SOME ASPECTS

OF

PHOSPHETAN CHEMISTRY

by

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STATEMENT

The experimental work described in this thesis has been carried out by the author in the laboratories of the Department of Chemistry of the University of Leicester between October 1969 and May 1972.

No part of this work has been presented or is concurrently being presented for any other degree.

Signed

R.K. Oram

August 1972. R.K. Oram
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#### SUBSTITUTION AT PHOSPHORUS IN OXYPHOSPHORANES

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1. THE SYNTHESIS OF PHOSPHETAN COMPOUNDS.

1.1 General Ring Synthesis.

A phosphetan is a four-membered heterocycle containing one phosphorus atom and three carbon atoms. Although many four-membered ring systems containing phosphorus are known, particularly as cyclic intermediates in the Wittig olefin synthesis, there have been few reports of the synthesis of phosphetans. One reason for this is that attempts to extend methods which have proved satisfactory for larger ring systems to the preparation of phosphetans have, in most cases, resulted in the formation of dimers, polymers, and open chain diphosphines. One general method of synthesis which has been found to be effective for the larger rings is the reaction of phosphides or phosphines with dihaloalkanes.\(^1,2,3\)

\[
\begin{align*}
R\overset{\text{P}}{\underset{\text{M}}{\text{H}}} + \overset{\text{X}}{(\text{CH}_2)_n} & \rightarrow R\overset{\text{P}}{\underset{\text{M}}{\text{O}}}(\text{CH}_2)_n \\
X &= \text{Cl, Br, I} & R &= \text{H, Alkyl, Aryl.} \\
M &= \text{H, Li, Na, K} & n &= 4, 5.
\end{align*}
\]

Although the method proved successful for the simplest phosphetan (1), attempts to replace one hydrogen of the phosphide by methyl or phenyl resulted in the formation of only biphosphines analogous to (2).

\[
\begin{align*}
\text{NaPH}_2 + \overset{\text{I}}{(\text{CH}_2)_3} & \rightarrow \overset{\text{P}}{\underset{\text{H}}{\text{O}}} + \overset{\text{I}}{\text{H}_2\text{P}(\text{CH}_2)_3\text{P}}_2 \\
(1) & \quad (2)
\end{align*}
\]
Intramolecular quaternisation of haloalkylphosphines has been used to synthesise phosphorus heterocycles, the haloalkylphosphines being the presumed intermediate products in the reaction of secondary phosphines and phosphides, or diphosphines with dihalogenoalkanes*.

\[
\text{Ph}_2\text{PK (H)} + X-(\text{CH}_2)_n-X \rightarrow [X-(\text{CH}_2)_n\text{PPh}_2]
\]

The attempted extension of this reaction to synthesise the analogous phosphetanium salt resulted in the formation of the bisphosphonium salt (3).

\[
\text{Ph}_2\text{PH} + \text{I(CH}_2)_3\text{I} \rightarrow \text{Ph}_2\text{P}+\text{PPh}_2^{+} \quad \text{2I}^{-}
\]

Under more favourable circumstances however this general method has proved successful. Intramolecular quaternisation of the intermediate chloroalkylphosphine (4) gave the phosphetanium salt (5).

In this example the bulky groups present force the intermediate (4) into a rotomer in which the phosphine and the chloromethyl group are in close enough proximity for intramolecular quaternisation to occur.
A similar explanation has been put forward⁰ to account for the observation that certain bulky substituents aid the analogous cyclisation of amines to azetidines (6). Increasing the bulk of the substituents by replacing A=H by A=CH₂OCH₃, or R=methyl by R= isopropyl, had the effect of making the rotomer (7) more preferential and thus increasing the yield of cyclic product.

A cyclisation reaction to give a phosphetan (8) was found⁰ to occur when phenyl bis(chloromethyl)phosphinate was treated with two equivalents of sodiodiethylmalonate. Again the large substituents
must force the conformation (9) on the intermediate.

\[
\text{PhOP(\text{CH}_2\text{Cl})_2} + \text{NaCH(CO}_2\text{Et)}_2 \rightarrow \text{PhOPCH}_2\text{C(CO}_2\text{Et)}_2
\]

Green\textsuperscript{10} prepared the highly substituted phosphetan oxide (10) from the reaction of bicyclo[2,2.1]heptadiene with methylphosphonous dichloride. Corfield\textsuperscript{11} found that by the use of catalytic quantities of aluminium chloride, this synthetic route could be extended to the preparation of the phenyl oxide from phenylphosphonous dichloride.

The synthesis of organophosphorus heterocycles has been accomplished\textsuperscript{12} by the photolysis, and by the partial oxidation of secondary phosphines (11) containing a terminally unsaturated alkenyl group.
However, allylphenylphosphine rapidly polymerised under u.v. radiation. No cyclic product was obtained.

\[(n+1) \text{CH}_2: \text{CHCH}_2\text{PH} \xrightarrow{\text{hv}} \text{CH}_2: \text{CHCH}_2\text{P(C}_3\text{H}_5\text{O})_n\text{PH} \]

1.2 2,2,3,4,4-Pentamethylphosphetan Oxides.

In the course of a systematic investigation into the reactions of phosphorus trichloride and olefins, Jungermann and co-workers found that the olefin 2,4,4-trimethylpent-2-ene underwent a cycloaddition reaction with an equimolar mixture of phosphorus trichloride and aluminium chloride to form the highly substituted phosphetan oxide (15) in good yield.
The product was found to be a single isomer even though the methyl substituent on the 3-carbon allowed the possibility of geometrical isomers.

An X-ray crystallographic study on this single diastereoisomer by Haque\textsuperscript{14} showed that (a) the 3-methyl substituent was trans to the 1-chlorine atom on phosphorus, (b) the four-membered ring was puckered, and (c) the ring C(2)-P(1)-C(4) angle of 85.9\textdegree was considerably distorted from the tetrahedral.

In order to adequately describe the stereochemistry of pentamethylphosphetan compounds, Corfield\textsuperscript{11} has suggested the use of the Belstein r-system\textsuperscript{15}, where the reference group on phosphorus is specified by the symbol r- and the geometrical relationship of this group to the ring 3-methyl is denoted by a cis or trans prefix.
1.3 The Synthesis of 2,2,3,4,4-Pentamethylphosphetan 1-Oxides.

1.3.1 By modification of Jungermann and McBride's Synthesis.

The synthesis of 2,2,3,4,4-pentamethyl-1-phenylphosphetan 1-oxide has been accomplished\textsuperscript{16,17} by the use of phenylphosphonous dichloride in place of phosphorus trichloride. The product was found to be a mixture of diastereoisomers, the isomer ratio of which being dependent on the workup procedure. Separation of the isomers has been achieved by fractional recrystallisation, and more readily by chromatography on basic alumina\textsuperscript{18}. An X-ray analysis\textsuperscript{19} on the separate isomers has shown that, like the acid chloride, both isomers have puckered ring systems, with C(2)-P(1)-C(4) angles of ca. 82°. It was found that the oxide with m.p. 126-127° had the 3-methyl trans to the 1-phenyl, while in the isomer with m.p. 117-118° there was a cis arrangement of the two groups.

The synthesis, and isomer separation of 1-p-methoxyphenyl-2,2,3,4,4-pentamethylphosphetan 1-oxide was accomplished using the methods for the 1-phenyl oxide. The isomer more readily eluted on chromatography on alumina had m.p. 151-153° while the other isomer had m.p. 113-115°. Tentative assignments of cis and trans geometries to these oxides may be made on the basis of the method of workup of the reaction mixture, and on the ease of elution of the oxides. Addition of the reaction mixture to water yielded a major isomer with the lower melting point, which was eluted from an alumina column with ether-methanol (100:1); these properties have been found for the 2,2,cis-3,4,4-pentamethyl-r-1-phenylphosphetan 1-oxide. Hence it is possible that the isomer with m.p. 113-115° is r-1-methoxyphenyl-2,2,cis-3,4,4-pentamethylphosphetan 1-oxide; the other isomer, m.p. 151-153°, may have the trans geometry.
1.3.2. By the Reaction of Grignard Reagents with r-1-Chloro-2,2, trans-3,4,4-pentamethylphosphetan 1-Oxide.

Grignard reagents react smoothly with r-1-chloro-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide to give single isomers of the 1-alkyl, and 1-arylphosphetan oxides (16). Corfield\textsuperscript{11} found that the 1-benzyl oxide produced by reaction of benzylmagnesium chloride with the acid chloride was identical in every respect to that produced using benzyl-lithium. This latter reaction\textsuperscript{20} is believed to proceed with retention of configuration which establishes that the stereochemical course of the Grignard reaction is also retention.

\[
\begin{align*}
\text{R'} & = \text{Isopropyl, 2-Methylallyl, p-Bromophenyl.} \\
\text{R''} & = \text{t-Butyl}
\end{align*}
\]

By use of the method of synthesis given by Corfield\textsuperscript{11} for the 1-benzyl oxide, the phosphetan oxides (16) were prepared.

1.4 Preparation of 2,2,3,4,4-Pentamethylphosphetans.

1.4.1. By Reduction of 2,2,3,4,4-Pentamethylphosphetan 1-Oxides.

Cremer\textsuperscript{16} has found that the isomers of 2,2,3,4,4-pentamethyl-1-phenylphosphetan 1-oxide could be reduced stereospecifically by trichlorosilane in the presence of triethylamine to give the phosphetan (17). Re-oxidation of the phosphetans with hydrogen peroxide gave back the original isomer in both cases. As oxidation occurs with retention of configuration\textsuperscript{21} the reduction must also proceed with retention.
The phosphetan oxides (16) from the reaction of Grignard reagents with the acid chloride were also found to be reduced stereospecifically; the adducts with hexafluoroacetone prepared from the phosphine solutions were found to be single isomers. That the stereochemistry of these reductions was also retention was established by re-oxidation of an aliquot of the 1-isopropylphosphetan solution to give back the starting isomer.

Phenylsilane has been found to reduce phospholan oxides and phosphorinan oxides with retention of configuration. Reduction of the alkylphosphetan oxides (16) prepared via the Grignard reagent was found to proceed with complete retention of configuration; however under identical conditions the 1-t-butylphosphetan oxide gave the phosphetan as a mixture of isomers. Similarly the oxides (18), \( R = p-\text{BrC}_6\text{H}_4 \) and \( p-\text{MeOC}_6\text{H}_4 \), were also found to give the phosphetan as a mixture of isomers.
It is possible that the reduction step is stereospecific in all cases, but that the product phosphetans have different pyramidal stabilities. That product equilibration is responsible for these results is supported by the data of Cremer and co-workers\textsuperscript{25}, who found that pyramidal inversion of the 1-t-butylphosphetan proceeded 8000 times faster than the 1-methylphosphetan. This was explained in terms of non-bonded interactions between the t-butyl group and the ring methyls. Mislow\textsuperscript{26} has suggested that the lower barrier to pyramidal inversion found for the 1-phenylphosphetan may be due to a combination of the steric factors and (\(p-p\))\(\pi\) bonding between the lone pair and the \(\pi\) orbitals of the phenyl group; this may also be true for the 1-\(p\)-BrC\(_6\)H\(_4\) and 1-\(p\)-MeOC\(_6\)H\(_4\) phosphetans.

The reduction of \(r\)-1-chloro-2,2,\(\text{trans}\)-3,4,4-pentamethylphosphetan 1-oxide with polymethylhydrogensiloxane\textsuperscript{27} has been found to give a mixture of the chlorophosphetan (19) and the secondary phosphetan (20).

\[
\begin{align*}
\begin{array}{c}
\text{Cl} \quad \to \\
\end{array}
\end{align*}
\]

(19) (20)

Treatment of the secondary phosphetan with one molar equivalent of chlorine gave the chlorophosphetan (19). The ratio of isomers of the chlorophosphetan was 3.8:1, the major isomer of which was found to be \textit{trans} as oxidation of the mixture of isomers (19) gave \(r\)-1-chloro-2,2,\(\text{trans}\)-3,4,4-pentamethylphosphetan 1-oxide as the major product.
Phenylsilane reduction of the acid chloride was found to give only 2,2,3,4,4-pentamethylphosphetan (20). When freshly and carefully distilled the phosphetan showed a P-H signal at \( \tau 6.28 \) (\( J_{PH} 170 \) Hz) which had been absent in previously prepared samples\(^{28}\). Attempts have been made to correlate the hybridisation of the phosphorus atom in secondary phosphetans with the coupling constant\(^{29}\). The low coupling constant found for 2,2,3,4,4-pentamethylphosphetan indicates a very high degree of \( p^3 \) hybridisation of the phosphorus atom, presumably in order to relieve strain in the four-membered ring.

1.4.2. By Nucleophilic Substitution at Phosphorus in 1-Chloro-2,2,3,4,4-pentamethylphosphetan.

Nucleophilic substitution of the chlorine atom in 1-chloro-2,2,3,4,4-pentamethylphosphetan (19) by benzylamine or ethoxide ion has been found to proceed with predominant inversion of configuration\(^{27,30}\), which was explained in terms of colinear attacking and departing groups.

\[
\begin{align*}
\text{(19)} & \quad \text{N}^- \quad \text{Cl}^- \\
\quad \text{Cl}^- & \quad \text{P} - \text{Cl} \\
\text{(21)} & \quad \text{P} - \text{Cl}^- \\
\text{(22)} & \quad \text{P} - \text{N} \\
\end{align*}
\]

\( N = \text{OMe, HNBz} \)

Here the increase in ring strain in (21) when the four-membered ring spans the two equatorial positions must be more than balanced by the stereoelectronic\(^{31}\) gain in having two electronegative substituents occupying the apical positions.
By adaptation of this reaction the 1-substituted phosphetans (22) were prepared.

![cis (22)](image)

![trans](image)

The phosphetans (22), \( N = N(CH_3)_2, N(CH_2)_4, \) and OPh were obtained as a mixture of isomers, the major isomer presumably cis.\(^{30}\)

The neat phosphines were found to slowly equilibrate to favour the other, presumed trans isomer.

On the basis of Mislow's prediction\(^ {32} \) that the presence of an electronegative heteroatom adjacent to phosphorus will raise the pyramidal inversion barrier as compared with the methyl analogue, it is unlikely that this process is responsible for the equilibration. Presumably, the presence of small quantities of the appropriate nucleophile in the crude product caused further substitution (with inversion\(^{30} \)) leading to equilibration of the isomers. The phosphetan (22), \( N = SPb \)

![Equilibration of Isomers](image)
was obtained with an isomer ratio close to unity; presumably equilibration was complete before isolation of the phosphetan in this case.

1.5 2,2,3,3-Tetramethyl-l-phenylphosphetan Compounds.

Cremer and Chorvat\textsuperscript{16} found that the phosphetan synthesis of Jungermann and McBride\textsuperscript{13} could be modified to synthesise other less substituted phosphetans. By the use of the olefin 2,3,3-trimethylbut-1-ene in the cycloaddition reaction with phenylphosphonous dichloride and aluminium chloride, 2,2,3,3-tetramethyl-l-phenylphosphetan 1-oxide (23) was prepared.

\[
\text{PhPCl}_2/\text{AlCl}_3 \xrightarrow{\text{H}_2\text{O}} \text{PhPCl}_2/\text{AlCl}_4 \xrightarrow{\text{Cl}} \text{PhPCl}_2/\text{AlCl}_4 \xrightarrow{\text{O}} (23)
\]

The reduction of this phosphetan oxide was readily accomplished by any of the methods enumerated for the related pentamethyl-1-phenylphosphetan 1-oxide. Quaternisation of the phosphetan with benzyl bromide yielded 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium bromide, the cation of which could be separated into its optical enantiomers\textsuperscript{33} by means of fractional crystallisation of its \text{D(-)} dibenzoyl hydrogenentartrate\textsuperscript{34,35} salt from propanol. Recovery of the optically active phosphetanium halide was achieved either by an adaption of a method given by Horner\textsuperscript{36}, or by metathesis with ammonium iodide. Shutt\textsuperscript{33} reported that the hydrolysis of this salt proceeded with complete retention of configuration at phosphorus;
attempts to repeat this work have shown that considerable inversion occurs. This will be discussed in a later Chapter.
2. PHOSPHORANES.

2.1 The Structure of Phosphoranes.

The structures of several stable pentacoordinate phosphoranes have been examined by X-ray crystallography and electron diffraction. These have included pentafluorophosphorus, pentaphenylphosphorus, two stable Wittig intermediates, and the two allotropic forms of the phenanthraquinone-triisopropylphosphite adduct (24).

![Chemical Structure](24)

Some of the more important observations made from these investigations are:

1). In every case the molecule was found to have trigonal bipyramidal geometry.

2). Those phosphoranes containing a small (four- or five-membered) ring had the ring occupying one apical and one equatorial position.

3). Apical bonds were longer than the corresponding equatorial bonds; for example in pentaphenylphosphorus the apical and equatorial P-C bond lengths were 1.987 Å and 1.850 Å respectively.

4). These structural determinations, together with $^{19}$F and $^1$H n.m.r. studies on fluorophosphoranes and oxyphosphoranes indicated a
preference of the more electronegative ligands for the apical position (the preference rule).

Molecular orbital calculations have shown that the bond length differences may be due to the fact that the apical orbitals are more electropositive than the equatorial orbitals, due to the smaller amount of \( s \) character in them. Hence electronegative ligands will prefer to bond to the apical position. More recently Ugi and Ramirez have suggested that the preference of a ligand for the apical or the equatorial position is governed not only by the electronegativity of the ligand but also by steric factors and by the ability of the ligand to \( \pi \)-bond with phosphorus; those ligands which are able to \( \pi \)-bond to the phosphorus \( d \)-orbitals will have an enhanced disposition to occupy the equatorial position over that predicted by simple electronegativity considerations. To avoid preconceived ideas as to the cause of the effect Ugi and Ramirez have introduced the term ‘apicophilicity’ to describe the preference of any group for the apical position over the equatorial position.

2.2. Pseudorotation.

The \(^{19}\text{F n.m.r.}\) of pentafluorophosphorus has been found to show only one kind of fluorine at temperatures as low as \(-157^\circ\) even though electron diffraction studies indicate a trigonal bipyramidal geometry. To account for this observation Berry postulated a method of intramolecular ligand exchange whereby equilibration of the apical and equatorial fluorines could occur. The process he suggested, which he called pseudorotation, consisted of simultaneous exchange of a pair of equatorial ligands and a pair of apical ligands by way of a square
pyramidal transition state (25). One ligand remains equatorial and has been designated the pivot.

This process has been widely used to account for the n.m.r. spectra of fluorophosphoranes, oxyphosphoranes and pentaarylphosphoranes.

2.3 Topological Representations of Pseudorotation Pathways.

The phosphorane (26) has three equatorial ligands which can serve as pivots in pseudorotation processes, i.e. three new phosphoranes are immediately accessible from (26), and from these a further six phosphoranes can be produced. As there are five ligands there are twenty different stereoisomers interconnected by thirty pseudorotation pathways. A number of topological representations of these processes have appeared, including that projection (27) of a Balaban twenty-vertex graph suggested by Mislow.

Here the stereoisomers are assigned to the vertices of the diagram with the interconnecting lines representing possible Berry pseudorotations. The enantiomeric pairs are designated by the identity of the apical groups, (1,2) and (1,2), for example. The chirality of the phosphorane is denoted by the barred symbol; if the ascending numerical order of the
equatorial ligands is clockwise when viewed from the vertex of the lowest numerical index the isomer is unbarred; if anticlockwise the isomer is barred (1,2).

2.4 Constraint.

Stereochemical constraints can readily be applied to the diagram (27), particularly those relevant to the effect of a small ring. For example, it is obviously impossible for a small ring to span the two apical positions, thus if the ring groupings are designated 1 and 2, the vertices (1,2) and (1,2), and the six pseudorotation pathways leading to them, may be removed from the diagram.
Phosphoranes which do not have either ligand 1 or ligand 2 in the apical position by necessity must have the ring in the diequatorial position, theoretically subtending a ring angle at phosphorus of 120°. The increase in ring strain on moving the four-membered ring from the apical-equatorial to the diequatorial position is believed to be considerable (estimated at approximately 20 kcal mol\(^{-1}\), see Chapter 7) and for this reason pseudorotation pathways via such high energy phosphoranes as (28) are thought not to enter into 'normal' pseudorotation processes\(^{22,44,46}\).

![Diagram](image)

The effect of neglecting pathways via such phosphoranes as (28) is to reduce the original diagram (27) to two non-interconnected six-membered cyclic pseudorotation pathways (29). As in this reduced diagram there is no access from one phosphorane to its enantiomer, stereomutation of a phosphorane cannot occur purely by pseudorotation processes.

![Diagram](image)
Mislow\textsuperscript{31} has pointed out, however, that under the most favourable circumstances the relief of stereoelectronic strain\textsuperscript{31} (the energetically unfavourable placement of electronegative ligands in the equatorial position) may balance out the increase in ring strain on the formation of phosphoranes such as (28). Under such circumstances pseudorotation pathways via these phosphoranes could become viable alternatives. However, when such a system was examined, the energy barrier to the formation of a species like (28) was still found to be high. Denney\textsuperscript{55} has determined the energy of activation for the process whereby the phosphorane (30) is converted into (31) by a two-pseudorotation process. A value of 15 kcal mol$^{-1}$ was given. Here the energetically favourable movement of the electronegative OEt ligand into an apical position did not come near to overcoming the increase in ring strain on putting the four-membered ring diequatorial. Only in association with the exceptionally electronegative ligand fluorine have such structures been found to have comparable energy. In the difluorophosphorane\textsuperscript{56} at low temperatures the two species (32) and (33) were present in the ratio 2.3:1, implying these species have almost the same energy.
In view of the magnitude of the barrier between (30) and (31) and the extreme nature of the fluorine ligand, it is probably reasonable to assume that in less favourable circumstances, where there is correspondingly less relief of stereoelectronic strain, such pseudorotations will not be viable alternatives to normal pseudorotations where the ring is retained in the apical-equatorial position. Accordingly, in the consideration of the pseudorotations of phosphorane intermediates in the hydrolysis of cyclic phosphonium salts the existence of these high energy pseudorotations will be neglected.

