me_2N, d, J_{PNCH} 13.5 Hz), 3.64 (CH_2O, d, J_{POCH} 7.2 Hz) and some bromomethane, δ_H 2.63(s). No dibromidite, $ROPBr_2$, δ_P ($CDCl_3$) 198.1 was detectable.

Thermal Decomposition of Bisdimethylamino(methyl)-neopentyloxyphosphonium Halides

(a) In anhydrous $CDCl_3$

Solutions of the halides (ca. 10%) in $CDCl_3$ were heated in sealed ^1H n.m.r. tubes at 100 °C. In each case, decomposition gave the neopentyl halides (δ_H as reported)[47] and methylphosphonic bisdimethylamide, δ_H 1.4 (MeP, d, J_{PCH} 13.2 Hz, 3H), 2.60 (Me_2N, d, J_{PNCH} 10.8 Hz, 12H), δ_P 36.9 (lit.[50] δ_P 38.0) as follows (%/h): Cl, 60/4, 94/9.5, 99/21; Br, 80/3.5, 98/7.5, 100/13.5.

(b) In the presence of water

A solution of the phosphonium bromide (0.1 g) in $CDCl_3$ (1 ml) was shaken with water (0.2 ml) and the mixture was then heated for 44 h at 100 °C (reaction complete) in a sealed tube. ^1H n.m.r. showed the presence of neopentyl bromide, δ 1.03 (Me_3C, s), 3.27 (CH_2, s), methanephosphonic bisdimethylamide, δ 1.40 (MeP, d, J_{PCH} 15.0 Hz), 2.61 (Me_2N, d, J_{PNCH} 10.0 Hz), and the dimethylammonium ion, δ 2.57 (s) (ca. 18 mole %). In two further experiments the bromide (0.58 g) was heated (44 h at 100 °C) with water alone: (a) 0.06 g (2 mol. equiv.); (b) 0.12 g (4 mol. equiv.). Tube (a) formed three layers, the upper layer slowly depositing white needle-like crystals of dimethylammonium bromide δ_H ($CDCl_3$) 2.69 (Me, s, 6H), 9.56 ($\overset{+}{N}H_2$, br s, 4H). The middle layer was dissolved in $CDCl_3$ and treated successively with ether and acetone to give an oily liquid which crystallised in 8 weeks. The crystals were washed with ether, dried, and identified as dimethylammonium neopentyl methanephosphonate, m.p. 95-100 °C, δ_H ($CDCl_3$) 0.91 (Me_3C, s, 9H), 1.24 (MeP, d, J_{PCH} 15.9 Hz, 3H), 2.53 ($\underline{Me}_2\overset{+}{N}H_2$, s, 6H), 3.45 ($CH_2O$, d, J_{POCH} 5.1 Hz, 2H), δ_P ($CDCl_3$) 24.0 (quartet of triplets), δ_C ($CDCl_3$) 11.8 (MeP, d, J_{PC} 137.3 Hz), 26.0 ($\underline{Me}_3C$, s), 32.0 ($Me_3\underline{C}$, d, J_{POCC} 7.3 Hz), 34.5 ($Me_2\overset{+}{N}H_2$, s), 74.5 (CH_2OP, d, J_{POC} 6.1 Hz).

Tube (b) formed two layers from which volatiles were removed under reduced pressure. The residue was dissolved in $CDCl_3$, and treated with ether/acetone to give a first crop of crystals which were washed with ether and dried to give bisdimethylammonium methanephosphonate (0.15 g), m.p. 60 °C, δ_H ($CDCl_3$) 1.30 (MeP, d, J_{PCH} 16.2 Hz, 3H), 2.66 ($Me_2\overset{+}{N}H_2$, s, 12H), 9.89 ($\overset{+}{N}H_2$, br s, 4H), δ_P ($CDCl_3$) 23.5 (quartet), δ_C ($CDCl_3$) 14.7 (MeP, d, J_{PC} 137.9 Hz), 34.9 ($Me_2\overset{+}{N}H_2$, s). A further crop of crystals consisted of dimethylammonium neopentyl methanephosphonate, m.p. 90-100 °C, with n.m.r. data as given above.

Absorption of Water by the Phosphonium Chloride

The chloride (0.18 g) was left open to the atmosphere when it absorbed water (0.033 g, 2.7 mol. equiv.) in 5 h, forming a liquid mixture. On standing in a desiccator with P_2O_5 overnight the water content fell to 0.023 g (1.9 mol. equiv.). The ^1H n.m.r. spectrum ($CDCl_3$) showed that no reaction had occurred. A signal which slowly appeared at δ 2.66 ($Me_2\overset{+}{N}H_2$) showed that ca. 27% hydrolysis occurred in the $CDCl_3$ solution in 16 weeks.

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FIGURES AND TABLES

VI

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