2.5 An Alternative Mechanism of Permutational Isomerisation

An analysis of the temperature-dependent $^{31}$P n.m.r. spectrum of dimethylaminotetrafluorophosphorane by Whitesides and Mitchell showed that in the temperature range $-50^\circ$ to $-100^\circ$ the apical pair of fluorines were replaced by an equatorial pair in a single concerted step. They concluded that the 'Berry pseudorotation mechanism' (BPR)

was the only mechanism out of the alternatives considered which satisfactorily explained this exchange process.
More recently, Ramirez and Ugi\textsuperscript{48, 58-60} have suggested an alternative mechanism for ligand exchange which also explained these results. This process, which they termed 'turnstile rotation' (TR), was characterised by a rotation of one apical and one equatorial ligand against the other three ligands. The result of a net rotation through $60^\circ$ was to form a new phosphorane in which the pair of apical ligands were exchanged for one pair of equatorial ligands. If ligands 1 and 3 were rotated against ligands 2, 4, and 5, the outcome was as shown below.

This is the identical result to a single pseudorotation via the BPR using ligand 5 as a pivot. They have shown that any ligand exchange which could be explained by the BPR could also be explained by the TR mechanism.

The rapid ligand position exchange observed in the cage oxyphosphorane (34) could readily be explained by the TR mechanism by a process of rotating the five-membered ring against the cage system, however the equivalent exchange via the BPR mechanism was suggested to have a prohibitively high energy barrier due to the high degree of ring strain involved in the square-pyramidal intermediate.
As a consequence of the results using this, and related cage systems, Ramirez and Ugi have suggested that although ligand reorganisation can proceed by either the BPR or the TR mechanism in acyclic phosphoranes, that in cyclic phosphoranes must proceed by the TR mechanism.

A recent molecular orbital analysis by Hoffmann and co-workers has suggested that this may not be so; the structure corresponding to the TR model has been shown to be higher in energy than the trigonal-bipyramidal structure, and the route involving the TR mechanism for ligand reorganisation was found to be an energetically less favourable pathway than the BPR mechanism via the square pyramidal intermediate. Hoffmann therefore suggested that, at least for symmetrically substituted phosphoranes of the R₅P type, ligand reorganisation via the TR mechanism was unlikely. In certain circumstances, however, this conclusion need not necessarily apply; possible circumstances were where the square pyramidal intermediate in the BPR mechanism was destabilised or when the trigonal bipyramidal ground state was geometrically distorted towards the TR model geometry. It may be that the cage oxyphosphorane of
Ramirez and Ugi is just such a system; in this case TR could operate even though in more normal cases the BPR mechanism is more likely.

In the absence of more conclusive evidence to the contrary, throughout this thesis ligand reorganisation in a trigonal bipyramidal phosphorane will be assumed to proceed via the Berry pseudorotation mechanism.
3. **THE ALKALINE HYDROLYSIS OF PHOSPHONIUM SALTS.**

3.1 *Alkylarylphosphonium Salts.*

The alkaline hydrolysis of quaternary phosphonium salts generally gives tertiary phosphine oxides and hydrocarbons, in contrast to the alkaline decomposition of quaternary ammonium salts which gives amines and olefins by α-elimination. This difference in behaviour has been suggested to be due to the inability of nitrogen to form a pentacordinate intermediate. It was also suggested that the relative extents of hydrolysis and α-elimination in phosphonium salts could be altered by introducing substituents on to the α-carbon; the introduction of a substituent which would increase the acidity of the α-proton should favour the formation of olefin and phosphine. Consequently it was found that while a α-phenylethylphosphonium salt gave mainly phosphine oxide and hydrocarbon by hydrolysis, a α,β-diphenylethylphosphonium salt (35) gave mainly olefin and phosphine.

\[
\text{Ph}^+ 
\begin{array}{c}
\text{CH}_2\cdot \text{CH}^+\text{Ph}_2 \\
\text{Br}^-
\end{array} 
\rightarrow 
\begin{array}{c}
\text{P}^- \\
\text{CH}_2\cdot \text{CPh}_2
\end{array}
\]

In the decomposition to hydrocarbon, Fenton and Ingold observed the following order for the ease of loss of groups: allyl, benzyl>phenyl> methyl>α-phenethyl>ethyl>higher alkanes.

More recently, Horner has studied the hydrolysis of tetra-aryl-phosphonium salts and has shown that aryl groups containing electron-withdrawing substituents are more readily lost than phenyl, whereas aryl groups bearing electron-releasing substituents are less readily lost than phenyl. This view has been confirmed by other workers. McEwen has found a similar pattern in the hydrolysis of monosubstituted tetra-
-benzylphosphonium salts; an analysis of the mixture of products showed that the presence of electron-withdrawing substituents on a group favoured the loss of that group and vice versa. Therefore, the relative ease of loss of groups on alkaline hydrolysis normally parallels their anionic stabilities. In cases where the stability of two or more groups present in a phosphonium salt are similar, hydrolysis has been found to give a mixture of products.\(^64,67\)

The ease of elimination of a group has also been found to be partially dependent upon the nature\(^67\) and the steric bulk\(^68,69\) of other groups present.

3.2 Kinetics and Mechanism.

Kinetic studies on the alkaline hydrolysis of phosphonium salts have demonstrated that almost all show third order kinetics, with a first order dependence on the concentration of phosphonium salt and a second order dependence on the concentration of hydroxyl ion\(^65-67,70-72\). Second order kinetics have been observed in a very few cases when the leaving group was an exceptionally stable anion such as p-nitrobenzyl\(^70\) or 1,4-diphenyl-1,3-butadienyl\(^73\) anion. The latter ion was lost in the hydrolysis of 1-methyl-1,2,5-triphenylphospholium iodide\(^73\) (36) to give ring-opened phosphine oxide. Similar behaviour was noted in (37).

In these few cases the hydrolyses were first order in both phosphonium salt and hydroxyl ion concentrations.

\[
\begin{align*}
\text{(36) } R & = H \\
\text{(37) } R & = \text{Ph}
\end{align*}
\]
The normal second order dependence on hydroxyl ion concentration indicates that two hydroxyl ions are involved prior to, or during the rate-determining step in the reaction. The mechanism proposed by McEwen to account for the observed kinetics involved fast, reversible formation of the pentacoordinate species (38). Fast reversible formation of the conjugate base of (38) preceded the rate-determinate step.

\[
\begin{align*}
R_4P^+ + OH^- & \quad \text{fast} \quad R_4POH \quad (38) \\
R_4POH + OH^- & \quad \text{fast} \quad R_4PO^- + H_2O \\
R_4PO^- & \quad \text{slow} \quad R_3PO + -R \\
R^- + H_2O & \quad \text{fast} \quad RH + -OH
\end{align*}
\]

This was loss of the carbanion from the conjugate base of (38). The final step was the conversion of the carbanion to the hydrocarbon by the aqueous medium.

The second order kinetics observed with the nitrobenzyl or butadienyl ion may indicate that in these cases the decomposition of the conjugate base of (38) to products is sufficiently fast to make the first step, the formation of the pentacoordinate species (38) rate determining. As only one hydroxyl ion is involved during the rate-determining step in this case, second order kinetics would be expected.

McEwen has proposed two variations on this mechanism which are consistent with the kinetic data. There could be synchronous attack of the second hydroxyl ion and departure of the anion.
Alternatively there could be a rapid formation of an unstable hexacoordinate intermediate with two hydroxide groups bonded to phosphorus. Collapse of this structure would lead to the formation of the phosphine oxide, the carbanion, and water.

Recently it has been shown\textsuperscript{74} that the final two steps of McEwen's mechanism, i.e. the rate determining loss of the carbanion and its protonation are concerted, the anion being protonated as it is formed. This was shown by the presence of a small kinetic isotope effect in the protonation of the R group on loss from the phosphonium salt; a free carbanion would not show such an isotope effect.

3.3 Stereochemistry of Hydrolysis.

The alkaline hydrolysis of benzylethylmethylphenylphosphonium iodide has been found to be completely stereospecific\textsuperscript{66} and to proceed with inversion of configuration at phosphorus.\textsuperscript{75,76} The oxide obtained from alkaline hydrolysis of a sample of the optically pure salt had exactly the opposite rotation to the phosphine oxide obtained from a Wittig reaction on a sample of the same enantiomer of the salt. Since the Wittig reaction is thought to proceed with complete retention of configuration\textsuperscript{76}, via a four-membered cyclic intermediate, then the
hydrolysis must be proceeding with complete inversion of configuration at phosphorus.

\[
(+) \text{SALT} \xrightarrow{-\text{OH}} (-) \text{OXIDE}
\]

Wittig

\[
(+) \text{OXIDE} \xleftarrow{-\text{OH}} (-) \text{SALT}
\]

Wittig (retention)

Wittig (inversion)

The hydrolysis of both enantiomers of benzylmethyl-n-propylphenyl-phosphonium bromide by Horner and coworkers\(^\text{77}\) has confirmed this result. They showed that the phosphine oxide from the hydrolysis of the salt had the opposite rotation to the phosphine oxide obtained by cathodic reduction of the salt followed by reoxidation of the resulting phosphine with hydrogen peroxide, the latter two processes proceeding with retention of configuration. They later showed\(^\text{78}\) that the phosphine oxide from a Wittig reaction on the optically active salt also had the opposite rotation to the phosphine oxide from the hydrolysis.

3.4 Structure of the intermediate.

The intermediates in bimolecular nucleophilic substitution at tetracoordinate phosphorus have been thought of as phosphoranes\(^\text{79,80}\). Displacement at phosphorus via a two-step process involving a pentacoordinate intermediate is a viable alternative to direct substitution because of the ability of phosphorus, like other second row elements, to achieve higher coordination numbers.

Although there are a number of possible geometries for a phosphorane intermediate\(^\text{81}\), most pentacoordinate species exist\(^\text{82}\) in the trigonal bipyramidal form (39) although the square pyramid structure (40) is
adopted primarily in the solid state for a small number of compounds. As all stable phosphoranes studied have been found to have the trigonal bipyramidal geometry it will be assumed throughout this thesis that the phosphorane intermediates in substitution reactions also have this geometry. However, the energy difference between the two structures 

![Diagram](image)

is accepted as being small; values as low as 1.5 kcal mol\(^{-1}\) have been suggested\(^{50}\).

3.5 **Formation and Decomposition of the Intermediate.**

There are two possible modes of attack of a hydroxyl ion on a tetrahedral phosphonium cation to form a trigonal bipyramid; attack on any one of the four faces or on any one of the six edges. Attack on a face is called apical attack as the attacking ion occupies an apical position in the resultant trigonal bipyramid, the equatorial positions being occupied by the three groups which formed the face being attacked. Attack on an edge is called equatorial attack as the attacking group occupies an equatorial position in the resultant phosphorane, the two groups forming the edge swinging into apical positions. Similarly the leaving group can depart from either an apical or an equatorial position.
An extended principle of microscopic reversibility (PMR) has been broadly applied to displacement reactions at tetracoordinate phosphorus\textsuperscript{44,47,83}. It states in effect that the stereochemistry (apical vs. equatorial) of entry and departure must be the same. In a discussion of this simplifying assumption Mislow\textsuperscript{31} has indicated that apical attack at phosphorus by a nucleophile followed by equatorial departure of the leaving group only violates the PMR when the energy profile has mirror symmetry. He has suggested that, in the final analysis, all that can be said on the basis of the PMR is that equatorial departure is rendered unfavourable to the same extent as apical attack is preferred over equatorial attack. Nevertheless, as a simplifying postulate, apical attack and apical departure will be assumed throughout this thesis.

That apical attack and apical departure are the preferred modes of bond making and breaking, at least when the ligands in question are relatively electronegative, follows from several lines of argument. Structural analyses of stable phosphoranes\textsuperscript{37-39, 41} have shown that apical bonds are longer, and therefore weaker and more readily broken than equatorial bonds. Theoretical calculations by Van der Voorn and
Drago have shown that the increased \( s \) character in equatorial bonds gives rise to apical bonds that are weaker and more polar than equatorial bonds. It is obvious therefore that electronegative nucleophiles will prefer to enter and depart via these electropositive apical positions. Also molecular orbital calculations by Boyd have borne out the essential features of Westheimer's mechanism for the hydrolysis of cyclic phosphate esters including the preference for apical attack and apical loss.

3.6 Stereochemistry of the Intermediate.

The stereochemistry of a substitution at phosphorus is governed by the position of entry and departure of the groups. The consequences of the possible combinations are shown in the following table.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Exit</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td>a.</td>
<td>I.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( I = ) Inversion.</td>
</tr>
<tr>
<td>a.</td>
<td>e.</td>
<td>R.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R = ) Retention.</td>
</tr>
<tr>
<td>e.</td>
<td>a.</td>
<td>R.</td>
</tr>
<tr>
<td>e.</td>
<td>e.</td>
<td>I.</td>
</tr>
</tbody>
</table>

As the hydrolysis of benzylethylmethylphenylphosphonium iodide (41) proceeds with inversion of configuration the choice of pathways is either apical attack and apical loss, or equatorial attack and equatorial
loss. For the reasons already enumerated the former is believed to be correct.\(^79\)

Here the electronegative hydroxy and benzyl groups (the more stable anion and hence the most electronegative of the four carbon functions present) occupy the apical positions corresponding to the phosphorane of lowest energy. However attack of the nucleophile can also occur opposite any one of the three other groups; in these cases loss of the benzyl group from the equatorial position would lead to retention. The observed complete inversion infers that decomposition of such intermediates to products does not occur; presumably dissociation to phosphonium cation and hydroxyl ion occurs. The complete stereospecificity of this hydrolysis also infers that loss of the resonance-stabilised benzyl from the phosphorane is very much faster than pseudorotation, for uncontrolled pseudorotation would lead to stereomutation of the optically active phosphorane. However if no good leaving group was present then the rate of decomposition of the intermediate phosphorane would decrease and a situation might then arise when the rate of pseudorotation is comparable with the rate of hydrolysis. In such a case an optically active phosphonium salt could hydrolyse with racemisation.
3.7 t-Butylphosphonium Salts.

The alkaline hydrolysis of the benzyl-t-butylphosphonium salt (42) has been shown to proceed with predominant retention of configuration in contrast to the ethyl analogue (41). This was rationalised in terms of attack of the hydroxyl ion opposite to the t-butyl group to give the phosphorane (43) with the t-butyl in the apical position.

Loss of the benzyl group can occur either after a single pseudorotation to place the benzyl apical or directly from an equatorial position to give the observed stereochemistry. As equatorial loss is believed not to occur the former mechanism is more likely.

This single pseudorotation is aided by both the decrease in stereoelectronic strain, i.e. the energetically favourable removal of
the highly electropositive t-butyl group from the apical position and its replacement with the more electronegative benzyl, and also by the decrease in steric crowding on moving the t-butyl group from the apical position. Further pseudorotation leading to stereomutation is presumably blocked by the inability to put the very bulky, very electropositive t-butyl back into the apical position.

The reason for this mode of attack is presumably steric; the bulky t-butyl group hinders attack of the hydroxyl ion on those faces of the tetrahedral phosphonium cation which contain the t-butyl group.
4. THE HYDROLYSIS OF CYCLIC PHOSPHONIUM SALTS.

4.1 The Phosphetan System.

There are two possible positions the four-membered ring can occupy in the phosphorane formed by attack of the hydroxyl ion on the phosphetan cation, either spanning one apical and one equatorial position (44) or two equatorial positions (45).

From the evidence provided by structural investigations into stable phosphoranes containing small rings, the structure (44) is believed to be correct. In addition there are two possible modes of attack of the hydroxyl group, either apical or equatorial. The arguments supporting apical attack have already been enumerated, but in addition equatorial attack would require equatorial departure of the benzyl leaving group from (46). The stereochemical outcome of this mode of substitution would be inversion, exactly as has been found for acyclic benzylphosphonium salts.

The observation that the small ring often has a profound effect on the stereochemical outcome of the hydrolysis indicates that equatorial attack is probably not the mode of phosphorane formation.

[Diagrams of chemical reactions and structures (44), (45), (46) are shown here.]
If the apical attack does occur, the phosphorane (47) can loose the benzyl anion either (a) directly from the equatorial position, or (b) after one pseudorotation to place the benzyl group in an apical position (48). The arguments in favour of apical loss of the carbonion have already been enumerated, but in either case the stereochemical course of the reaction would be the same, retention of stereochemistry would be observed.

The important difference between these two alternatives is that if one accepts that one pseudorotation to place benzyl apical can occur, then providing the electronegativity (or more correctly the apicophilicity) of the benzyl and the other carbon function R are comparable, other pseudorotations leading to loss of stereospecificity or optical activity during the hydrolysis should also be possible. The stereochemical consequences of the hydrolysis of phosphetanium salts suggest that mechanism (b) is probably correct.
4.2 The Pentamethylphosphetan System.

In contrast to an earlier report, Cremer and coworkers have found that the alkaline hydrolysis of various mixtures of the cis and trans stereoisomers of 1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium bromide always gave the same mixture of isomers of 2,2,3,4,4-pentamethyl-1-phenylphosphetan 1-oxide. Corfield has found identical results using the pure single isomers.
In addition it was found\(^3\)\(^3\) that while the cis salt (49) underwent a Wittig olefin synthesis to give the trans oxide (51) (retention), the trans salt (50) gave the oxide as a mixture of stereoisomers. That the stereomutation occurred at the ylide stage (by ylide isomerisation) was demonstrated by the regeneration of the salt from the ylide derived from the trans salt as a mixture of stereoisomers of identical isomer ratio to the product oxide from the Wittig synthesis using the ylide.

\[
\begin{align*}
(50) + (49) \\
49 : 51 \\
\end{align*}
\]

In the hydrolysis of 1-benzyl-1,2,2,3,4,4-hexamethylphosphetanium iodide, Trippett and coworkers\(^3\)\(^3\) have found that while the hydrolysis of the cis salt goes with complete retention to yield the trans oxide, the trans salt (53) hydrolysed with partial inversion. The product isomer ratio in the hydrolysis of the trans salt (53) was found\(^1\)\(^1\) to be very sensitive to the reaction conditions; in aqueous ethanol the hydrolysis went with predominant retention while in water predominant inversion was observed.
Cremer and coworkers\textsuperscript{87} however have reported that both isomers on hydrolysis gave a mixture of the stereoisomeric oxides. Stereo-rotation of the ylides derived from both the cis and trans isomers was observed in this case.

The lack of stereospecificity in the hydrolysis of 1-benzylpentamethylphosphetanium salts can be accounted for in a number of ways but the following possibilities have been suggested to be the most likely.

(a) Ylide isomerisation.

In view of the occurrence of isomerisation of the ylides derived from 1-benzylpentamethylphosphetanium salts, the hydrolysis of these salts may involve prior ylide formation and isomerisation by removal of one of the benzyl CH\textsubscript{2} protons. Reformation of the salts followed a stereospecific hydrolysis would give the phosphetan oxide as a mixture of isomers.

(b) Stereomutation \textit{via} pseudorotation.

In view of the stereochemical non-rigidity of phosphoranes, an alternative involves the pseudorotation of the intermediate phosphoranes prior to their decomposition to products.
Corfield\textsuperscript{11} has suggested that the latter explanation may be correct in view of the observed stereomutation of \(1\text{-cumyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium iodide}\) on alkaline hydrolysis. This phosphetanium salt is incapable of forming an ylide and thus stereomutation \textit{via} such an intermediate cannot occur. Pseudorotation of the phosphorane intermediate must therefore be responsible for the lack of stereospecificity on hydrolysis; presumably the same phenomenon is responsible for the stereochemical courses of the alkaline hydrolyses of similar \(1\text{-benzylphosphetanium salts}\). The actual mechanism of ylide isomerisation has also been suggested\textsuperscript{11} to involve the formation of phosphoranes such as (54) by the metal halide and the ylide which can pseudorotate and then decompose to give the equilibrated ylide, as ylides formed from salts with non-nucleophilic anions showed greatly decreased rates of isomerisation.
4.3 The Trimethylphosphetan System.

Shutt has reported\textsuperscript{88} that while one isomer of 1-benzyl-2,2,3-trimethyl-1-phenylphosphetanium bromide underwent both the Wittig reaction and alkaline hydrolysis with retention of configuration, the other isomer underwent both reactions with partial inversion.

4.4 The Tetramethylphosphetan System.

The presence of a chiral centre but no geometrical isomerism in 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium halides makes possible a more direct determination of the stereochemical changes involved in the hydrolysis of a phosphetanium salt than is possible in the pentamethyl or trimethyl phosphetan systems.

The separation of the cation of the phosphetanium salt into its optical enantiomers by means of the fractional crystallisation of its D(-) dibenzoyl hydrogen tartrate salt from propanol has been accomplished\textsuperscript{88}. The alkaline hydrolysis was reported to proceed with complete retention of configuration\textsuperscript{33} as the oxide from the hydrolysis of a sample of the optically pure phosphetanium iodide had the same rotation as that obtained from a Wittig reaction on a sample of the salt.
In view of the report by Shutt\(^8\) that in the hydrolysis of the related 1-benzyl-2,2,3,4,4-pentamethyl-1-phenylphosphetanium bromide a partial hydrolysis gave back the salt of unchanged stereoisomeric composition to the starting material, while Cremer and coworkers\(^87\) have since shown that the phosphetanium salt is actually rapidly equilibrated by aqueous sodium hydroxide, the hydrolysis of the optically active tetramethylphosphetanium salt (55) seemed worthy of re-examination.

The isolation of the laevorotatory diastereoisomer was accomplished using the method given by Shutt\(^8\), having \([\alpha]_D^{\text{MeOH}} = -56^\circ\) as compared to a reported value of \(-49^\circ\). The metathesis of phosphonium dibenzoyl hydrogen tartrates has been accomplished in a number of ways; Kumli and coworkers\(^35\) have achieved exchange using ammonium iodide in methanol, while Horner and Balzer\(^36\) have used an alkyl halide in acetonitrile. The results using these methods and the tartrate \([\alpha]_D^{\text{MeOH}} = -56^\circ\) are summarised below;
1)  MeI  CH$_3$CN  15.8°  14.0°
2)  EtBr  CH$_3$CN  18.0°  13.5°
3)  NH$_4$I  CH$_3$OH  18.8°  17.0°

Further recrystallisation of the halides from dichloromethane achieved a maximum rotation of +22.0° for the iodide and +19.5° for the bromide.

Addition of small quantities of water to a methanolic solution of the salt resulted in slow racemisation which was greatly accelerated by the addition of trace quantities of aqueous sodium hydroxide. The actual hydrolysis was found to proceed with considerable inversion, the relative extent of which could be altered by variation of the reaction conditions.

a) Salt [α]$^D_{MeOH}$ Hydrolysis, $\frac{N}{10}$ NaOH/MeOH. Wittig.
   $P^+Br^-$ + 18.0° + 11.6° + 34.0°
   $P^+I^-$ + 22.0° + 18.5° + 37.0°

b) Bromide [α]$^D_{MeOH}$ = + 18.0°.

(MeOH:aq. NaOH, 1:1) $\frac{N}{100}$ $\frac{N}{10}$ $\frac{N}{1}$
Oxide [α]$^D_{MeOH}$ + 12.3° + 11.6° + 8.7°

c) Bromide [α]$^D_{MeOH}$ = + 18.0°, 1:1 $\frac{N}{10}$ aqueous NaOH: solvent.
Solvent  H$_2$O  MeOH  EtOH
Oxide [α]$^D_{MeOH}$ + 5.9° + 11.6° + 13.4°
4.5 **Mechanism of Alkaline Hydrolysis of 1-Benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium Halides.**

McEwen's basic hydrolysis mechanism\(^7^6\), which was proposed for acyclic phosphonium salts and which explains configurational inversion, demands linearity between the attacking hydroxyl ion and the departing benzyl ion. Such a diapical situation is impossible in phosphetanium salts because of the increase in ring strain as the ring would have to occupy two equatorial positions. The distinctive stereochemical outcome of the hydrolysis of phosphetanium salts is a consequence of the different course the reaction has to take.

The racemisation of the optically active tetramethylphosphetanium salt prior to hydrolysis, and the partial inversion during hydrolysis may be rationalised by reversible\(^6^6\) apical attack of the hydroxyl ion on the tetrahedral phosphetanium cation to give the phosphoranes (57) and (58) in which the ring spans the apical-equatorial position, which can pseudorotate to allow the benzyl group to depart from an apical position. However, due to the reasonably comparable electronegativities of the benzyl and the phenyl groups, other pseudorotations can also occur and as a result the reaction is not stereospecific.

It will be noted that two non-enantiomeric phosphoranes can be formed by attack of the hydroxyl group opposite either of the ring junctions; because of the t-butyl-like nature of the CMe\(_2\) junction, attack of the hydroxyl ion is more likely to occur opposite this junction for steric reasons.\(^8^4\) If this is so the Scheme I could possibly be a description of the hydrolysis and racemisation routes of the cation (59); a corresponding scheme could be drawn for the other enantiomer.
If (57) is the initially formed phosphorane pseudorotation of this species can proceed along either the clockwise or the counterclockwise pathway in Scheme I. While the initial pseudorotation of the clockwise path leading to the 'retention oxide' precursor (60) is sterically favourable and stereoelectronically favourable as compared with that leading to (61), further pseudorotation along the clockwise path to (62) is certain to be much less facile as it produces a phosphorane which is both sterically and stereoelectronically less favourable than (61). Accordingly the clockwise path may proceed only as far as the phosphorane (60), and may therefore be the reaction pathway of retention.

The counterclockwise path has to provide both the oxide with inversion (63) and the inverted salt (64). A superficial analysis of the relative energies of the phosphoranes leading to the inverted oxide (63) in this pathway indicates that neither is likely to be as favourable as the product from the single pseudorotation of the clockwise, retention pathway. This is in agreement with the predominant retention actually observed.

Formation of the conjugate bases of the phosphoranes (60) and (65) will precede hydrolysis, while dissociation of the phosphoranes (57) and (58) will result in racemisation of the enantiomeric cations. A simple consideration might predict a first order dependence on hydroxyl ion concentration for racemisation of the phosphetanium salts, in contrast to the second order dependence of phosphonium salt hydrolyses. If the inverted oxide is formed by prior formation of the inverted salt by pseudorotation then an increase in the base strength might be predicted to decrease the quantity of inverted oxide produced. Such a simple trend is not observed however; a small but reproducible increase in inversion was actually observed. This could infer that the inverted
oxide is formed directly from (57) by pseudorotation, without prior formation of the inverted salt.

The predominant retention observed during hydrolysis may be an indication of the relative favourability of the clockwise, single pseudorotation pathway as compared with the clockwise two-pseudorotation path leading to inversion. The relative extent of the inversion, and its change with external conditions, suggests that the relative energetics of the two pathways are quite similar; a small change in the external conditions of the hydrolysis must induce minor variations in the energetics of the processes involved sufficient to markedly affect the feasibility of the inversion process. The increase in the percentage of inversion on changing the solvent system from aqueous ethanol to water has been previously observed by Corfield in the hydrolysis of the 1-benzyl-1,2,2,3,4,4-hexamethylphosphetanium salt.

The reason why the optically active phosphetanium salt racemises under conditions where acyclic salts do not may be connected with the strain in the tetrahedral phosphetanium cation; the relief of this strain on the formation of a pentacoordinate species by attack of hydroxyl or any other nucleophile present may result in the equilibrium of this reaction lying very much more on the side of the phosphorane than for acyclic salts. As phosphoranes are stereochemically non-rigid, by
greatly increasing the concentration of the phosphorane the rate of racemisation may also be increased. The extremely rapid rate of hydrolysis of phosphetanium salts (up to $10^7$ times as fast as acyclic analogues\(^\text{20}\)) has been identified with this relief of ring strain on forming a pentacoordinate species; if a comparable acceleration of the rate of racemisation is so produced then the observed result is not surprising.

Pseudorotation of cyclic phosphoranes has been suggested\(^\text{89}\) to be more rapid than that of acyclic systems due to a preferential decrease in non-bonded interactions in the square pyramidal intermediate for cyclic phosphoranes; if this is so stereomutation of phosphetanium salts would again be expected to be more rapid than with their acyclic analogues.

4.6 The Alkaline Hydrolysis of Some Other Cyclic Phosphonium Salts.

Marsi and coworkers\(^\text{22,85}\) have reported that the alkaline hydrolysis of both the cis and trans isomers of 1-benzyl-3-methylphospholanium bromides (67, $R = \text{Me, Ph}$) gave the oxides (68, $R = \text{Me, Ph}$) with complete retention of configuration at phosphorus.

The phospholan ring is similar to the phosphetan ring in its
stereochemical requirement in that during the hydrolysis of the phosphoranium salt the ring will span one apical and one equatorial position in the trigonal bipyramidal intermediate (69) formed by apical attack of hydroxide ion. The observed retention of configuration has been explained by equatorial departure of the benzyl anion from this intermediate, or by formation of the conjugate base of (69) followed by pseudorotation to place the very electropositive $O^-$ in the preferred equatorial position, and loss the the benzyl anion from the apical position.

As the ring size increases, the requirement that the ring has to occupy the apical-equatorial position becomes less rigorous and as a result, the phosphorane in which the benzyl and the hydroxyl are apical (and the ring diequatorial) becomes more comparable in energy to that with the apical-equatorial ring. Marsi has reported that the hydrolysis of the pure cis and trans isomers of 1-benzyl-4-methyl-1-phenylphosphorinanium bromide (70) gave different mixtures of the cis and trans isomers of 4-methyl-1-phenylphosphorinan 1-oxide (71), which was explained in terms of two competing mechanisms. One was a hydrolysis mechanism analogous to the phosphoranium salt in which the hydroxide ion attacked opposite the ring junction leading to retention, and the other a normal 'McEwen' type
hydrolysis in which the hydroxyl and the benzyl were colinear (and the ring diequatorial) in the phosphorane leading to inversion. The different oxide isomer compositions from the different isomers of the phosphonium salt is presumably due to greater steric interactions between the 4-methyl and the incoming hydroxyl group in the 'McEwen' mechanism for one (possibly the trans methyl/benzyl) isomer. Other hydrolyses of single geometrical isomers of 6-membered cyclic phosphonium salts leading to mixtures of product oxides have been reported.\textsuperscript{92,93}

In view of the partial inversion via the 'McEwen' mechanism observed in the hydrolysis of the six-membered cyclic phosphonium salt, the hydrolysis of the next homologue would be expected to give a correspondingly larger percentage of the inverted oxide as the strain involved in placing the ring diequatorial would be greatly reduced. The hydrolysis of the single cis and trans isomers of 1-benzyl-5-methyl-1-phenylphosphaninium bromide (72) has been shown by Marsi\textsuperscript{91} to proceed with complete inversion of configuration analogous to an acyclic benzyl phosphonium salt; presumably the greater flexibility of the seven-membered ring permits the accommodation of the ring in a comparatively unstrained diequatorial position (73).

\begin{itemize}
  \item \textbf{(72)}
  \item \textbf{(73)}
\end{itemize}
4.7 Hydrolysis of 3-Phospholenium Salts.

The hydrolysis of 1,3,4-trimethyl-1-phenyl-3-phospholenium iodide (74) has been reported\textsuperscript{18} to proceed with exclusive ring opening, which was explained in terms of the greater stability of the allyl carbanion formed by ring opening over the phenyl carbanion. However, examples which exhibit both ring opening and ring retention have been reported.\textsuperscript{69,94} Corfield\textsuperscript{69} has found that the hydrolysis of 1,3,4,5,5-pentamethyl-1-phenyl-3-phospholenium iodide (75) gave predominantly loss of phenyl in spite of the theoretically greater stability of the allyl carbanion.

The explanation which was offered suggested that ring constraint
led to lack of overlap of the double bond with the incipient carbanion resulting in a decrease in the allyl character of the ring opening carbanion. If this suggestion is correct then the hydrolysis of a 3-phospholenium salt which has as one substituent on phosphorus a true allyl group could lead to complete ring retention.

The quaternisation of 3,4-dimethyl-1-phenyl-3-phospholen (76) with 2-methylallyl chloride gave the phosphonium salt (77). Hydrolysis yielded entirely 3,4-dimethyl-1-phenyl-3-phospholen 1-oxide (78) and isobutene. It therefore seems reasonable to assume that loss of allyl character does indeed occur on the incorporation of the group into a ring system.

A possible explanation of the results of the hydrolyses of these three phosphonium salts (74), (75), and (77) lies in the identity of the initial phosphorane; (74) and (77) have the structures (79) and (80), while (by analogy to the hydrolysis of t-butyl phosphonium salts\textsuperscript{84} the salt (77) will form an initial phosphorane (81) with the t-butyl-like group in the apical position. For (81) and (80) to ring open and loose allyl respectively the phosphoranes need to pseudorotate.
In the case of (81) this pseudorotation will be greatly accelerated compared to (79) by the relief of steric compression around the 't-butyl' group while for (80) this will be accelerated by the
stereoelectronically favourable placement of the electronegative allyl group in the apical position. The mode of decomposition of these phosphoranes now becomes a question of the relative anionic stabilities of phenyl or allyl against the ring allyl group. The greatly decreased allyl character in the ring group results in exocyclic cleavage being the preferred mode of decomposition.

In the case of the phosphorane (79) there is no acceleration of the pseudorotation to place phenyl apical and presumably the rate of decomposition of (79) is now faster than its pseudorotation, instead of slower as in the other two examples. As there is no opportunity for the choice between loss of phenyl or the ring allyl, exocyclic cleavage is the mode of decomposition.

Priestley and Snyder\textsuperscript{94} have suggested that the phosphoranes of similar 1-alkyl-1-phenyl-3-phospholenium salts do indeed decompose rapidly, before pseudorotation to place the phenyl apical can occur.

4.8 Hydrolysis of 2-Phospholenium Salts.

An analysis of the hydrolysis of 2-phospholenium salts is complicated by the presence, and the nature of the two different substituents adjacent to phosphorus. Simple electronegativity\textsuperscript{95} considerations would predict that attack of the hydroxyl group would preferentially occur opposite the ring vinyl group to form a phosphorane of the general structure (82). However the very low apicophilicity of the vinyl group (Chapter 7) would

\begin{equation}
\begin{array}{c}
\text{(82)} \\
\text{(83)}
\end{array}
\end{equation}
suggest that attack of the hydroxyl group would occur opposite the ring CH₂ group (83); in this position the maximum stabilising overlap between the vinyl π system and the phosphorus d-orbitals may be obtained.⁴⁸,⁶¹

This problem may be largely academic, however, because the high pKa values of the olefin and the benzene groups⁹⁶ should ensure that the rate of decomposition of the hydroxyphosphoranes to products will be comparatively slow; probably slow enough for an equilibrium to be set up throughout the pseudorotation pathways of Scheme II. Under these conditions the nature of the products will be dependent on both the relative energies of the different phosphoranes and on the leaving group abilities of the groups present in the apical positions in these phosphoranes.

Hawes¹⁸ has reported that the hydrolysis of 1,3-dimethyl-1-phenyl-2-phospholenium iodide (84) proceeded with complete ring cleavage to the product oxide (85). Priestley and Snyder⁹⁶, however, have found that the hydrolysis of the tetradecyl 2-phospholenium bromide (86) can lead

![Chemical Structures](https://example.com/chemical_structures.png)

(84) \( R = \text{Me} \)  
(86) \( R = \text{C}_{14}\text{H}_{29} \)  

(85)

to a complete spectrum of product mixtures, ranging from complete ring opening to complete loss of phenyl depending on the reaction conditions.
(84) $R = \text{Me}, R_i = \text{H}$
(86) $R = \text{C}_{14}\text{H}_{29}, R_i = \text{H}$
(87) $R = \text{Me}, R_i = \text{Me}$
This would infer that a fine balance exists between the energetics of the processes involved such that altering the external conditions can make either decomposition route the most favourable.

Introduction of methyl substituents into the ring system also had an effect on the product distribution; both ring open and ring intact products were obtained from the hydrolysis of 1,3,4,4-tetramethyl-1-phenyl-2-phospholenium iodide (87).

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{P} & \quad \text{I}^- \\
\text{Me} & \quad \text{Ph} \\
\end{align*}
\xrightarrow{-\text{OH}}
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{P} & \quad \text{O} \\
\text{Me} & \quad \text{Ph} \\
\end{align*}
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\end{align*}

(87)

An attempt was made to investigate the effect of incorporation of the vinyl group into the ring system on its leaving group ability by the synthesis of a 1-vinyl-2-phospholenium salt. Vinylphosphonium salts have been prepared by the base-catalysed rearrangement of allylphosphonium salts via the ylide; bases used include benzyltrimethylammonium methoxide\(^97\) and basic alumina\(^98\). Neither of these methods was successful at rearranging 3-methyl-1-(2'-methylallyl)-1-phenyl-2-phospholenium chloride (88).

\[
\begin{align*}
\text{P} & \quad \text{CH}_2\text{CH} & \quad \text{CH}_2\text{CH} \\
\text{P} & \quad \text{CH}_2\text{CH} & \quad \text{CH}_2\text{CH} \\
\end{align*}

\xrightarrow{\text{B}^-} \quad \begin{align*}
\text{P} & \quad \text{CH}_2\text{CH} & \quad \text{CH}_2\text{CH} \\
\end{align*}
\xrightarrow{\text{H}^+} \quad \begin{align*}
\text{P} & \quad \text{CH}_2\text{CH} & \quad \text{CH}_2\text{CH} \\
\end{align*}

\]
The phospholenium salt was finally treated with butyl-lithium to generate the ylide, which gave 3-methyl-1-phenyl-2-phospholen 1-oxide (89) on treatment with aqueous sodium hydroxide. In view of the apparently correct orientation of the incipient ring-opening carbanion for maximum vinyl character, it is unlikely that the obvious conclusion of decreased vinyl character on ring-incorporation is correct.

A more likely explanation is that although the original isomerisation of the allyl to the vinyl group was successful, the low anionic stability of the vinyl and phenyl anions ensures that hydrolysis is slow enough for base-catalysed reisomerisation of the 2'-methylprop-1-yl salt (90) back to the methylallyl salt (88) to occur. The very rapid hydrolysis
of the allyl-2-phospholenium salt (88), due to the much greater anionic stability of this allyl group, ensures that the hydrolysis proceeds with complete exocyclic cleavage. As expected, the hydrolysis of the methylallyl-2-phospholenium salt (88) was found to proceed with complete loss of the allyl group.
5. RING OPENING REACTIONS OF PHOSPHETANS.

5.1 The Phosphetan System.

A characteristic feature of the phosphetans is their readiness to undergo ring opening and ring expansion reactions. This may be partly attributable to two properties of the phosphetan system; (a) the very rapid attack of nucleophiles at phosphorus in order to reduce ring strain by the formation of a pentacoordinate species in which the ring occupies an apical-equatorial position, and (b) the existence of ring strain even in the pentacoordinate structure, which is relieved on ring opening or ring expansion.

Typical of these reactions is the behaviour on hydrolysis of the 1-methyl-1-phenylphosphetanium salts (90) via the phosphorane\(^{17,99}\) (91). The ring opening reactions for the 2,2,3,3-tetramethylphosphetan system

\[
\begin{align*}
(90) & \\
(91) & \\
(90, R_1 = Me, R_2 = H) \text{ and the } 2,2,3\text{-trimethylphosphetan system (90, } R_1 = R_2 = H) \text{ occur at the } P-CH_2 \text{ junction to give the more stable}
\end{align*}
\]
carbanion, while the decreased stability of the \( \text{CMe}_2 \) anion formed by ring opening of the \( 2,2,3,4,4 \)-pentamethylphosphetan system (90, \( R_1 = H, R_2 = \text{Me} \)) causes rapid attack of the incipient carbanion on the aromatic system rather than separation of the carbanion and subsequent protonation as in the other systems.

A series of ring expansion reactions corresponding to that for the hydrolysis of the \( 1,2,2,3,4,4 \)-hexamethyl-1-phenylphosphetanium iodide and conforming to the general pattern (92) has been reported\(^{100}\), where the ring grouping occupying an apical position migrates to an \( \alpha \)-carbon bearing a substituent \( X \) capable of accommodating a negative charge.

\[
\begin{align*}
\text{P} & \quad \text{C} & \quad \text{X} \\
\text{H} & \quad \text{Ph} \\
\end{align*}
\]

(92)

5.2 **The Tetramethylphosphetan System.**

The structure of the \( 2,2,3,3 \)-tetramethylphosphetan ring system makes possible the observation of ring opening and ring expansion reactions involving either the \( \text{CH}_2 \) or the \( \text{CMe}_2 \) group. Fission of the \( \text{P-CH}_2 \) linkage has been suggested\(^{100}\) to be favoured when the leaving or migrating group has some anionic character in the transition state, while fission of the \( \text{P-C(Me)}_2 \) linkage could be favoured by steric factors, such as ease of access of the nucleophile, or when the migrating group has cationic character.
Although both ring opening and ring expansion reactions involving the P-CH₂ linkage have been reported, only ring expansion reactions have been found for the CMe₂ group. Typical carbanion-character ring opening and expansion reactions are found in the hydrolyses of the 1-methyl, and the 1-iodomethyl phosphetanium iodide salts (93) and (94).

In the latter reaction a small amount (8%) of the other isomer was found, corresponding to ring expansion from the other junction presumably due to the more ready access of the hydroxyl opposite the CMe₂ group.

A reported example of ring expansion involving the P-C(Me)₂ linkage has been the reaction of 1-phenyl-2,2,3,3-tetramethylphosphetane with dimethyl acetylenedicarboxylate to give the stable ylide (95). The preferential migration of the CMe₂ group may indicate that the migrating centre in (96) acquires a positive charge in the transition state.
5.3 Reaction of Potassium Cyanide with 1,2,2,3,3-Pentamethyl-1-phenylphosphetanium Iodide.

Treatment of the salt (93) with potassium cyanide in refluxing methanol gave, after oxidation, the tertiary alcohol (97). The identity of the ring junction cleaved and the nature of the product indicated that in this case ring opening did not involve the anion. Presumably instead the powerful inductive effect of the nitrile group induced ring opening to give the carbonium ion. In the mass spectrum of (97) no molecular ion was observed; that dehydration of the alcohol
was occurring in the mass spectrometer was confirmed by dehydration
of the alcohol with toluene-\(p\)-sulphonic acid to give the olefin (98)
whose mass spectrum was identical to that of the alcohol (97).

5.4 Reaction of Cyanogen Bromide with 2,2,3,3-Tetramethyl-1-phenylphos-
phetan.

The observation that potassium cyanide induced ring opening at
the \(P-C(Me)\,_2\) linkage in 1,2,2,3,3-pentamethyl-1-phenylphosphetanium
iodide via the cyanophosphorane (99, \(R = Me\)) prompted an investigation
of the possibility of an analogous ring opening from the reaction of
cyanogen bromide with 2,2,3,3-tetramethyl-1-phenylphosphetan via the
phosphorane (99, \(R = Br\)).

\[
\begin{array}{c}
\text{Ph} \\
\text{CN} \\
\text{R}
\end{array}
\]

(99)

The phosphetan reacted with an equimolar quantity of cyanogen
bromide to give, after oxidation an alkaline hydrolysis, a mixture
of acidic and neutral products. The neutral phosphine oxide product
was found to be 3,4,4-trimethyl-1-phenyl-2-phospholen 1-oxide (100, 65%)
while chromatography of the acidic products on acidic silica gave
4,4,5,5-tetramethyl-2-phenyl-1,2-oxaphospholan 2-oxide (101, 13%)
 together with trace quantities of phenyl (2,2,3-trimethylbut-3-enyl)
phosphinic acid (102)
A similar reaction of the phosphetan with 2 moles of cyanogen bromide gave an increased yield of the phospholen oxide (100, 72%), the 1,2-oxaphospholan 2-oxide (101, 6%), and a further acidic product (4-bromo-2,2,3-trimethylbut-3-enyl)phenylphosphinic acid (103, 13%). The mass spectrum of this acid (103) showed peaks corresponding to dimeric species. This behaviour of phosphinic acids has previously been noted by Dimroth\textsuperscript{101}, and Trippett and coworkers\textsuperscript{100}. The absence of any quantity of phenyl(2,2,3-trimethylbut-3-enyl)phosphinic acid (102) was traced to its ready cyclisation to the oxaphospholan oxide (101) during chromatography on silica. Cyclisation could also be induced by treatment of the phosphinic acid with dilute hydrochloric acid, presumably by the mechanism illustrated, protonation giving the tertiary carbonium ion rather than the less stable primary ion.
The isolation of the bromobutenylphosphinic acid (103) only from the reaction of the phosphetan with excess cyanogen bromide could indicate that its origin lies in the bromination of the intermediate butenylphosphine (104) by bromine present in the reaction mixture.

\[
\begin{align*}
\text{Ph} & \quad \text{CN (Br)} \\
\text{P} & \quad \text{Br} \\
\text{CH}_2\text{Br} & \\
\text{Ph} & \quad \text{CN (Br)} \\
\text{H}_2\text{O}_2 & \quad \text{OH} \\
\text{Ph} & \quad \text{CN (Br)} \\
\text{CHBr} & \\
\end{align*}
\]

(104)  
(103)

Finding that the reaction of cyanogen bromide resulted in the formation of these unusual products prompted an investigation of the reactions of other halogens with 2,2,3,3-tetramethyl-1-phenylphosphetan.

5.5 Reaction of Chlorine with 2,2,3,3-Tetramethyl-1-phenylphosphetan.

Treatment of 2,2,3,3-tetramethyl-1-phenylphosphetan (105) with slightly less than one mole of chlorine in 1,2-dichloroethane at -20° gave initially a white solid, which on pyrolysis and distillation at temperatures below 100° gave the acyclic chlorophosphine (106). Presumably the white solid was the addition compound which underwent a ring opening reaction via the carbonium ion. Dehydrohalogenation gave the chlorophosphine.

\[
\begin{align*}
\text{Ph} & \quad \text{P} \\
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \\
\text{Ph} & \quad \text{P} \\
\text{Cl} & \\
\end{align*}
\]

(105)  
(106)
The structure of the acyclic chlorophosphine was confirmed by oxidation and alkaline hydrolysis to the phosphinic acid (102), which was in turn characterised as the 1,2-oxaphospholan oxide (101) after chromatography on silica.

The outcome of the reaction was found to be very dependent on the reaction conditions; addition of slightly more than one mole of chlorine, or distillation at temperatures in excess of 120° resulted in the near-quantitative production of the 2-phospholen, (107), characterised as the oxide (100).

The chlorophosphine was also produced in high yield by the pyrolysis of the adduct from the reaction of the phosphetan with phosgene.

5.6 Reaction of Bromine with 2,2,3,3-Tetramethyl-1-phenylphosphetan.

Treatment of a solution of the phosphetan in dichloromethane with one mole of bromine gave a crystalline adduct which on pyrolysis gave the 2-phospholen hydrobromide (108) as a glassy solid.
The presence of a phosphorus-hydrogen bond in the molecule was shown by a broad doublet in the $^1$H n.m.r. spectrum at $\tau$ 0.40 ($J_{PH}$ 540 Hz) and by an i.r. spectrum which showed $v_{\text{max}}$ 2400 and 2250 cm$^{-1}$. The structure was confirmed by its synthesis from hydrogen bromide and 3,4,4-tetramethyl-1-phenyl-2-phospholen (107) produced by the phenylsilane reduction of the phospholen oxide (100), and by titration of the adduct with sodium hydroxide; one mole of sodium hydroxide neutralised one mole of the hydrobromide.

An interesting feature of the $^1$H n.m.r. spectrum of the hydrobromide was that the signals due to the hydrobromide were shifted downfield relative to those of the corresponding phospholen (107) and the phospholen oxide (100). A similar effect was noted in the spectrum of 1,3,4,4-tetramethyl-1-phenyl-2-phospholenium iodide (87). This could suggest that, at least in solution, the hydrobromide exists in the ionic form (108) rather than in the covalent pentacoordinate structure (109). Unfortunately no signal could be detected in the $^{31}$P n.m.r. spectrum of the hydrobromide.

\[ \text{[Diagram: Structures 108 and 109]} \]

The 2-phospholen was evidently a reasonable base; addition of D$_2$O to an n.m.r. solution of the hydrobromide in deuteriochloroform resulted in the collapse of the signal from the P-H proton, but the
remainder of the spectrum was unchanged. In order to remove the hydrogen bromide from the phospholen hydrobromide it was necessary to add dilute sodium hydroxide. Removal of the hydrogen bromide was also accomplished by refluxing a suspension of the hydrobromide in tetrahydrofuran with magnesium.

Unlike the reaction of the phosphetan with chlorine no evidence for the formation of an acyclic bromophosphine corresponding to the chlorophosphine (106) could be found. The use of less than one mole of bromine only resulted in the depression of the yield of the hydrobromide and the recovery of unchanged phosphetan.

5.7 Cyclisation of But-3-enyl(chloro)phenylphosphines.

The observation that pyrolysis of the phosphetan-chlorine adduct (110) and distillation at temperatures below 100° afforded the chlorophosphine while distillation at temperatures in excess of 120° gave the phospholen could be interpreted as evidence that the phospholen has its origin in the acyclic butenylchlorophosphine (106). This may indeed be so; at 170° the butenylchlorophosphine cyclised with the evolution of hydrogen chloride to give the phospholen (107).
It was found that the thermal cyclisation was aided by the presence of a 3-methyl substituent. Thus but-3-enyl(chloro)phenylphosphine (111, R = H) would not cyclise at 230°. This and the nature of the product from the cyclisation suggests the mechanism shown.

In view of the readiness of this thermal cyclisation the possibility of cyclisation by other means was investigated. Examples are known of addition of olefins to phosphorus pentachloride and its derivatives, presumably via the \( \text{PCl}_4^+ \) species. Olefins are also known to add to chlorophosphines in the presence of aluminium chloride.

Addition of one mole of chlorine to the butenylchlorophosphine (106) gave the phospholen, isolated as the oxide (100) after treatment with hydrogen peroxide. Again cyclisation was aided by a 3-methyl substituent, thus but-3-enyl(chloro)phenylphosphine (111, R = H) was unaffected by chlorine and bromine.
Cyclisation of the but-3-enylchlorophosphine (106) was also catalysed by aluminium chloride. Oxidative work-up gave a mixture of 2,2,3,3-tetramethyl-1-phenylphosphetan 1-oxide (56) and the 2-phospholen 1-oxide (112, R = Me); however the but-3-enylchlorophosphine (111, R = H) gave only the 2-phospholen 1-oxide (112, R = H). Thus phosphetan formation is favoured by a 3-methyl substituent.

Presumably formation of the phospholen ring involves the coordination of the aluminium chloride to the phosphorus, while phosphetan formation involves coordination to the olefin.

5.8 Heterocyclic Synthesis.

The general methods available for the synthesis of simple carbon-phosphorus heterocycles containing one phosphorus are few in number and limited in extendability; in particular the synthesis of
mono-unsaturated heterocycles of the general structure (113) is essentially limited to the synthesis of five-membered heterocycles (phospholens) by the McCormack synthesis.\(^{107}\)

![Diagram of structure (113)]

The restrictions on the number and distribution of the substituents on the diene of the McCormack synthesis, together with the slow reaction and low yields often obtained enhances the value of the alternative phospholen synthesis by the cyclisation of but-3-enylchlorophenylphosphines.

As the higher and lower homologues of the series have not been reported as isolated products, an investigation of the extendibility of the cyclisation procedure to these systems appeared worthwhile.

(a) Chloropent-4-enylphenylphosphine.

The aluminium chloride catalysed cyclisation of the phenylphosphine (114) gave the required phosphorinen 1-oxide (115) in low yield,

![Chemical structures](114) \(\rightarrow\) (115)

The major product being a polymeric material. It would appear that
intramolecular reaction is suppressed relative to intermolecular reaction possibly due to the high degree of ordering required to place the terminus of the long chain in the correct orientation for intramolecular reaction.

(b) Chloro(2-methylallyl)phenylphosphine.

Although the unsaturated 4-membered ring system has been postulated as an intermediate in the reactions of ylides with benzyne and certain acetylenes, such a ring system has not as yet been characterised. Not unexpectedly the attempted cyclisation of the methylallylphosphine with aluminium chloride to this ring system was unsuccessful; it may be that although the alkene terminus can readily approach the phosphorus centre, the π system of the vinyl group cannot effectively overlap with the acceptor orbitals on the electron-deficient phosphorus due to the shortness of the chain length.

Presumably the balance of these opposing effects of the chain length comes out strongly in favour of intramolecular reaction for the butenyl system, but against cyclisation in the other homologues.
6. THE OXYPHOSPHORANES.

6.1 Synthesis.

The oxyphosphoranes comprise perhaps the largest class of isolated pentacoordinate phosphorus compounds. Although many acyclic examples are known\textsuperscript{113-117} the cyclic oxyphosphoranes have received the greatest study due in part to their relatively increased stability and their ease of synthesis compared to their acyclic analogues. The first reported cyclic oxyphosphorane was as a postulated intermediate in the reactions of trialkyl phosphites and biacetyl to yield $\alpha,\beta$-unsaturated methyl phosphates via an alkyl group translocation reaction. Since this initial report by Kukhtin\textsuperscript{118} intensive work in this field primarily by Ramirez and coworkers\textsuperscript{46} has introduced a variety of new cyclic oxyphosphoranes.

Dioxaphospholens.

Ramirez and coworkers\textsuperscript{21,119} have found that the reaction of phosphites, phosphonites and phosphinites with $\alpha$-diketones and $o$-quinones can form the unsaturated 1,3,2-dioxaphospholens (116).

\[
\begin{align*}
\text{(MeO)}_3P & \quad \text{+(Me.CO)}_2 \quad \rightarrow \quad \text{MeO} \quad \text{MeO} \\
\begin{array}{c}
\text{MeO} \\
\text{P} \\
\text{O} \\
\text{O} \\
\text{Me} \\
\text{Me}
\end{array} & \quad \begin{array}{c}
\text{MeO} \\
\text{P} \\
\text{O} \\
\text{O} \\
\text{Me} \\
\text{Me}
\end{array} & \quad \begin{array}{c}
\text{MeO} \\
\text{P} \\
\text{O} \\
\text{O} \\
\text{Me} \\
\text{Me}
\end{array}
\end{align*}
\]

These 1:1 adducts have the useful property of combining with a further molecule or molecules of the same, or different carbonyl compound to form 1,3,2-dioxaphospholans such as (117). As methods
are available for the removal of the phosphorus moiety this represents an approach to the creation of C-C single bonds in polyoxygenated compounds\textsuperscript{21,119,120}. 1,3,2-Dioxaphospholen phosphoranes have also been synthesised from catechol\textsuperscript{121,122}.

1,2-Oxaphospholen

The reaction of equimolar quantities of benzylidene acetylacetone and phosphites, phosphonites or phosphinites gives the 1,2-oxaphospholen adduct\textsuperscript{45,123} (118). The general reaction has been extended to the use of a variety of \(\alpha,\beta\)-unsaturated ketones\textsuperscript{43,124,125} and esters\textsuperscript{43,126}.

On heating in solution, the 1,2-oxaphospholen adducts have a marked tendency to ring open to form the zwitterion (119), the tendency to ring open being enhanced by the replacement of the alkoxy groups in the phosphite with alkyl or aryl groups. Thus ring opening in the trimethyl phosphite adduct shows in the \(^{1}H\) n.m.r. spectrum at \(+150^\circ\), while dimethyl phenylphosphonite and methyl diphenylphosphinite adducts show ring opening at \(125^\circ\). The adducts from trialkylphosphines exist as the zwitterions (119) even at \(0^\circ\)\textsuperscript{127}.

\[
\begin{align*}
\text{(MeO)}_3\text{P} \ + \ \text{PhHC:C(COMe)}_2 \rightarrow \ & \quad \text{MeO} \\
& \quad \text{MeO} \\
& \quad \text{MeO} \\
& \quad \text{MeO} \\
\end{align*}
\]

![Diagram](image-url)

\(R = \text{Alkoxy, Alkyl}\)

\[
(119)
\]
Dioxaphospholans.

The reaction of activated monocarbonyl compounds such as hexafluoroacetone\(^\text{128}\), \(\alpha\)- and \(\beta\)-nitrobenzaldehydes\(^\text{129}\), fluorenone\(^\text{130}\), or phthalaldehydes\(^\text{120}\) with trialkyl phosphites gives the 2:1 adducts, the 1,3,2-dioxaphospholans (120). The reaction is believed to go stepwise via the unstable 1:1 adduct such as (121). The negative charge which forms on the carbonyl carbon during the formation of the 1:1 adduct is stabilised by interaction with the electron-withdrawing substituents.

In the absence of activating groups the initial 1:1 adduct analogous to (121) would be considerably destabilised; accordingly simple aliphatic aldehydes and trialkyl phosphites form the alternative 2:1 adducts, the 1,4,2-dioxaphospholans (122)\(^\text{21,119}\). The intermediate 1:1 adduct (123) will have the negative charge on the oxygen; nucleophilic attack on a second aldehyde group followed by ring-closure gives the adduct (122).
Ramirez has demonstrated\textsuperscript{46} that the initial 2:1 adduct from perfluorobenzaldehyde and a trialkyl phosphite has the 1,4,2-ring system which slowly isomerises to the more stable 1,3,2-dioxaphospholan. However, in other 1,3,2-dioxaphospholan syntheses, for example with hexafluoroacetone, he found no evidence for assuming these also went via such a ring system.

More recently, Denney and coworkers\textsuperscript{131} have introduced a method of synthesis of 1,3,2-dioxaphospholans (124) and (125) by means of an exchange reaction, whereby alkoxy groups in an acyclic oxyphosphorane (126) are displaced as alcohols by simple, or substituted ethylene glycols. The simple ethylene glycol ring can be replaced\textsuperscript{132} by a more substituted ring by the use of tetramethylethylene glycol to form a new spiro oxyphosphorane (127).
Pentacoordinate 1,3,2-dioxaphospholans (128) have also been synthesised by the reaction of tris(dimethylamino)phosphine with ethylene glycols; the cyclisation of the intermediate phosphite ester of ethylene glycol (129) to the phosphorane must be due to the decrease in the ring strain on moving from a distorted tetrahedral geometry to the pentacoordinate state.

\[
\text{(Me}_2\text{N)}_3\text{P} \xrightarrow{(\text{CH}_2\text{OH})_2} \text{Me}_2\text{N} - \overset{\text{P}}{\text{O}} \quad \overset{\text{(CH}_2\text{OH})_2}{\xrightarrow{} \overset{\text{O}}{\text{P}}} \\
\text{(130)} \quad \text{(129)}
\]

Modification of this synthesis whereby (130) was reacted with 2-aminoethanol gave the adduct (131).

6.2 Stability of Oxyphosphoranes.

The reactions of trivalent phosphorus compounds with carbonyl compounds need not form pentacoordinate oxyphosphoranes, and even amongst those which do form oxyphosphoranes their stability may vary considerably. The stabilisation of the pentacoordinate structure can be effected by (a) the introduction of a small ring system into the
molecule, and (b) by increasing the electronegativity of the substituents attached to phosphorus.

(a) Ring systems. X-ray diffraction techniques have shown that considerable crowding exists in the oxyphosphorane trigonal bipyramid. The enhanced stability of cyclic oxyphosphoranes may be due to the small ring partly offsetting these crowding difficulties, and also to the ring being less strained when spanning an apical-equatorial position of a trigonal bipyramid than when it contains a tetrahedral phosphorus.

Denney and coworkers have found that while the reactions of diethyl peroxide with trimethylphosphine or dimethylphenylphosphine lead to materials whose properties are best rationalised in terms of an equilibrium between the oxyphosphorane and the phosphonium ethoxide structures, the phosphetans (132) and (133) give stable oxyphosphoranes (134) and (135).

\[
\begin{align*}
&\text{(132) } R_1 = H, R_2 = Me. \\
&\text{(133) } R_1 = Me, R_2 = H. \\
&\text{(134) } R_1 = H, R_2 = Me. \\
&\text{(135) } R_1 = Me, R_2 = H.
\end{align*}
\]

The product from the reaction of tris(dimethylamino)phosphine with 9,10-phenanthraquinone was found to be an open dipolar ion (136) in both the crystal and in solution, while that from a cyclic aminophosphine was
a stable oxyphosphorane (137)\textsuperscript{135}.

Similarly, tris(dimethylamino)phosphine gave \textsuperscript{136} the unstable 1:1 adduct (138) with hexafluoroacetone, while a stable 2:1 adduct was formed from a cyclic aminophosphine.

In the case of the adducts from benzil, that from the acyclic aminophosphine could be isolated\textsuperscript{135} in two crystalline forms (140) and (141), while that from the cyclic aminophosphine was a stable oxyphosphorane (142).
The reaction of the pentaphenoxyphosphorane (142) with catechol to form the cyclic oxyphosphoranes (144) and (145), and that of pentaethoxyphosphorane (146) with glycols to give (147) and (148) is also strong evidence in favour of an increase in stability on the introduction of a small ring into a phosphorane.

(b) Electronegativity of the substituents. The electronegativity of the elements attached to phosphorus can be a major influence on whether the adduct from the reaction of a trivalent phosphorus compound and a carbonyl compound exists as an oxyphosphorane or in the open dipolar form.
While trimethyl phosphite forms the oxyphosphoranes (149) and (120) with phenanthraquinone\textsuperscript{21,119} and hexafluoroacetone\textsuperscript{128}, tris(dimethylamino)-phosphine gives the zwitterions (139) and (138).

![Chemical structures](image)

The adduct from benzil and tris(dimethylamino)phosphine can be isolated\textsuperscript{135} in two crystalline forms, the stable oxyphosphorane (140) and the metastable open dipolar form (141); in solution these two forms are in rapid equilibrium giving a single solvent-dependent $^3\text{P}$ n.m.r. signal. In contrast the adduct from trimethyl phosphite and benzil is a very stable oxyphosphorane (150)\textsuperscript{21,119}. Similarly, tertiary phosphines resemble aminophosphines in their reluctance to form pentacoordinate species\textsuperscript{46}.

![Chemical structure](image)

However, in any comparison of the stabilities of their adducts the electronegativity difference between, for example, $\text{NMMe}_2$ and OMe is not the sole variable; the larger steric requirement\textsuperscript{137} of the $\text{NMMe}_2$ group would also be expected to destabilise the pentacoordinate state of its
adducts. This steric effect may be related to the significant intramolecular crowding which exists in the trigonal bipyramidal structure of phosphoranes.

6.3 **Mechanism of Adduct Formation.**

Three of the most likely possibilities for the mechanism of formation of a cyclic oxyphosphorane (151) from an α-diketone and a trialkyl phosphite are:

1. *Nucleophilic attack of phosphorus on the carbonyl oxygen followed by cyclisation of the zwitterion (152).*

\[
\text{(RO)}_3\text{P} : + \quad \text{(151)} \quad \rightarrow \quad \text{(152)}
\]

2. *Nucleophilic attack of phosphorus on the carbonyl carbon followed by rearrangement and cyclisation of the zwitterion (152).*

\[
\text{(RO)}_3\text{P} : + \quad \text{(151)} \quad \rightarrow \quad \text{(152)}
\]
(3) Concerted cyclisation, analogous to the Diels-Alder reaction.

\[
\begin{align*}
\text{(151)} \\
(R\text{O})_3\text{P} & \quad + \quad \begin{array}{c}
\text{O} \\
\text{C} \\
\text{R}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{O} \\
\text{C} \\
\text{R}
\end{array} \quad \begin{array}{c}
\text{O} \\
\text{C} \\
\text{R}
\end{array} \\
\text{(RO)}_3\text{P}
\end{align*}
\]

Although nucleophilic attack of trivalent phosphorus on carbonyl oxygen has been suggested \(^{46,129,138}\) to be particularly facile when the carbonyl group is substituted with electron-withdrawing groups, a kinetic study of the reaction of trialkyl phosphites with benzil by Ogata and Yamashita \(^{139}\) has led them to favour mechanism (2) involving attack on the carbonyl carbon.

The reactions were followed spectrophotometrically at various temperatures and in a variety of solvents. Some of the more pertinent results are summarised below.

(a) The reaction was irreversible, and was found to be second order, first order in both [phosphite] and in [benzil].

(b) Temperature variation gave the energy and entropy of activation as 8.41 kcal mol\(^{-1}\) and -47.5 eu respectively.

(c) The rate constant increased with increase in the dielectric constant of the solvent.

(d) The rate constant was increased by the presence of organic acids in the reaction mixture, but decreased by the presence of tertiary aliphatic amines. Aromatic amines had no effect on the rate constant.

On the basis of the large negative entropy of activation the Diels-Alder type reaction was said to be unlikely, as this reaction
in general exhibits entropies of activation of not more than \(-30\) eu\(^{140}\).

In addition, the normal Diels-Alder reaction is accelerated by both tertiary amines and organic acids\(^{141}\) in contrast to these findings.

The accelerating effect of organic acids was identified with hydrogen bonding between the carbonyl oxygen and the acid, resulting in an activation of the carbonyl carbon for nucleophilic attack. The changes in the extinction coefficient of the benzil UV carbonyl absorption in the presence of acid was interpreted as evidence for this hydrogen bonding. The retarding effect of base was suggested to be due to the coordination of the base to the carbonyl carbon atom, weakening its electrophilicity.

The full mechanism suggested by Ogata and Yamashita is shown below.
The reversibility of the first step was suggested on the basis of the low value of the energy of activation of the reaction. An example of reversible nucleophilic attack by trivalent phosphorus on the carbonyl carbon has been suggested by Hudson and Mancuso\textsuperscript{142}.

The conclusion that the overall reaction was irreversible is in contrast to a more recent statement by Ramirez and coworkers\textsuperscript{60}. To explain the reluctance of certain caged phosphites, notably (153), to form oxyphosphoranes with biacetyl, Ramirez suggested that the reactions of trivalent phosphorus compounds with biacetyl were reversible in all their stages and that in the case of the caged phosphites ring strain and intramolecular crowding in the trigonal bipyramidal products precluded their isolation. However, the nucleophilic attack of cyclic tertiary phosphorus compounds on carbonyl groups is expected to be slower than that of their acyclic analogues\textsuperscript{143}, purely on the grounds of increased ring strain on forming a more tetrahedral phosphorus. For the caged phosphites
this increase in ring strain on changing to an intermediate with a more tetrahedral geometry (154) may result in product formation being very slow.

\[
\begin{align*}
\text{(153)} & \quad \xrightarrow{(\text{MeCO})_2} \quad \text{(154)} \\
\end{align*}
\]

That the reason for the failure by Ramirez to isolate pentacoordinate products from these reactions may have been kinetic rather than thermodynamic is suggested by the work of Bernard and Burgarda\textsuperscript{144}, who found that heating the similar cyclic phosphite (155) with biacetyl at 60° for eight days was necessary for adduct formation. The product isolated was the 1:2 adduct (156) in this case.

\[
\begin{align*}
\text{(155)} & \quad \xrightarrow{(\text{MeCO})_2} \quad \text{(156)} \\
\end{align*}
\]

In addition Brennan\textsuperscript{145} has reported the reaction of ozone with the cage phosphite (157) to give the remarkably stable adduct (158). This

\[
\begin{align*}
\text{(157)} & \quad \text{(158)} \\
\end{align*}
\]
decomposed only at temperatures above 0°, in contrast to the fleeting existence of (EtO)₃PO even at -95°. This stability was attributed to the relatively strain-free bicyclic system (158).

6.4 Phosphoranes Containing Four-membered Rings.

Certain phosphinimines are known to exist as dimeric species; typical are N-methyltrichlorophosphinimine (159)¹⁴⁶ and its phenyldifluoro ¹⁴⁷,¹⁴⁸ and trifluoro¹⁴⁸,¹⁴⁹ analogues. In these dimers trigonal-bipyramidal geometry exists at the phosphorus atoms with the four-membered ring spanning the apical-equatorial positions.

Beck-Gohring and coworkers¹⁵⁰ treated (159) with bis(methylamino)sulphate and produced the stable phosphorane (160).

The reaction of PF₃Cl₂ with one mole of N,N'-bis(trimethylsilyl)-N,N'-dimethylsulphamide has been reported¹⁵¹ to give the fluorophosphorane (161), which reacts further with the sulphamide to give the phosphorane (162) or with N,N'-bis(trimethylsilyl)-N,N'-dimethylurea to give (163).
Ramirez and coworkers have found that the 1,3,2-dioxaphospholan adducts (164) from the reaction of tertiary phosphines with hexafluoroacetone underwent thermal rearrangements to give the 1,2-oxaphosphetan adducts (165).

6.5 Adducts of the Phosphetans.

Although the presence of the phosphetan ring spanning the apical-equatorial positions would be expected to enhance the stability of their phosphoranes, published work in this field has been largely confined to the synthesis of the diethoxy and difluorophosphoranes of 2,2,4,4-tetramethyl-1-phenylphosphetan and its 2,2,3,3-analogue by Denney and coworkers; relatively little attention has been paid to the α-diketone, α-quinone and α,β-unsaturated ketone adducts of the phosphetans.
Shutt found that the 1:1 adducts of trimethylphenylphosphetan and pentamethylphenylphosphetan with phenanthraquinone and benzil had spectroscopic properties characteristic of pentacoordinate adducts of these diketones. The high thermal stability reported for these adducts suggested the use of similar phosphetan adducts in the study of high-energy pseudorotation processes.

The pseudorotation processes available to an adduct of a phosphetan are shown below. The energy barrier for pseudorotation between equivalent forms such as (166) and (167) is not known but is expected to be very low, however the other two processes in which the four-membered ring (168) or the five-membered ring (169) is placed diequatorial are expected to have a high energy barrier due to the considerable ring strain increases involved.

The pseudorotation (170) to (171) in which the five-membered ring is placed diequatorial requires the loss of the cis/trans geometrical relationship of the pairs of phosphetan ring methyls R and R' with the
phenyl group; accordingly the n.m.r. signals of these groups can be used to monitor this process. Unlike the trimethyl- and pentamethyl-1-phenylphosphetan systems the 2,2,3,3-tetramethyl-1-phenylphosphetan system has the requisite substitution pattern (i.e. \( R_1 = R'_1, R_2 = R'_2, \) and \( R_3 = R'_3 \)).

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{O} & \quad \text{O} \\
\end{align*}
\]

(170) \quad (171)

6.6 The Adducts of 2,2,3,3-Tetramethyl-1-phenylphosphetan.

Pentacoordinate adducts of the 2,2,3,3-tetramethylphosphetan system would be expected to have enhanced stability over those of the pentamethylphosphetan system on steric grounds, due to the decrease in crowding, and possibly on electronegativity grounds.

Phenanthraquinone.

2,2,3,3-Tetramethyl-1-phenylphosphetan reacted exothermically with phenanthraquinone to give the very stable 1:1 adduct, which exhibited \( ^{31}P \) n.m.r. shifts of +4.5 p.p.m. in chloroform and 4.8 p.p.m. in benzene. The i.r. spectra in the solid state and in chloroform solution were essentially identical to one another and showed absorptions at 1048 cm\(^{-1} \) and 1022 cm\(^{-1} \), which are found in pentacoordinate adducts of 9,10-phenanthraquinone\(^{161} \). These two absorptions are not exhibited by dipolar adducts of phenanthraquinone, and the characteristic 1550 cm\(^{-1} \) absorption\(^{135} \) of the dipolar adducts was absent. This i.r. data
together with the $^{31}\text{P}$ n.m.r. values would suggest a pentacoordinate geometry (172) for the adduct.

The $^1\text{H}$ spectrum of the adduct was unchanged from $-60^\circ$ to $+150^\circ$ which indicates the energy barriers to pseudorotation (172) to (173), and (172) to (174) are less than 10 kcal mol$^{-1}$ and greater than 21 kcal mol$^{-1}$ respectively.

Biacetyl

Biacetyl reacted readily, but not exothermically, with the tetramethylphosphetan to give the distillable 1:1 adduct which crystallised on standing. The adduct was very soluble in pentane but could be partially purified by crystallisation from this solvent at low temperatures. The adduct was readily hydrolysed to acetoin and the phosphetan oxide; this hydrolytic instability is quite typical of biacetyl adducts and those of $\alpha$-diketones in general$^{161}$.

The $^{31}\text{P}$ n.m.r. shifts of the adduct of +16 p.p.m. in chloroform and +16.5 p.p.m. in benzene indicate a pentacoordinate structure (175) for this adduct, which is confirmed by the absence of an 'enolate' i.r. absorption$^{134,161}$ in the region 1650-1530 cm$^{-1}$.

Like the phenanthraquinone adduct, the $^1\text{H}$ n.m.r. spectrum of the adduct was essentially unchanged from $-60^\circ$ to $+150^\circ$. 

\begin{align*}
(173) & \iff (172) \iff (174) \\
(173) & \iff (172) \iff (174)
\end{align*}
The failure to observe the pseudorotation in which the 1,3,2-dioxa-
phospholen ring of the biacetyl and phenanthraquinone adducts is
placed diequatorial implies that the activation energy for such a
process is greater than 21 kcal mol⁻¹. A similar result with a
1,3,2-dioxaphospholan adduct has been reported by Denney and coworkers.¹³¹

**Hexafluoroacetone.**

Ramirez and coworkers¹³⁷ found that tertiary phosphines reacted
with excess hexafluoroacetone to give the 1,3,2-dioxaphospholan adducts,
which were believed to be completely pentacoordinate in contrast to
1,3,2-dioxaphospholen adducts from α-diketones and ο-quinones which
exist as an equilibrium between open dipolar forms and the oxyphosphoranes.
The enhanced stability of the pentacoordinate state in the adducts of
hexafluoroacetone compared to those of the ο-quinones is believed to be
a general phenomenon for trivalent phosphorus.¹³⁷

The formation of 1,4,2-dioxaphospholan adducts from hexafluoroacetone
has never been reported although the 1,3,2-dioxaphospholan adduct from
perfluorobenzaldehyde has been shown⁴⁶ to be formed by rearrangement of
such a 1,4,2-dioxaphospholan.

Hexafluoroacetone was found to react with the tetramethylphosphetan
at -78° to give a colourless crystalline adduct which was stable in the solid state. On the basis of the method of synthesis, the spectroscopic properties, and the identity of the rearrangement products this adduct is believed to have the 1,4,2-dioxaphospholan ring system (176). In solution at temperatures at or above ambient this adduct rearranged to a mixture of a new crystalline adduct, believed to be the 1,3,2-dioxaphospholan adduct (177), and the phosphinate (178).

The initial adduct exhibited a $^{19}$F spectrum consisting of two pairs of multiplets separated by 12 p.p.m., consistent with the two distinctly different types of fluorine environments of the 1,4,2-dioxaphospholan structure (176). In contrast, the rearranged adduct exhibited three multiplets in the ratio 2:1:1 spread over only 2.6 p.p.m., consistent with the slight differences between the fluorine environments of the 1,3,2-dioxaphospholan structure (177).

A possible mechanism for this rearrangement is shown below in which the 1,4,2-dioxaphospholan adduct is the kinetic product while the alternative 1,3,2-dioxaphospholan is the thermodynamically favoured product. The trifluoromethyl groups could be expected to activate the carbonyl carbon towards nucleophilic attack to give the 1:1 adduct (179), although the incipient carbanion in the formation of the alternative adduct (180) has been suggested to be stabilised by these
groups. The steps involved in the synthesis of the 1,4,2-dioxa-
phospholan adduct could be expected to be reversible; that

\[ \begin{align*}
\text{(180)} & \quad \text{Ph} \quad \text{O} \quad \text{Ph} \\
\text{(181)} & \quad \text{OCH(CF}_3\text{)}_2 \\
\text{(182)} & \quad \text{heat} \\
\text{(176)} & \quad \text{Ph} \quad \text{O} \quad \text{Ph} \\
\text{(177)} & \quad \text{OCH(CF}_3\text{)}_2 \\
\text{(178)} & \quad \text{Ph} \quad \text{O} \quad \text{Ph} \\
\text{(179)} & \quad \text{OCH(CF}_3\text{)}_2 \\
\text{(182)} & \quad \text{heat} \\
\text{(176)} & \quad \text{Ph} \quad \text{O} \quad \text{Ph} \\
\text{(177)} & \quad \text{OCH(CF}_3\text{)}_2 \\
\text{(178)} & \quad \text{Ph} \quad \text{O} \quad \text{Ph} \\
\text{(179)} & \quad \text{OCH(CF}_3\text{)}_2 \\
\end{align*} \]

adduct isolation is possible in this example may be a reflection of
the decrease in ring strain in the phosphetan ring on formation of a
pentacoordinate species. If ring opening is a prerequisite for decomposition of this adduct then the low solubility of the adduct coupled with the preferred oxyphosphorane crystal structure\textsuperscript{18,135} could also aid its isolation.

In solution at temperatures above ambient ring opening and decomposition of this adduct may occur, initially to give the 1:1 adduct (179). Direct rearrangement, or complete decomposition and carbonyl oxygen attack by phosphorus, will give the alternative, possibly more stable\textsuperscript{46} 1:1 adduct (180).

Formation of the 1,3,2-dioxaphospholan adduct will become competitive with loss of hexafluoroacetone if any one step in its formation is essentially irreversible under the reaction conditions. Although the formation of a C-C bond to give (181) has been suggested\textsuperscript{60} to be irreversible, the absence of a change in the $^{31}$P n.m.r. shift of (176) in xylene and 2-methoxyethanol would suggest that the adduct has very little tendency to ring open. Such $^{31}$P solvent effects have been used\textsuperscript{46,48} as a probe for the existence of equilibria between oxyphosphorane and dipolar structures.

The formation of the phosphinate (178) may be due to proton transfer to give the ylide (182) and the Wittig reaction with hexafluoroacetone. Internal ylide formation in phosphetanium systems may not be particularly facile as the Wittig synthesis with 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium salts and benzaldehyde gave only the oxide resulting from benzylidene ylide formation. This could indicate that attack of the carbanion of (180) on the hexafluoroacetone carbonyl carbon is not particularly rapid in order for ylide formation to take place. It will be shown that the reaction of the 1-benzylphosphetan (183) with hexafluoroacetone gave only the product (184) from
ylide formation and no 1,3,2-dioxaphospholan adduct; this is the expected result on the grounds of the increased acidity of the α-proton.

That the phosphinate (178) has its origin other than in the 1,3,2-dioxaphospholan adduct (176) is indicated by the complete stability of this adduct at temperatures in excess of 150°. This is in agreement with the earlier proposition that at least one of the steps between (180) and (176) may be irreversible, but is in contrast to the findings of Ramirez and coworkers. The analogous hexafluoroacetone adducts of acyclic tertiary phosphines (164) underwent just such a rearrangement at 80° to give the 1,2-oxaphosphetans (165) which decomposed to the phosphinates on further heating. Two possible mechanisms for this rearrangement were suggested, both of which involved
the opening of the dioxaphospholan ring\textsuperscript{137,152}. The significant difference in behaviour of the acyclic phosphine and the phosphetan adducts could be reconciled with the facility of this process; ring strain considerations would predict such a process to be much slower for a phosphetan adduct than for the acyclic tertiary phosphine adduct.

A similar reluctance to undergo this rearrangement has been reported\textsuperscript{157} for the hexafluoroacetone adducts of certain acyclic phosphonites. Here the increased stability of the phosphorane structure (185) and instability of the ring open form (186) was the result of the introduction of two electronegative substituents, but the end result was

\[
\text{(185)} \quad \text{(186)}
\]

the same as that of introducing the phosphetan ring; in both cases the prerequisite ring opening reaction was suppressed.

Although the 1,3,2-dioxaphospholen adducts from biacetyl and phenanthraquinone failed to show \textsuperscript{1}H n.m.r. spectral changes identifiable with the high energy pseudorotation (187) to (188), the increase in the OPO angle of the 1,3,2-dioxaphospholen system could suggest that the activation energy for such a process may be lower in this system (176). As the \textsuperscript{1}H n.m.r. spectrum of this adduct was also unchanged at temperatures up to 160° the activation energy of the pseudorotation to
(189) is obviously still greater than 22 kcal mol$^{-1}$.

Benzylidene Acetylacetone.

The adducts of benzyldiene acetylacetone and acyclic trialkyl or alkylarylphosphines are known to exist as dipolar species even at -40°. This has been attributed to the stereoelectronically unfavourable placing of carbon functions in one apical and three equatorial positions on ring closure preventing phosphorane formation. The presence of a small ring in the phosphine might however be expected to enhance the stability of the phosphorane form for the reasons previously enumerated. Indeed cyclic alkylphosphoranes have been reported in which all five positions in the trigonal bipyramid are occupied by carbon functions.

On the basis of these considerations the adducts of benzyldiene acetylacetone and the phosphetans would be expected to have an increased disposition towards phosphorane formation.

Hawes found that 2,2,3,4,4-pentamethyl-1-phenylphosphetan on reaction with benzyldiene acetylacetone gave a 1:1 adduct which was pentacovalent in the solid state but existed as the dipolar form in solution. A consideration of the increased rate of hydrolysis of phosphetanium salts with only one P-CMe$_2$ linkage (attributed to
decreased steric hindrance to attack of hydroxyl to form the phosphorane compared with the pentamethylphosphetan series), and the decrease in crowding in the phosphorane with fewer substituents, might suggest an increased likelihood of phosphorane formation with $2,2,3,3$-tetramethyl-1-phenylphosphetan.

\[ R_1=H, R_2=Me, \quad R_1=R_2=H \]

hydrolysis, rel. rate 1 300

Benzylidene acetylacetone reacted with the tetramethylphosphetan in refluxing dichloromethane to form the 1:1 adduct, a composition confirmed by elemental analysis. A pentacoordinate geometry for this adduct was suggested by the following spectroscopic data.

(a) The i.r. spectra of the adduct in the solid state and in solution in benzene and in chloroform were essentially identical and showed a strong absorption at 1630 cm$^{-1}$, indicating a conjugated carbonyl group, in contrast to the adduct of Hawes.\(^{18}\)

(b) The $^1$H n.m.r. spectrum exhibited two sharp singlets at $\tau 7.52$
and \( 8.17 \), corresponding to the two different methyl groups of the 1,2-oxaphospholan ring; a dipolar form would show a single signal corresponding to equivalent methyl groups.

(c) The adduct exhibited a \(^{31}\text{P} \) n.m.r. signal at +31 p.p.m., a value comparable to the pentacovalent adduct from trimethyl phosphite \(^{123}\) (+28 p.p.m.)

Although the geometries of the ketone and the phosphetan permit the existence of four geometrical isomers (190)-(193), preparation of the adduct at 40° and recrystallisation of the crude product afforded

![Diagram of isomers](image)

an adduct with a \(^1\text{H} \) n.m.r. spectrum consistent with the presence of only one isomer.

On heating, the \(^1\text{H} \) n.m.r. spectrum in \( o \)-dichlorobenzene showed broadening of the signals above 60°, and at 85° the methyl signals from the benzylidene acetylacetone residue coalesced. Further heating resulted in the sharpening of this signal. These changes are consistent with a ring opening process to give the betaine, in which the two methyls would be identical. These changes were not completely reversible; on cooling the spectrum of the product was consistent with the presence of two isomers, ratio 18:7, the 'new' (minor) isomer showing a
characteristic methine CH doublet at \( \tau 6.30 \) (d, \( J_{PH} 12 \, \text{Hz} \)).

A closer examination of the crude product from the preparation of the adduct at 40° and prior to recrystallisation showed an identical isomer ratio, but preferential crystallisation of the major isomer and re-equilibration of the enriched mother liquors on concentration effectively prevented isolation of the minor isomer. Reaction of the phosphetan and benzylidene acetylacetone at 0° was also found to give a mixture of isomers but on this occasion the ratio of products was 1:1.

A consideration of molecular models would suggest that approach of the benzylidene acetylacetone to the phosphorus may preferentially occur in the orientation (194), resulting in the dipolar ion (195).

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{COMe} & \quad \text{COMe} \\
\text{Me} & \quad \text{Me} \\
\text{P} & \quad \text{P}
\end{align*}
\]

(194) (195)

Cyclisation of the zwitterion (195) can occur opposite the ring CH\(_2\) or the ring CMe\(_2\). Attack of hydroxyl ion on t-butylphosphonium salts has been suggested to preferentially occur opposite the t-butyl group for steric reasons; similar reasoning could predict that the phosphorane (190) resulting from attack opposite the ring C(Me\(_2\)) would be most readily formed. In addition such a phosphorane would involve the minimum of non-bonded interactions between the two phenyl groups. Thus the major, more stable isomer may be (190), while the less stable isomer may be (193).
That the methine P-CH signal of the minor isomer is +0.77 p.p.m. upfield of that of the major isomer could also be interpreted as evidence in favour of assigning a 'trans' relationship to the phenyl groups of the major, more stable isomer, as in this configuration the methine proton would be deshielded by diamagnetic effects from both of the aromatic groups, while in a cis geometry for the phenyl groups, deshielding would be confined to only one phenyl group.

Presumably the product isomer ratio is governed by the final step, the cyclisation of the zwitterion (195). At 0° the cyclisation is under kinetic control and selectivity between the pathways to each isomer does not occur in spite of their slightly different product energies, while at 40° the products can equilibrate at a rapid enough rate for the thermodynamically favoured product ratio to be obtained.
7. THE HEXAFLUOROACETONE ADDUCTS OF 2,2,3,4,4-PENTAMETHYLPHOSPHETANS.

7.1 The Structure of Phosphetan Phosphoranes.

In pentacoordinate trigonal bipyramids containing the phosphetan ring system, either isolated as stable phosphoranes or as nucleophilic substitution intermediates, there is a conflict between the desire of the ring to occupy the apical-equatorial position as opposed to the diequatorial position (the strain factor) and the preference of more electronegative substituents for the apical position (the stereoelectronic factor). The retention stereochemistry observed\textsuperscript{11,20,165,166} in phosphetan substitution reactions infers that the strain factor is normally the larger, and therefore pseudorotation pathways involving species with the phosphetan ring in the diequatorial position are of high energy. As such this process is amenable to n.m.r. study using stable pentacoordinate phosphetan adducts.\textsuperscript{55}

In order to study the pseudorotation process (196) to (197) of cyclic phosphetan adducts in which the four-membered ring is placed diequatorial, the loss of geometrical non-equivalence of substituents of the five-membered ring against the phosphetan 1-substituent has to be monitored. For this reason the 1,3,2-dioxaphospholen adducts, where the substituents are in the plane of the ring, cannot be used. The hexafluoroacetone adducts of the pentamethylphosphetans do meet the geometrical requirements, i.e. cis and trans substituents on the five-membered ring and identical phosphetan ring junctions.
7.2 The 2,2,cis-3,4,4-Pentamethyl-r-1-phenylphosphetan Adduct.

Trichlorosilane reduction of the diastereoisomerically pure cis phosphetan oxide and reaction of the cis phosphetan solution with hexafluoroacetone gave a crystalline single isomer of the adduct, presumably with the cis-phenyl geometry. The $^1$H n.m.r. spectrum was consistent with a 1,3,2-dioxaphospholan ring system (198) rather than the 1,4,2-dioxaphospholan system. In contrast to the hydrolytically unstable adducts from acyclic phosphines\textsuperscript{137}, this adduct was stable to aqueous solvents. As previously mentioned, this stability may be interpreted\textsuperscript{48} as an indication of the absence of significant amounts of ring opening to a tetrahedral phosphetanium system as a prior step to hydrolysis.

The $^1$H n.m.r. spectrum was unchanged from $-60^\circ$ to $+160^\circ$, with no interconversion to the trans isomer. This showed that the five-membered ring was not placed diequatorial up to this temperature, in
agreement with the results obtained with the tetramethylphosphetan adduct and those reported by Denney and coworkers \(^{131}\).

The \(^{19}\)F n.m.r. spectrum consisted of two signals showing fine structure. On heating the fine structure disappeared, the signals broadened and collapsed, and then finally coalesced at 140°. The process was reversible with no decomposition and the coalescence temperature was unchanged in 1-bromonaphthalene and ethylene glycol. The absence of a solvent effect on the coalescence temperature rules out a process producing equilibration via a betaine (199); solvation of the incipient carbanion of (200) by the hydroxylic solvent would be expected to lower the temperature at which ring rupture occurs.

\[
\begin{align*}
(198) & \quad \begin{array}{c}
\text{Ph} \\
0 \\
\text{P}
\end{array} \\
\begin{array}{c}
0 \\
2 \\
3 \\
4
\end{array} & \quad \begin{array}{c}
\text{Ph} \\
0 \\
\text{P}
\end{array} \\
\begin{array}{c}
0 \\
2 \\
3 \\
4
\end{array} & \quad \begin{array}{c}
\text{Ph} \\
0 \\
\text{P}
\end{array} \\
\begin{array}{c}
0 \\
2 \\
3 \\
4
\end{array} & \quad \begin{array}{c}
\text{Ph} \\
0 \\
\text{P}
\end{array} \\
\begin{array}{c}
0 \\
2 \\
3 \\
4
\end{array}
\end{align*}
\]

\(1,2,3,4 = \text{CF}_3\)

The activation energy for the equilibration process at 140° was 19.6 kcal mol\(^{-1}\). The free energy of activation (\(\Delta G^*\)) will be equivalent
to this only if the entropy of activation is small; an intramolecular
process such as pseudorotation where no bond rupture or formation
occurs would be expected\textsuperscript{167} to meet this criterion. Gorenstein\textsuperscript{168}
has found that the values of $\Delta S^*$ for pseudorotation processes in cyclic
oxyphosphoranes could never be clearly distinguished from zero and
suggested that this value should be treated as such.

On the basis of molecular orbital calculations, Mislow\textsuperscript{31} has
suggested that structures such as (201) are best considered merely as
transition states in pseudorotation processes between 'normal'
phosphoranes in which the phosphetan ring spans the apical-equatorial
position, rather than as discrete intermediates with activation
energies to their breakdown. If this is so, the $\Delta G^*$ is the difference
in energy between the structures (198) and (201), i.e. the energy
required to move the four-membered ring into the diequatorial position ($S_4$)

\begin{center}
\begin{tabular}{ccc}
\includegraphics[width=0.3\textwidth]{198.png} & \includegraphics[width=0.3\textwidth]{201.png} & \includegraphics[width=0.3\textwidth]{196.png}
\end{tabular}
\end{center}

minus a stereoelectronic factor corresponding to the difference in
apicophilicities\textsuperscript{48} of the ring CMe$_2$ and the phenyl groups ($A_{\text{Ph}} - A_{\text{CMe}_2}$).

If we represent this by a simple expression such as

$$\Delta G^* \geq S_4 - A_{\text{Ph}} + A_{\text{CMe}_2}$$
(where the \( \geq \) sign is to take account of the possible existence of a small potential energy minimum corresponding to the high energy structure (201), see later), then if other possible variables are kept constant, a study of the variation of the \( \Delta G^* \) with the identity of the phosphetan 1-substituent (R) of the adduct (196) should provide data on the relative apicophilicities of the R groups, the use of which will be discussed later.

### 7.3 Relative Apicophilicities.

Using the methods of preparation given in Chapter 1, a range of 1-substituted 2,2,3,4,4-pentamethylphosphetans was synthesised and the adducts with hexafluroracetone prepared. Values of coalescence temperatures (\( T^C \)) and other physical and spectroscopic data for some of these adducts are given in the following table.

#### Data for Hexafluoracetone Adducts of Pentamethylphosphetans.

<table>
<thead>
<tr>
<th>R Group</th>
<th>Ph(trans)</th>
<th>Ph(cis)</th>
<th>CH:CM(_2)</th>
<th>iPr(_a)</th>
<th>Me(_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{19})F ( T^C )</td>
<td>180(^c)</td>
<td>140(^c)</td>
<td>135(^d)</td>
<td>93(^d)</td>
<td>85(^d)</td>
</tr>
<tr>
<td>( \Delta\nu ) Hz</td>
<td>133</td>
<td>153</td>
<td>219</td>
<td>83</td>
<td>166</td>
</tr>
<tr>
<td>( \Delta G^* ) (kcal mol(^{-1}))</td>
<td>&gt; 22</td>
<td>19.6</td>
<td>19.1</td>
<td>17.8</td>
<td>16.9</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>2.49</td>
<td>2.49</td>
<td>2.37</td>
<td>2.28</td>
<td>2.27</td>
</tr>
<tr>
<td>( ^{31})P(^e)</td>
<td>-3.4</td>
<td>-7.7</td>
<td>+0.5</td>
<td>-19.5</td>
<td>-6.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R Group</th>
<th>NMe(_2)</th>
<th>OPh(^b)</th>
<th>OCH(CF(_3))(_2)</th>
<th>H(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{19})F ( T^C )</td>
<td>63(^f)</td>
<td>-77(^g)</td>
<td>-125(^h)</td>
<td>-115(^i)</td>
</tr>
<tr>
<td>( \Delta\nu ) Hz</td>
<td>86</td>
<td>ca. -220</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \Delta G^* ) (kcal mol(^{-1}))</td>
<td>16.2</td>
<td>ca. 9</td>
<td>&lt; 7.5</td>
<td>(&lt; 8.0)</td>
</tr>
<tr>
<td>Electronegativity</td>
<td>2.40</td>
<td>2.68</td>
<td>3.74</td>
<td>2.2</td>
</tr>
<tr>
<td>( ^{31})P(^e)</td>
<td>-15.5</td>
<td>-16.0</td>
<td>-15.3</td>
<td></td>
</tr>
</tbody>
</table>
c. 1-Bromonaphthalene.  d. o-Dichlorobenzene.  e. Benzene
f. Toluene.  g. Trichlorofluoromethane.  h. Broad singlet at this
temperature.  i. Sharp singlet at this temperature.

Although the general ordering of these values of $T^C$ and $\Delta G^*$ are
broadly in line with those expected on the basis of the nature of the
group attached to phosphorus, i.e. C>N>0, they differ in several respects
from those expected on the basis of the preference rule\textsuperscript{42} i.e. that the
more electronegative substituents will prefer to occupy the apical
position.

(a) Carbon substituents. The apicophilicities of the carbon functions
are clearly in the inverse order of their electronegativities; the
phenyl group has previously been assumed to be more apicophilic than
alkyl groups.

(b) The dimethylamino group. Although the apicophilicity of this
group is, as expected, between those of carbon and oxygen ligands, on
the basis of electronegativity alone the dimethylamino group would be
expected to be much more apicophilic relative to the similarly sized
isopropyl group.

(c) The difference ($>13 \text{ kcal mol}^{-1}$) in the activation energies for
placing Ph and OPh in the apical positions is larger than that expected
on the basis of previous work by Denney and coworkers\textsuperscript{55,115} relating
Ph and OEt, where values in the region of 10 to 11 kcal mol$^{-1}$ are
suggested.

Recent molecular orbital calculations have suggested\textsuperscript{61} that the
electronegativity is not the sole determinant of the apicophilicity of
a group. Ugi and coworkers' results\textsuperscript{48} indicated that the greater
stabilising interaction between ligand filled π orbitals and the phosphorus d-orbitals in the equatorial position compared with the apical position could play a substantial role in the determination of ligand positions on the trigonal bipyramidal skeleton. Ligands in the apical positions must be able to accommodate considerable amounts of electronic charge since the ability to lower this electron density by π-bonding is smaller. Hence the most electronegative ligands show a pronounced disposition towards apical site occupation, in agreement with the preference rule. However, the preferential π-bonding from the equatorial position will result in a tendency for any ligand with filled π-orbitals or lone pairs of electrons to occupy an equatorial position. These two factors can be in opposition to one another, and the apicophilicity of a group then becomes a balance of its electronegativity and its π-bonding ability, with steric factors playing an undetermined role.

The relative importance of the π-bonding ability must be judged individually for each ligand; for the very electronegative ligands such as fluorine the electronegativity effect has been shown by molecular orbital calculations to be dominant. As the electronegativity decreases, the π-bonding effect becomes an important determinant of the relative apicophilicity of a group.

These conclusions can readily be applied to the interpretation of the data given in the table; the results imply a high degree of back-bonding from equatorial amino, vinyl and phenyl groups which is essentially absent in the 1-isopropyl adduct.

Similar results, where the apicophilicity of a group may be reduced by preferential equatorial π-bonding are rare in the
literature, however one possible example may have been provided by Cowley and Taylor\textsuperscript{167}.

Trifluorobis(perfluoroalkyl)phosphoranes such as (202) normally exhibit\textsuperscript{153} equivalent phosphorus fluorines at temperatures as low as -$120^\circ$, the fluoroalkyl groups being very electronegative ligands. By contrast trifluorobis(perfluorovinyl)phosphorane (203) exhibits\textsuperscript{167} different apical and equatorial fluorines at temperatures as high as -$20^\circ$, which implies that the CF$_2$:CF group is at least 5 kcal mol$^{-1}$ less apicophilic than C$_2$F$_5$. Presumably a similar explanation holds for the reduced apicophilicity of this group as for those of certain of the hexafluoroacetone adducts; preferential $\pi$-bonding is again a possibility.

It may be of major significance that the effects of ($p$-$d$)$\pi$-bonding are observed here in a system in which very electronegative ligands are bonded to phosphorus. As discussed later these are the normal circumstances in which $\pi$-bonding is believed to occur.

As previously noted, the consideration that the activation energy for the pseudorotation process where the four-membered ring is placed diequatorial is similar to the difference in energy between the two structures such as (196) and (197) is based on Mislow's molecular
orbital calculations, where structures such as (197) are of very high energy. However as the electronegativity of the phosphetan 1-substituent R is increased structures such as (197) will become progressively more stable, and thus the consideration of these species merely as transition states becomes less valid. The effect of this stabilisation of structures such as (197) by electronegative substituents may be to make those values of relative apicophilicity obtained for the electronegative ligands more correctly minimum values. Thus although the difference in apicophilicity between isopropyl and phenoxy is apparently 8 kcal mol$^{-1}$ on the basis of these investigations, the true difference is very probably larger than this.

7.4 Applications and Limitations of the Apicophilicity Values.

(a) Applications

An apicophilicity value measures the energetic preference of a ligand to occupy an apical site in the phosphorane trigonal bipyramid over occupation of an equatorial site. Complete tables of these values should in theory provide a means of estimating the relative energies of the different arrangements of five ligands on the trigonal bipyramidal skeleton, providing that the apicophilicity values available are applicable to the phosphorane system under consideration. Such information could be of considerable value in the investigation of the course of a substitution reaction at phosphorus.

As an example, if there are two obvious phosphoranes which can be formed by attack of a nucleophile on phosphorus then an estimation of their relative energies should be possible. If the more stable arrangement of ligands has the leaving group in an equatorial position, then either equatorial loss of that ligand or pseudorotation to place the ligand apical and subsequent apical loss may occur. Such pathways
could lead to retention of configuration.

An illustration of this could be the alkaline hydrolysis of alkoxy(methylthio)phosphonium salts such as (204). The two most obvious ligand arrangements are (205) and (206); (205) has the more electronegative OR group apical, while (206) has the better leaving group SR in the apical position. As discussed in Chapter 3, the hydrolysis of acyclic phosphonium salts is taken to involve attack of the hydroxyl group opposite the best leaving group, and therefore inversion of configuration via (206) could be expected.

\[
\begin{align*}
\text{OMen} & \quad \text{OMen} & \quad \text{SMe} \\
\text{Me} & \quad \text{P} & \quad \text{MeS} & \quad \text{Ph} & \quad \text{SMe} \\
\text{Ph} & \quad \text{SMe} & \quad \text{OH} & \quad \text{MenO} & \quad \text{Ph}
\end{align*}
\]

\(\text{SbCl}_6\)  \(\text{(204)}\)  \(\text{(205)}\)  \(\text{(206)}\)

The reaction is found to proceed with retention of configuration\(^{169}\). Presumably complete apicophilicity values would have semi-quantitatively predicted the greater stability of (205) as a guide to prediction of the reaction course.

Apicophilicity values could also be useful in predicting the course of a substitution where extensive pseudorotation is possible. For example in Scheme I, it might be possible to obtain a semi-quantitative prediction of the magnitude of the suggested barrier provided by the presumed energetically unfavourable phosphorane (62).

(b) Limitations.

These derive both from the meaning of apicophilicity values and from their method of evaluation.
Although apicophilicity values should provide a means of estimating the relative energies of phosphoranes involved in substitution reactions, they provide no information on the relative activation energies to the formation or decomposition of these phosphoranes, or to the pseudorotation barriers to the interconversion of phosphoranes by pseudorotation processes. The hydrolysis of the acyclic t-butylphosphonium salt (42) and the methanolysis of menthyl S-methyl phenylphosphonothioate (207) provide illustrations of these points.

The hydrolysis of the t-butylphosphonium salt proceeds\textsuperscript{84} with retention of configuration. Apicophilicity considerations would probably predict the opposite result as they provide no information on the steric hindrance to nucleophilic attack.

Methoxide substitution of the methylthio group of (207) could be envisaged as occurring via either of the phosphoranes (208) and (209). Apicophilicity considerations would probably predict retention of configuration in this reaction via (209). Actually almost complete inversion is observed\textsuperscript{170}. This could be a reflection of the relative activation energies to decomposition by loss of methylthio from (208) or (209), or the pseudorotation barrier to placing SM\textsubscript{e} apical from (209).

In the analysis of a substitution reaction where extensive pseudorotation may be involved, although the relative energies of two
phosphoranes connected by a pseudorotation may be estimated using apicophilicity data, the pseudorotation energy barrier is essentially unknown. Apicophilicity values will normally only provide an estimate of the minimum value of that barrier, and will only give a more specific estimation of this barrier in the extreme case, i.e. when there is essentially no activation energy to the pseudorotation in one direction.

The system used to obtain the apicophilicity values also limits their generality. The values were obtained from a phosphorane in which two extremely electronegative ligands were bonded to phosphetan phosphorus. The apicophilicity values have been suggested to be partly dependent on two factors, the electronegativity of a ligand and the extent of its back-bonding ability. The magnitude of these factors should not be constant throughout phosphorane chemistry.

The extent of \( \pi \)-donation to phosphorus from a ligand has been suggested\(^{171} \) to be affected by the inductive withdrawal ability of the other ligands bonded to phosphorus. Thus in the phosphorane (210) there has been suggested\(^{172} \) to be very little \( \pi \)-donation to phosphorus, in contrast to (211) where very considerable donation is believed to occur\(^{116} \). This triggering off of \( \pi \)-bonding has been attributed\(^{174,175} \) to the powerful inductive effect of the four fluorines in (211) creating a high

\begin{center}
\begin{tikzpicture}
\node[draw,shape=circle,inner sep=1pt] (a) at (0,0) {\( \text{OEt} \)};
\node[draw,shape=circle,inner sep=1pt] (b) at (1,0) {\( \text{F} \)};
\node[draw,shape=circle,inner sep=1pt] (c) at (2,0) {\( \text{OEt} \)};
\node[draw,shape=circle,inner sep=1pt] (d) at (1,1) {\( \text{F} \)};
\node[draw,shape=circle,inner sep=1pt] (e) at (1,-1) {\( \text{F} \)};

\draw[thick] (a) -- (b);
\draw[thick] (b) -- (c);
\draw[thick] (d) -- (e);
\end{tikzpicture}

(210)
\begin{tikzpicture}
\node[draw,shape=circle,inner sep=1pt] (a) at (0,0) {\( \text{F} \)};
\node[draw,shape=circle,inner sep=1pt] (b) at (1,0) {\( \text{OEt} \)};
\node[draw,shape=circle,inner sep=1pt] (c) at (2,0) {\( \text{F} \)};
\node[draw,shape=circle,inner sep=1pt] (d) at (1,1) {\( \text{F} \)};
\node[draw,shape=circle,inner sep=1pt] (e) at (1,-1) {\( \text{F} \)};

\draw[thick] (a) -- (b);
\draw[thick] (b) -- (c);
\draw[thick] (d) -- (e);
\end{tikzpicture}

(211)
\end{center}
polarity difference between phosphorus and its ligand set, and also to a reduction in the diffuse nature of the d-orbitals on bonding very electronegative substituents to phosphorus, presumably making \( \pi \)-bonding more efficient. The reduction of the polarity difference between phosphorus and its ligand set which occurs on this donation has been shown to stabilise the phosphorane. The extent of \( \pi \)-donation will almost certainly vary with that from the other ligands; the bonding from one ligand is clearly going to be restricted if extensive donation is occurring from other ligands.

The effective electronegativity of a ligand may also vary according to the nature of the other phosphorus substituents. The reduction of the phosphorus electron density which occurs on bonding other, more electronegative, ligands to phosphorus may limit the electronegativity of a ligand very considerably. However, the \( \pi \)-donation to phosphorus from any available \( \pi \)-bonding ligands which may occur under these circumstances may tend to increase the ligand electronegativity once more. Clearly therefore, the ligand apicophilicity is likely to be considerably affected by the nature of the other ligands present.

A consideration of the electronegativity of the OC(CF\(_3\))\(_2\) ligands in the phosphorane used in this investigation would suggest that \( \pi \)-bonding may be very considerable. The effect of the phosphetan ring in this respect is uncertain, but may also affect the ligand \( \pi \)-bonding ability and the effective electronegativity of ligands in its phosphoranes. Therefore, when one attempts to extend these apicophilicity values to more 'normal' phosphoranes where \( \pi \)-bonding may not be so extensive, the results obtained are certain to be of somewhat limited value.
Finally, it is worthy of note that the apicophilicities of several ligands to which 'abnormal' stereochemistry has been found to be associated (t-butyl and alkylthio) as well as those of the halogens and good leaving group carbon functions (e.g. benzyl and allyl) are absent from the table. This was not intentional; their adduct preparations were attempted but non-typical chemistry was observed.

7.5 The 2,2,3,4,4-Pentamethyl-1-t-butylphosphetan Adduct.

The reaction of the phosphetan with hexafluoroacetone gave the 2:1 adduct in low yield. On the basis of the $^{19}$F n.m.r. spectrum this adduct is believed to have the 1,3,2-dioxaphospholan ring system (212). Unfortunately a value of $T^\circ$ could not be obtained as solutions of the adduct in non-hydroxylic solvents decomposed with gas evolution at temperatures above 60° to give the phosphetan as a mixture of isomers, characterised as the phosphetan oxide after aerial oxidation. The temperature at which decomposition occurred at a significant rate was dependent on the polarity of the solvent. Similar decomposition rates in toluene, anhydrous methanol and 1:1 aqueous ethanol were observed at temperatures of 70°, 25° and 0° respectively.

These results could be consistent with decomposition occurring via a ring opening mechanism involving the betaine (213); the solvation of the incipient carbanion by hydroxylic solvents should decrease the activation energy for ring opening and thus decomposition.

This instability contrasts with other 1,3,2-dioxaphospholan adducts of alkyl and aryl phosphetans which are in general stable.
at temperatures in excess of 120°.

As previously noted, phosphoranes are believed to possess a high degree of intramolecular crowding\textsuperscript{40,41}. In spite of the decrease in these non-bonded repulsions due to the presence of the two small rings in the phosphorane and the increased phosphetan ring strain on the formation of a tetracoordinate species such as (213), it would appear that the pentacoordinate state can barely accommodate a further increase in these crowding difficulties when a t-butyl group is introduced and ring opening readily occurs.

7.6 Reaction of Hexafluoroacetone with 2,2,3,4,4-Pentamethyl-1-phenylthiophosphetan.

Relatively little is known of the chemistry of phosphoranes in which sulphur is bonded to phosphorus. In general those that are known have the sulphur atom incorporated into a ring system. Stewart and Trippett\textsuperscript{176,177} have synthesised a variety of adducts of the ethylene phosphonothioites (214). These adducts resembled that (215) synthesised by French workers\textsuperscript{178} in that a thiiran was eliminated on heating.
De'ath and Denney have synthesised a number of sulphur-containing phosphoranes from tertiary phosphorus compounds and (216). Again, a notable feature of these adducts was their stability; in a qualitative way these sulphur-containing phosphoranes were less stable than oxyphosphoranes. Thus the adduct (217) decomposed at ambient temperatures, in contrast to the stability of the biacetyl adduct (116) of trimethyl phosphite at temperatures in excess of 100°.

Treatment of 2,2,3,4,4-pentamethyl-1-phenylthiophosphetan with hexafluoroacetone at its boiling point for twelve hours resulted in the near-quantitative recovery of the phosphetan. The failure to isolate products under these conditions may be due to both kinetic and thermodynamic causes; ampouling the phosphine and hexafluoroacetone for ten days at ambient temperatures gave a precipitate of diphenyl disulphide in moderate yield. Aerial oxidation of the residue gave an inseparable
mixture of products. A possible mechanism for the formation of diphenyl disulphide involves an intermolecular displacement reaction, in keeping with the leaving group ability of the phenylthio group; however the dimeric species (218) formed in this mechanism could not be isolated.

\[
\begin{align*}
\text{(218)} \\
\end{align*}
\]

Similar decomposition of the hexafluoroacetone adduct (219, \( R = \text{SPh} \)) has been observed by Whittle. This readily decomposed with the production of diphenyl disulphide as the only isolated product.

\[
\begin{align*}
\text{(219)} \\
\end{align*}
\]

\[
\begin{align*}
\text{(220)} \\
\end{align*}
\]

The finding that both the phenoxyphosphetan adduct (220) and the phenoxy adduct (219, \( R = \text{OPh} \)) were perfectly stable under these conditions is in keeping with the general conclusion of Denney concerning the relative stability of oxygen- and sulphur-containing phosphoranes.
7.7 The 1-Chloro-2,2,3,4,4-pentamethylphosphetan Adduct.

The problem of the structure of haloxyphosphoranes in solution and in the solid state is largely unsolved. Acyclic examples such as chlorotetraphenoxyphosphorane have been suggested to exist in solution as equilibria between the quasiphosphonium salt and the phosphorane structures; however the product from the reaction of two moles of catechol with phosphorus pentachloride has been formulated with the pentacoordinate structure (221). Presumably this difference is a reflection of the enhancement of the pentacoordinate structure by the presence of small ring systems.

The tendency towards covalence has been suggested to increase in the order I<Br<Cl<F, as expected on the basis of phosphorus-halogen bond strength considerations. Thus while fluoroxyphosphoranes such as (222) are accepted as being pentacoordinate, the similar chloro compound (223) may actually be largely ionic in solution.

Hexafluoroacetone reacted with the chlorophosphetan to give a crystalline 2:1 adduct, solutions of which at temperatures above ambient readily lost hexafluoroacetone to regenerate the isomerically-identical chlorophosphine. The high solubility of the adduct in
pentane may indicate a pentacoordinate rather than a pseudophosphonium salt structure. Unfortunately a $^{31}$P n.m.r. shift could not be obtained for this adduct.

There are two possible pentacoordinate structures for this adduct, the 1,3,2- or the 1,4,2-dioxaphospholan systems (224) or (225). The $^{19}$F spectrum, showing two signals separated by 17 p.p.m., may be more consistent with the 1,4,2-dioxaphospholan structure (225). It would definitely appear to be inconsistent with a bicyclic pseudophosphonium salt structure (226) or an equilibrium involving this species. As the $^{19}$F spectrum was unchanged from -60° to +35° no energetic data concerning apicophilicities could be obtained.

7.8 Reaction of Hexafluoroacetone with 1-Benzyl- and 1-(2'-Methylallyl)-2,2,trans-3,4,4-pentamethylphosphetans; The 1,2-Oxaphosphetan System.

The reaction of hexafluoroacetone with the 1-benzylphosphetan at -78° gave a dense mass of crystals which rapidly disappeared. Removal of the solvent and chromatography on alumina gave a liquid 2:1
adduct, to which the 1,2-oxaphosphetan structure (227, R = Ph) was assigned, on the basis of its $^1$H, $^{19}$F and $^{31}$P spectroscopic properties. The atmospheric stability of this adduct is in contrast to those synthesised by Ramirez and coworkers$^{152,186}$.

The $^1$H n.m.r. spectrum indicated the presence of only one isomer although the system permits the existence of four geometrical isomers even when the ring oxygen is restricted to the apical position. This conclusion was confirmed by the hydrolytic and thermal decomposition reactions of this adduct. At temperatures above 70° decomposition proceeded rapidly to give the olefin (228, R = Ph) and the phosphinate as a single geometrical isomer. This decomposition reaction is in keeping with the nature of (227) as a Wittig intermediate in the olefin synthesis. At ambient temperatures decomposition was complete within 30 days. An analysis of the reaction path suggests a cis geometry

![Reaction Pathway](image)

for the phosphinate (229).

Acid catalysed hydrolysis could readily be achieved by treating a chloroform solution of the adduct with acidified water or one mole of toluene-$p$-sulphonic acid monohydrate, or by chromatography on acidic silica. In each case the product was the alcohol (230, R = Ph), apparently as a single geometrical isomer of the phosphetan. The observed non-equivalence of the phosphetan α-methyl groups in the $^1$H
n.m.r. spectrum is possibly a result of the chiral centre at C1'.

The mechanism of this reaction may involve acid-catalysed ring opening of the oxaphosphetan system followed by hydrolysis of the alkoxyphosphetanium system (231) (with retention). Such a mechanism should give the alcohol as the trans isomer. Alternative mechanisms to give the cis isomer can be envisaged however.

\[ (227) \xrightarrow{\text{H}^+} (231) \xrightarrow{\text{H}_2\text{O}} (230) \]

The 1-(2'-methylallyl)phosphetan reacted similarly with hexafluoroacetone although in this case only the phosphinate (229) and the diene (228, R = Me:CH₂) were isolated. Presumably the intermediate 1,2-oxaphosphetan was thermally less stable than that from the 1-benzylphosphetan.

In the synthesis of the 1,3,2-dioxaphospholan adduct of the 1-methylphosphetan a minor product (230, R = H) analogous to that formed by the hydrolysis of the 1,2-oxaphosphetan adduct was obtained. Presumably the 1,2-oxaphosphetan (227, R = H) was hydrolytically less stable than (227, R = Ph). The decreased yield of this product is in keeping with the decreased acidity of the α-proton of the methyl group compared to those of the benzyl and allyl groups.

As previously mentioned, the first step in the formation of 1,3,2-dioxaphospholan adducts is the formation of a 1:1 intermediate adduct, by either nucleophilic attack of phosphorus on carbonyl oxygen
or rearrangement of the alternative 1:1 adduct. In the absence of an acidic \( \alpha \)-proton on the phosphorus \( \lambda \)-substituent this then reacts with a further molecule of hexafluoroacetone to give the \( 1,3,2 \)-dioxaphospholan adduct after ring closure. Depending on the acidity of any \( \alpha \)-proton present in the \( \lambda \)-substituent, ylide and thus oxaphosphetan formation may become competitive with this reaction. For the benzyl and allyl groups the high acidity of their \( \alpha \)-protons results in complete formation of the \( 1,2 \)-oxaphosphetan. The decreased acidity of these protons of the \( 1 \)-methylphosphetan must result in this reaction having a comparable activation energy to that of \( 1,3,2 \)-dioxaphospholan formation, as both products are formed. As expected the \( 1 \)-isopropylphosphetan gave only the dioxaphospholan adduct; its \( \alpha \)-proton being even less acidic than those of the methyl group.

7.9 Reaction of Hexafluoroacetone with \( 2,2,3,4,4 \)-Pentamethylphosphetan.

Very little work has been published on the reaction of primary and secondary phosphines with hexafluoroacetone. Stockel\(^{162}\) has reported that the reaction of hexafluoroacetone with diphenylphosphine gave the phosphinite (232), rather than the \( 1,3,2 \)-dioxaphospholan adduct (233), inferring that proton transfer proceeds at a faster rate than attack of the carbanion of (234) on the hexafluoroacetone carbonyl carbon. That this product was formed rather than the phosphine (235) was suggested to indicate that initial attack of phosphorus occurs at carbonyl oxygen rather than at carbonyl carbon of hexafluoroacetone.

This conclusion is only valid however if formation of the alternative product, the phosphine (235) is irreversible under the reaction conditions. This may not be so; the acidic properties of
trifluoromethyl-substituted alcohols and the suggested reversibility of phosphorus nucleophilic attack on carbonyl carbon could indicate that the formation of (235) may actually be reversible. If this is so, then as decomposition of (232) back to the secondary phosphine may be irreversible, the formation of (232) as the thermodynamically favoured product from the initial product (235) could have occurred.

2,2,3,4,4-Pentamethylphosphetan reacted with hexafluoroacetone to give a highly crystalline 1:2 adduct. This readily decomposed at temperatures above 35° to give the hexafluoroisopropoxyphosphetan (236) and hexafluoroacetone. Although alternative formulations can be envisaged, the two most obvious structures for this adduct are the dioxaphospholans (237) and (238). Unfortunately no $^{31}$P n.m.r. signal could be observed and instability problems precluded the obtaining of a mass spectrum. The $^{19}$F n.m.r. spectrum showed two sharp singlets
of different intensity separated by only 0.3 p.p.m.; this would seem inconsistent with the 1,4,2-dioxaphospholan structure (237) but could be compatible with separate signals from the cis and trans isomers of the 1,3,2-dioxaphospholan adduct (238).

If this structure is correct, then the variable temperature results imply a very high apicophilicity value for hydrogen, definitely higher than phenoxy and probably higher than the very electronegative OCH(CF₃)₂, even though its electronegativity is very low. This may be an illustration of the naivety in always expecting an association between electronegativity and apicophilicity as a high apicophilicity value for hydrogen has been implied by the results of several workers. Therefore the activation energy of the process of placing the five-membered ring diequatorial in the phosphorane (239) has been found to be 15.6 kcal mol⁻¹, while the equivalent process in the methoxyphosphorane (240) has an activation energy of approximately 22 kcal mol⁻¹. If a difference
in apicophilicity between H and OMe of approximately 6 kcal mol$^{-1}$ is correct then the results with the adduct (238) are reasonable; separation of the signals would be expected only below -180°. A high apicophilicity value for hydrogen has also been suggested$^{48}$ by molecular orbital calculations with PH$_2$F$_3$.

The mode of decomposition and the stereoisomeric changes involved could also indicate a 1,3,2-dioxaphospholan structure. The thermolysis of a sample of the adduct with a (presumed) isomer ratio 4:3, as estimated from the $^{19}$F n.m.r. spectrum, gave the phosphinite (236) as a mixture of geometrical isomers with composition 4:3. Addition of sulphur to the phosphinite gave the sulphide (241) whose isomeric composition was 7:5.

The apparent preservation of isomer ratios involved in these processes is reconcilable with decomposition of the 1,3,2-dioxaphospholan adduct by the mechanism shown below. Proton transfer in (242) might be expected to be rapid, as a slight relief of ring strain may be involved in this transformation.

- 129 -
7.10 Effect of the Hexafluoroacetone Adduct Ring System.

As well as causing an increased tendency towards pentacoordinacy, the 4,4,5,5-tetrakistrifluoromethyl-1,3,2-dioxaphospholan ring system formed from the reaction of tertiary phosphines with hexafluoroacetone apparently has another effect which may best be illustrated by a comparison of the results obtained with the phosphetan adducts with those in the literature.

Denney and coworkers have reported that the activation energy for the two pseudorotation process (30) to (31) is approximately 15 kcal mol\(^{-1}\). This can be represented by the simple equation:
The activation energy for the process in the phenoxyphosphetan hexafluoroacetone adduct (220) where the phosphetan ring is placed diequatorial has been found to be 9 kcal mol\(^{-1}\), i.e.

\[
9 > S_e - A_{0\text{Ph}} + A_{\text{CMe}_2}
\]

Admittedly there is an unknown factor corresponding to the difference in apicophilicity between ethoxy and phenoxy, but nevertheless a difference in \(\Delta G^*\) of the general magnitude of 6 kcal mol\(^{-1}\) is apparent.

A similar effect has been found by Duff\(^{189}\) with the hexafluoroacetone adduct (243). The activation energy for the pseudorotation (243) to (244) was found to be 9.5 kcal mol\(^{-1}\), however the activation energy for the similar pseudorotation of the phosphorane (240) has been reported\(^{131}\) to be approximately 22 kcal mol\(^{-1}\). Again a very considerable difference in the activation energy is observed.

Although the reason for this effect is unknown, in some way this ring system apparently lowers the activation energy for processes whereby a small ring is placed diequatorial. It may be that the intense electronegativity of the OC(CF\(_3\))\(_2\) group in some way alters the
hybridisation of the phosphorus in such a way that the angle between the other two 'equatorial' ligands is reduced from the 120° of a trigonal bipyramid to a value more amenable to small ring occupation.

Unfortunately very few X-ray structures are available of molecules containing the suggested very electronegative OC(CF₃)₂ ligand. The only suitable system may be that of the oxaphosphetan (245), which contains two such ligands, although both occupy apical positions in this phosphorane. The required distortion from the idealised trigonal bipyramidal geometry is indeed observed⁴⁰, with the angle between the two equatorial phenyl groups decreased to 112.7° from the theoretical 120°.

If a comparable diequatorial angle exists in the phosphetan hexafluoroacetone adducts then the observed considerable decrease in the activation energy for the process of placing the phosphetan ring diequatorial is not surprising. The difference in ring strain in a five-membered ring with phosphorus ring angles of 109.5° and 120° has been estimated¹⁹⁰ at 5-7 kcal mol⁻¹; a comparable phosphetan ring
Strain difference with ring angles at phosphorus of 120° and approximately 113° could be quite reasonable.

7.11 π-Bonding in Aromatic Systems: Substituent Effects.

Substituent effects on the rates of reaction at centres adjacent to aromatic systems are widely interpreted in terms of the electron-donating and withdrawing properties of the substituent. Suitable substituents might be expected to alter the extent of the suggested (p-d) π-bonding between aromatic systems and $P^v$ phosphorus. To examine this effect two pentamethylphosphetan-hexafluoroacetone adducts with substituted 1-phenyl groups were prepared; the p-bromo and p-methoxy substituents were chosen on the basis of their opposite effects on the rate of these reactions. Preparation could readily be achieved by the standard methods although the p-methoxy substituted adduct could only be obtained in low yield. The results obtained were not exactly those which might have been predicted.

(a) The p-Bromophenyl Adduct. Within experimental error the $T^c$ for the cis isomer of the adduct mixture was the same as that for the cis-phenyl adduct, while the trans isomer showed no coalescence up to 170°, resembling the trans-phenyl adduct in this respect. The frequency separation ($\Delta v$) between the pairs of $^{19}F$ signals for the phenyl and p-bromophenyl adducts were also almost identical.

(b) The p-Methoxy Adduct. The mixture of isomers of this adduct showed progressive decomposition above 80°, but although the $^{19}F$ spectrum showed this decomposition, no coalescence of the two multiplets was observed at temperatures up to 160°. Two possible explanations for this result could be offered; either the $T^c$ of the cis-methoxyphenyl
adduct is raised to above 160° by the substituent effect, or preferential decomposition of the cis adduct had occurred such that the cis isomer was essentially absent before its T<sup>c</sup> could be reached. Unfortunately the latter explanation could not be examined due to the complexity of the <sup>1</sup>H n.m.r. spectrum of the partially decomposed mixture and the difficulty in separating the components for detailed examination.

The resonance donor properties of the p-methoxy substituent as indicated by its σ<sup>+</sup> constant<sup>191</sup> could indicate that the former explanation is correct; however if this is so then an opposite, albeit smaller, effect on the T<sup>c</sup> of the p-bromophenyl adduct could also be expected. This was not observed.

The difficulty in attempting to correlate substituent effects on (π-π)π-bonding with σ constants may be connected with the nature of the processes involved. The resonance contribution to the σ<sup>σ</sup><sub>p</sub> values measures the strength of the π-donor interaction between the substituent (S) and an essentially vacant π orbital through an aromatic σ system.

However here we are attempting to observe substituent effects on the extent of the π-bonding between the aromatic π system and the vacant
phosphorus $d$ orbitals. Perhaps there is actually little similarity between these two processes and thus substituent effects of the former type may be entirely different from the latter.

7.12 $^{31}$P N.M.R. Shift Values for the Hexafluoroacetone Adducts.

The reduced apicophilicities of several ligands have been discussed in terms of extensive $\pi$-bonding between the ligands and phosphorus. The resulting increase in the electron density at phosphorus might be expected to be reflected in the $^{31}$P n.m.r. chemical shifts of these adducts. The values obtained are listed below.

<table>
<thead>
<tr>
<th>1-Substituent.</th>
<th>Geometrical Isomer.</th>
<th>$^{31}$P Value (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isopropyl</td>
<td>trans</td>
<td>-19.5</td>
</tr>
<tr>
<td>Phenoxy</td>
<td>mainly trans</td>
<td>-16.0</td>
</tr>
<tr>
<td>Dimethylamino</td>
<td>trans</td>
<td>-15.5</td>
</tr>
<tr>
<td>OCH(CF$_3$)$_2$</td>
<td>unknown</td>
<td>-15.3</td>
</tr>
<tr>
<td>Phenyl</td>
<td>cis</td>
<td>-7.7</td>
</tr>
<tr>
<td></td>
<td>trans</td>
<td>-3.4</td>
</tr>
<tr>
<td>Methyl</td>
<td>trans</td>
<td>-6.2</td>
</tr>
<tr>
<td>p-Bromophenyl</td>
<td>cis</td>
<td>-6.3</td>
</tr>
<tr>
<td></td>
<td>trans</td>
<td>-3.7</td>
</tr>
<tr>
<td>p-Methoxyphenyl</td>
<td>cis</td>
<td>-6.0</td>
</tr>
<tr>
<td></td>
<td>trans</td>
<td>-3.3</td>
</tr>
<tr>
<td>CH:CMe$_2$</td>
<td>trans</td>
<td>+0.5</td>
</tr>
</tbody>
</table>

A ready correlation between chemical shift and the suggested $\pi$-bonding ability or even the electronegativity of the substituent is
not apparent; the isopropyl and dimethylamino adducts both exhibit low values which would appear to invalidate the obvious predictions of an increase in shielding of the phosphorus on bonding to it electropositive or π-bonding ligands.

In fact the difficulty in readily interpreting these results in terms of the separate effects of ligand electronegativity and π-donation is not surprising in the light of the work of Van Vazer and Letcher. Molecular orbital calculations have indicated that any reduction of the electron density at phosphorus by inductive withdrawal stimulates π-donation to the phosphorus, in order to reduce the polarity difference between phosphorus and its ligand shell. This stabilising π-donation has been suggested to involve modification of the d-orbitals by the inductive withdrawal effect of electronegative ligands. Thus the observed decrease in the 31P n.m.r. shifts in the series X = Ph, OEt, F, for the PX₅ system is not merely the effect of increasing inductive withdrawal but rather the result of the progressive increase of both inductive withdrawal and π-donation in this series. π-Donation may be essentially absent in PPh₅, where inductive withdrawal should be low.

The actual effect of π-donation on the 31P n.m.r. shift is uncertain, due to the near-impossibility of separating this phenomenon from the electronegativity effect as indicated above, but it may result in a deshielding of the phosphorus, i.e. the opposite to naive arguments. This could be due to some electro-magnetic property of the d-orbitals involved.

Although this goes against the ideas mentioned above, it is tempting to link π-bonding from carbon ligands in the hexafluoroacetone adducts
with a shielding of the phosphorus, as the vinyl and aryl group adducts have significantly higher shifts than the isopropyl adduct. It is difficult to rationalise the high $^{31}\text{P}$ shift of the methyl adduct in these terms however, as $\pi$-donation from this group would not have been expected. Theoretical calculations$^{48}$ have indicated that such a process could be possible however.

Presumably when the processes involved in determining the $^{31}\text{P}$ shift are more clearly understood a satisfactory explanation of these values will be possible; until that time it is probably unwise to attempt any sort of detailed analysis.

7.13 $\pi$-Bonding and Hindered Rotation.

Pseudorotation processes have been widely investigated using fluorophosphoranes$^{42}$. Anomalies in the n.m.r. spectroscopic properties of these compounds have been observed when another ligand bearing a $\pi$ system or a lone pair of electrons is bonded to phosphorus. (a) Amine Ligands. The molecular orbital calculations of Hoffmann and coworkers$^{61}$ indicate that a donor ligand bonded to phosphorus and occupying an equatorial position can preferentially $\pi$-bond to the phosphorus when the ligand lone pair or $\pi$ system occupies an equatorial position (246). The difference in energy between the axial (247) and

![Diagram](246) ![Diagram](247) ![Diagram](248)
equatorial orientation (246) was calculated to be considerable, of the order of magnitude 6.5-18 kcal mol$^{-1}$. This was borne out by the experimental measurement of the barrier to rotation about the P-N bond in diaminotrifluorophosphorane (248); a value of 11 kcal mol$^{-1}$ was obtained.

The activation energies of the processes for the equilibration of the fluorines in a variety of aminofluoro phosphoranes have been found to be in the range 5-12 kcal mol$^{-1}$, which could similarly be interpreted in terms of restricted bond rotation.\textsuperscript{153,192-194}

(b) Sulphur Ligands. Schmutzler and coworkers\textsuperscript{195} have observed non-equivalence of the axial fluorines, but not of the equatorial fluorines, in a variety of alkylthio- and arylthiotetrafluorophosphoranes (249). This was interpreted in terms of a freezing out of the P-S bond rotation with the thio-substituent in the apical plane and the sulphur $p$-type lone pair in the equatorial plane, as predicted by theoretical calculations\textsuperscript{61}. Similar behaviour was noted in the trifluoro and difluoro analogues.

\begin{center}
\includegraphics[width=0.2\textwidth]{structure.png}
\end{center}

(249) $R = \text{Me, Et, Ph.}$

(c) Aromatic Systems. In view of the suggestion of an association between $\pi$-donation from a ligand into phosphorus $d$ orbitals and the magnitude of the phosphorus-ligand rotational energy barrier in the above systems, it seemed possible that the high degree of $\pi$-bonding
suggested to account for the decreased apicophilicity of the phenyl group might similarly be reflected in a high phosphorus-aryl rotational barrier. The observation of such an enhanced barrier could provide confirmation of the existence of this effect.

The unsymmetrically-substituted aryltetrafluorophosphoranes could be used in such an investigation, but such systems would have the same disadvantages as the amino and thiotetrafluorophosphoranes in that the process which is slowed first at low temperatures could be either pseudorotation or bond rotation. The substituted aryltrimethylfluorophosphoranes (250) are unambiguous in this respect, and in addition provide a ready means of determining the plane in which the aromatic system becomes 'frozen'. Axial plane freezing (251) would result in non-equivalent apical fluorines being observed, while equatorial freezing would show non-equivalent methyl groups (252). An extension of Hoffmann and coworkers' predictions\textsuperscript{61} to aryl systems would suggest an axial plane occupation of the aryl group.

\begin{align*}
&(250) \quad \begin{array}{c}
\begin{tikzpicture}
\draw[thick,dashed] (0,0) -- (0.5,0);
\draw[thick] (0,0) -- (0,0.5);
\draw[thick] (1,0) -- (1,0.5);
\draw[thick] (0,0) -- (1,0);
\draw[thick] (0,0) -- (0,1);
\draw[thick] (1,0) -- (1,1);
\draw[thick] (0,1) -- (1,0);
\fill[white] (0,0) circle (0.05);
\fill[white] (0,1) circle (0.05);
\fill[white] (1,0) circle (0.05);
\fill[white] (1,1) circle (0.05);
\fill[white] (0.5,0) circle (0.05);
\fill[white] (0.5,0.5) circle (0.05);
\fill[white] (0.25,0) circle (0.05);
\fill[white] (0.25,0.5) circle (0.05);
\fill[white] (0.75,0) circle (0.05);
\fill[white] (0.75,0.5) circle (0.05);
\fill[white] (0.5,0.75) circle (0.05);
\fill[white] (0.5,0.25) circle (0.05);
\end{tikzpicture}
\end{array} \\
&(251) \quad \begin{array}{c}
\begin{tikzpicture}
\draw[thick,dashed] (0,0) -- (0.5,0);
\draw[thick] (0,0) -- (0,0.5);
\draw[thick] (1,0) -- (1,0.5);
\draw[thick] (0,0) -- (1,0);
\draw[thick] (0,0) -- (0,1);
\draw[thick] (1,0) -- (1,1);
\draw[thick] (0,1) -- (1,0);
\fill[white] (0,0) circle (0.05);
\fill[white] (0,1) circle (0.05);
\fill[white] (1,0) circle (0.05);
\fill[white] (1,1) circle (0.05);
\fill[white] (0.5,0) circle (0.05);
\fill[white] (0.5,0.5) circle (0.05);
\fill[white] (0.25,0) circle (0.05);
\fill[white] (0.25,0.5) circle (0.05);
\fill[white] (0.75,0) circle (0.05);
\fill[white] (0.75,0.5) circle (0.05);
\fill[white] (0.5,0.75) circle (0.05);
\fill[white] (0.5,0.25) circle (0.05);
\end{tikzpicture}
\end{array} \\
&(252) \quad \begin{array}{c}
\begin{tikzpicture}
\draw[thick,dashed] (0,0) -- (0.5,0);
\draw[thick] (0,0) -- (0,0.5);
\draw[thick] (1,0) -- (1,0.5);
\draw[thick] (0,0) -- (1,0);
\draw[thick] (0,0) -- (0,1);
\draw[thick] (1,0) -- (1,1);
\draw[thick] (0,1) -- (1,0);
\fill[white] (0,0) circle (0.05);
\fill[white] (0,1) circle (0.05);
\fill[white] (1,0) circle (0.05);
\fill[white] (1,1) circle (0.05);
\fill[white] (0.5,0) circle (0.05);
\fill[white] (0.5,0.5) circle (0.05);
\fill[white] (0.25,0) circle (0.05);
\fill[white] (0.25,0.5) circle (0.05);
\fill[white] (0.75,0) circle (0.05);
\fill[white] (0.75,0.5) circle (0.05);
\fill[white] (0.5,0.75) circle (0.05);
\fill[white] (0.5,0.25) circle (0.05);
\end{tikzpicture}
\end{array}
\end{align*}

The two substituted phosphoranes (250, Ar = o-anisyl) and (250, Ar = a-naphthyl) were synthesised, together with the phenyl analogue (250, Ar = phenyl) for comparative purposes, from the appropriate aryltrimethylphosphine sulphide and antimony trifluoride\textsuperscript{196,197}. 
The phenyl and o-anisyl compounds were colourless mobile liquids, while the α-naphthyl analogue was a solid. All however were extremely sensitive to atmospheric moisture and could be handled only in a dry-box; because of this sensitivity synthesis could only be satisfactorily accomplished under reduced pressure.

At -20° these adducts exhibited $^{19}$F n.m.r. spectra consisting of a poorly defined doublet with a P-F coupling constant consistent with an axial fluorine. On cooling the resolution steadily improved to an optimum at approximately -70°. At this temperature fine structure consistent with coupling to six identical protons was observed. At -90° these spectra were unchanged apart from a slight loss of resolution consistent with freezing out of the adduct from solution. The spectra from the naphthyl and o-anisylphosphoranes were entirely analogous to that of the phenylphosphorane at this temperature. Further lowering of the temperature was rendered impossible by solubility problems.

The $^1$H n.m.r. spectra of all three adducts at room temperature consisted of a simple doublet, corresponding to P-H coupling, with no discernable P-F coupling. As the temperature was lowered fine structure appeared, consistent with coupling to two identical fluorines. At -80° these spectra were unchanged other than a slight loss of resolution. The $^1$H n.m.r. spectral data are summarised in the table.

It is unlikely that no loss of degeneracy of the pairs of groups would occur if such freezing out of rotation had taken place in view of the aryl groups chosen for study. In the naphthylphosphorane with a hypothetical axial plane restriction (253) the fluorine
**1H N.M.R. Data for the Aryldimethyldifluorophosphoranes.**

<table>
<thead>
<tr>
<th>Aryl Group</th>
<th>Solvent</th>
<th>Conc. $V_a/V_s$</th>
<th>Temp.</th>
<th>$\tau$</th>
<th>$J_{PH}$</th>
<th>$J_{FH}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl</td>
<td>CH$_2$Cl$_2$</td>
<td>0.1</td>
<td>+35°</td>
<td>8.2</td>
<td>18 Hz</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>CFCl$_3$</td>
<td>0.5</td>
<td>-60°</td>
<td>8.15</td>
<td>18.5 Hz</td>
<td>11.5 Hz</td>
</tr>
<tr>
<td>o-Anisyl</td>
<td>CH$_2$Cl$_2$</td>
<td>0.1</td>
<td>+35°</td>
<td>8.03</td>
<td>17.5 Hz</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>CFCl$_3$</td>
<td>0.5</td>
<td>-60°</td>
<td>8.0</td>
<td>18 Hz</td>
<td>12.5 Hz</td>
</tr>
<tr>
<td>t-Naphthyl</td>
<td>CFCl$_3$</td>
<td>0.1</td>
<td>+35°</td>
<td>7.88</td>
<td>21 Hz</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Toluene</td>
<td>0.5</td>
<td>-60°</td>
<td>7.92</td>
<td>21 Hz</td>
<td>12.5 Hz</td>
</tr>
</tbody>
</table>

Nearest to the aromatic system would be expected to be deshielded by ring current effects, and therefore distinct fluorine environments would be expected to show in the $^1$H n.m.r. spectrum, and possibly the effects of this non-equivalence of the fluorines in the $^1$H n.m.r. spectrum fine structure. Equatorial freezing (254) should similarly affect the methyl groups.

These results need not invalidate the suggestion of extensive $\pi$-bonding from aryl systems; to expect to slow rotation to the required extent for n.m.r. observation at temperatures in the range -80° to -90° requires the rotation process to have an activation energy.
of approximately 9 kcal mol$^{-1}$. A value of 7-8 kcal mol$^{-1}$ could still be consistent with extensive $\pi$-bonding but would be outside the scope of measurement under the conditions of this experiment. In addition, although axial plane freezing of the aryl group should maximise the stabilising (p-d)$\pi$ bonding, it may also maximise the destabilising non-bonded repulsions between the aryl group and the other substituents. Thus these steric factors may partially mask any enhancement in the rotational barrier due to $\pi$-bonding.

In retrospect, the likelihood of observation of the restriction of rotation of the P-aryl bond may have been higher in the aryltetrafluorophosphoranes. The extent of $\pi$-bonding between ligands and the phosphorus d-orbitals has been suggested to be increased by the reduction in the diffuse nature of the phosphorus d-orbitals on bonding very electronegative ligands to phosphorus. On bonding two additional fluorines to phosphorus in the aryltetrafluorophosphoranes the extent of the $\pi$-bonding could possibly be increased to the required magnitude for the observation of restricted rotation at accessible temperatures. 

Intramolecular Fluorine Exchange in Fluorophosphoranes.

The $^{19}$F n.m.r. spectra of the difluorophosphoranes investigated showed both a temperature and concentration dependence. At high concentrations (1:1, v/v) a single, very broad absorption (10 p.p.m. wide) was observed at temperatures down to $+10^\circ$. Lowering the temperature at this fixed concentration, or lowering the concentration at this temperature, resulted in the change to two absorptions, corresponding to phosphorus coupling to two identical fluorines. Lowering the temperature still further gave the fine structure previously mentioned, while raising the temperature sharpened the above broad absorption.
considerably; at 90° the signal from the solution discussed above was 2 p.p.m. wide. These processes were unchanged in the presence of the HF scavenger sodium fluoride.

The reasons for these changes in a discrete fluorophosphorane are not immediately obvious, although similar spectral results have been linked with 'exchange processes' without further elaboration on their exact nature.

A possible explanation of these phenomena is suggested by the work of Cowley and coworkers. By a computer study of related changes in the 1H n.m.r. spectra of trifluorodimethyl- and difluorotrimethyl-phosphoranes they found that the process involved had a 'molecularity' of approximately two. A fluorine-bridged dimeric species (255) was suggested as the intermediate by which exchange occurred in the difluorophosphorane. Neither the mode of formation of such a structure from the difluorophosphorane nor its mode of decomposition was mentioned.

![Diagram](255)

Presumably a similar process is responsible for the fluorine exchange in the aryltrimethyldifluorophosphoranes (250).

In the aryltrimethyldifluorophosphoranes H-F coupling is lost
before P-F coupling as the temperature is raised from -80°. This would be expected on the basis of the much larger P-F coupling, as the activation energy derived from the observation of a coalescence of two n.m.r. signals is dependent on both the $T^C$ and the frequency separation $\Delta \nu$ between the two signals. Thus for any given coalescence the larger the $\Delta \nu$ the higher the temperature that will be needed to observe coalescence.
8. SUBSTITUTION AT PHOSPHORUS IN OXYPHOSPHORANES.

8.1 Base-Catalysed Substitution.

A number of examples of displacement reactions involving pentacoordinate oxyphosphoranes have been reported. These normally involve the reaction of alcohols with oxyphosphoranes to displace alkoxy groups as their alcohols. The reactions of diethoxyphosphoranes with ethylene glycol\textsuperscript{131} and pentaphenoxyphosphorane with catechol\textsuperscript{121} have previously been mentioned. In addition, Ramirez and coworkers\textsuperscript{186} have shown that alkoxy groups of the biacetyl adducts of phosphites can be replaced by those of alcohols.

Reactions of this type have recently been suggested to be base-catalysed\textsuperscript{186}; the reaction of methanol with the 1,2-oxaphosphetan adduct (256) has been interpreted as a nucleophilic displacement of the hexafluoroisoproxy group by the methoxide ion via the hexacoordinate species (257). Exchange of the methoxy groups occurred simultaneously with the replacement reaction.

![Chemical diagram]

R = CH(CF\textsubscript{3})\textsubscript{2}
Such a mechanism should involve inversion of configuration at phosphorus, although none of the adducts mentioned above is suitable to demonstrate this stereochemical change. The geometrical isomerism in the adducts of the pentamethylphosphetan system can however be used in such an investigation.

8.2 Displacement Reactions in 1,3,2-Dioxaphospholan Adducts.

In an attempt to observe the predicted increase in the apicophilicity of the dimethylamino group on protonation, a sample of the single isomer (trans) of the dimethylaminophosphetan adduct (258) was dissolved in the acidic hexafluoroisopropanol. However immediate and complete replacement of the amino group occurred to give the hexafluoroisopropoxyphosphetan adduct (259), as a single geometrical isomer.

Two possible mechanisms for such a replacement can readily be envisaged, either (a) a dissociative mechanism via a phosphonium system, or (b) a nucleophilic substitution reaction.

(a) Dissociation. Protonation of the amino group of the adduct (258) could be envisaged as preceding loss of this group as dimethylamine to give the alkoxyphosphonium salt (260). Combination of the ions would give the adduct (259).
It can be shown that the recombination procedure can give either isomer of the adduct (259). The production of a single isomer as in this example would require the recombination steps leading to each isomer to have different activation energies. However a consideration of the ring strain increases involved in the formation of a bicyclic phosphonium system such as (260), and the possible difficulties encountered in the development of a positive charge in the presence of two very electronegative substituents, could indicate that such a dissociative mechanism is improbable.

(b) Nucleophilic Substitution. Protonation of the amino group may be followed by the displacement of this group by the alkoxide ion. The substitution mechanism suggested by Ramirez and coworkers\(^{188}\) implies that inversion of configuration at phosphorus should take place, and thus a cis geometry for the product (259a) would be expected from this reaction.
Strong support for a nucleophilic substitution by such a mechanism would be provided by a demonstration of inversion stereochemistry for the replacement reaction. However, the most obvious method of investigation where the adduct (259) of known stereochemical composition is independently synthesised, was not possible in this system.

The phosphinite (236) can be synthesised as a mixture of isomers by the decomposition of the secondary phosphetan hexafluoroacetone adduct and its isomeric composition measured by comparison of the n.m.r. spectrum of its phosphinate with that of the separately prepared cis isomer (229) of the phosphinate. The reaction of the phosphinite with hexafluoroacetone gave the adduct (259) but examination of its $^1$H n.m.r. spectrum showed that the product contained at least 80% of one isomer, whereas the phosphinite isomer ratio was approximately 4:3. This anomaly could be explained by a consideration of the nature of the intermediate 1:1 adduct. Formation of the 2:1 adduct by nucleophilic attack by the carbanion of (261) on the carbonyl carbon is probably unlikely to be rapid enough to compete with proton transfer between the hexafluoro-isopropoxy groups of (261). On this basis the observed loss of
stereochemical identity of the phosphinite and its adduct could be expected.

\[
\begin{align*}
\text{P} & \quad (\text{CF}_3)_2\text{CO} \\
\text{OCH(CF}_3)_2 & \quad + \quad \text{P} \quad - \quad \text{OC(CF}_3)_2 \\
\text{OCH(CF}_3)_2 & \quad \rightarrow \quad \text{OCH(CF}_3)_2
\end{align*}
\]

(261)

Attempted displacement reactions with methanol and thiophenol under both acidic and basic conditions were unsuccessful. At ambient temperatures under these conditions the dimethylaminophosphetan adduct (258) was perfectly stable, while at 60° slow decomposition could be observed by $^1\text{H}$ and $^{19}\text{F}$ n.m.r. spectroscopy to give complex mixtures of products without the production of the adducts. The adducts (220) and (259) were unaffected by hexafluoroisopropanol under both acidic and basic conditions.

8.3 Displacement Reactions in 1,2-Oxaphosphetans.

Treatment of a chloroform solution of the 1,2-oxaphosphetan (184) with a one molar excess of hexafluoroisopropanol gave a steady conversion of this adduct to another with a decreased P-H coupling constant for the P-CH methine proton (8 Hz). An equilibrium mixture of isomers was achieved within 18 hours, with the 'new' isomer predominating in the ratio 10:1.

Thermolysis of the mixture of adducts gave a mixture of the phosphinates (229) and (262), in which the trans isomer (262) predominated.
The 'new' adduct could therefore be assigned a trans geometrical relationship between the hexafluoroisopropoxy group and the phosphetan methyl group (263).

Ramirez and coworkers\textsuperscript{186} have observed nucleophilic substitution in 1,2-oxaphosphetan adducts under basic conditions. Under acidic conditions, such as in the presence of hexafluoroisopropanol, a different reaction\textsuperscript{60} took place whereby interconversion of the diastereoisomeric adducts (264) and (265) occurred via an opening of the oxaphosphetan ring.
However, the equivalent inversion at phosphorus in the phosphetan-oxyphosphetan adduct (266) may not occur due to the effect of the small ring on the stereochemical course of the intermediate nucleophilic substitution in the phosphonium system (267). Unlike their acyclic analogues the alkaline hydrolysis of monoalkoxyphosphetanium salts proceeds\textsuperscript{166} with retention of configuration. If the alkoxy group exchange proceeds in a similar manner then the stereochemistry at the phosphorus in relation to the phosphetan ring substituent would be unaffected by this reaction. The stereochemistry at the oxyphosphetan ring 3-position could however be reversed by the ring closure reaction, as shown below.

As the thermolysis product stereochemistry implies that inversion at the phosphetan phosphorus actually occurs to give (268), this could indicate that the mechanism of isomerism actually involves a nucleophilic
substitution via the hexacoordinate species (269) rather than such a ring opening mechanism.

\[
\begin{align*}
\text{(266)} & \quad R = (\text{CF}_3)_2\text{CH} \\
\text{(269)} & \quad \text{Ph} \\
\text{(268)} & \quad \text{Ph}
\end{align*}
\]

In fact ring strain considerations would suggest that the ring opening reaction may be slow in the adduct (266). Ramirez has found that the isomeric oxaphosphetan adducts (270) and (271) are not interconverted in the presence of hexafluoroisopropanol unlike (264) and (265). The reluctance of these adducts to undergo ring opening was attributed to the increased stability of the pentacoordinate structure due to the additional electronegative substituent. In this respect the phosphetan ring should have the similar effect of decreasing the facility of ring opening by enhancing the stability of the pentacoordinate form and destabilising the ring-open phosphonium system (267).

The exact nature of the stereochemical changes occurring at the
1,2-oxaphosphetan ring 3-position are not clear, however the downfield shift of the $^1$H n.m.r. signal from the OCH(CF$_3$)$_2$ proton of 0.73 p.p.m. could infer that the phenyl substituent on the oxaphosphetan 3-position may be moving from a trans geometry to the OCH(CF$_3$)$_2$ to the cis arrangement during the substitution. In the cis geometry of the phenyl and OCH(CF$_3$)$_2$ groups deshielding of the OCH(CF$_3$)$_2$ proton by the aromatic system should occur, which should be essentially absent in the trans arrangement of these groups. Thus the original isomer may have the trans configuration at the oxaphosphetan ring 3-position as shown in (266), rather than the cis configuration (268).

As this stereochemical change at the oxaphosphetan ring 3-position would be expected from a substitution reaction at phosphorus via (269), this could also be interpreted as evidence in favour of such a mechanism.
EXPERIMENTAL

Instrumentation.

I.r. spectra were recorded on a Perkin-Elmer 237 grating spectrometer for samples in Nujol except as otherwise noted. Mass spectra were determined with an A.E.I. MS9 instrument; in each case the molecular ion is given first followed by peaks of structural significance. Routine $^1$H n.m.r. spectra were recorded with a Varian T-60 spectrometer with tetramethylsilane as internal standard. Variable temperature $^1$H n.m.r. spectra were recorded with a Varian A-60 spectrometer. Variable temperature $^{19}$F n.m.r. spectra were recorded with a Varian D.A.-60 spectrometer, as were $^{31}$P n.m.r. spectra.

General.

Evaporation was performed with a rotary evaporator, and solutions in organic solvents were dried over magnesium sulphate. All reactions involving air sensitive reactants or products were carried out under an atmosphere of dry, oxygen free, nitrogen. The butyl-lithium used was a solution in pentane supplied by the Aldrich Chemical Company. Light petroleum had b.p. 40-60°.

Solvents were dried as follows. Tetrahydrofuran was refluxed over calcium hydride and distilled onto sodium wire; when required a portion was refluxed over, and distilled from, lithium aluminium hydride. Diethyl ether when required very dry was purified in a similar manner; otherwise it was dried over sodium as was petroleum spirit. Methanol and ethanol were refluxed over their magnesium alkoxides and distilled. Acetonitrile, benzene, dichloromethane and toluene were distilled from calcium hydride.
Preparation of 2,2,3,3-Tetramethyl-1-phenylphosphetan 1-Oxide.

High yields of this phosphetan oxide were obtained by the method of J.R. Shutt, m.p. and mixed m.p. 82-83°.

Preparation of 2,2,trans-3,4,4-Pentamethyl-r-phenylphosphetan 1-Oxide.

This was prepared by the method of Hawes, m.p. and mixed m.p. 126-127°.

Preparation of 2,2,cis-3,4,4-Pentamethyl-r-1-phenylphosphetan 1-Oxide.

This was prepared by the method of Corfield, m.p. and mixed m.p. 117-118°.

Preparation of 1-p-Methoxyphenyl-2,2,3,4,4-pentamethylphosphetan 1-Oxide.

2,4,4-Trimethylpent-2-ene (4.5 g) in dichloromethane (50 ml) was added dropwise to a stirred solution of p-methoxyphenylphosphonous dichloride (8.4 g) and aluminium chloride (5.2 g) in dichloromethane (100 ml), the temperature being maintained below 10°. After stirring for 1 hour the solution was added slowly to an ice-water slurry (1 kg). The organic layer was washed with water, aqueous sodium hydroxide (N/2, 2 x 100 ml), and water, dried, and evaporated. The residue was chromatographed on basic alumina (100 g). Elution with ether-light petroleum (1:1) yielded the (presumed trans-) p-methoxyphenyl phosphetan oxide (1.1 g, 10%) m.p. 151-153° (from light petroleum) \( \nu_{\text{max}} \) 1600, 1503, 1292, 1261, 1190, 1153, 1102, 829, and 803 cm\(^{-1}\), m/e 266, 251, 224, 196, 158, 134, and 107, \( \tau \) 1.90-3.00 (4H, m), 6.17 (3H, s), 8.62 (6H, d, J = 16 Hz),
8.00 (6H, d, J = 24 Hz), and 9.00 (3H, d, J = 7 Hz); the ring 3-H signal could not be identified (Found: C, 67.5; H, 2.7; P, 11.6. C₁₅H₂₃O₂P requires C, 67.65; H, 8.65; P, 11.65%). Elution with ether-methanol (100:1) yields the (presumed cis-) p-methoxyphenyl phosphetan oxide (1.6g, 15%). m.p. 113-115° (from light petroleum), vmax. and m/o as for the other isomer, τ 1.93-3.07 (4H, m), 6.17 (3H, s), 7.73 (1H, q, J = 7 Hz), 8.65 (6H, d, J = 16 Hz), 8.62 (6H, d, J = 19 Hz), and 9.00 (3H, d, J = 7 Hz) (Found: C, 67.9; H, 8.65; P, 11.6. C₁₅H₂₃O₂P requires C, 67.65; H, 8.65; P, 11.65%).

Preparation of Phosphetan Oxides from Grignard Reagents and r-1-Chloro-2,2,trans-3,4,4-pentamethylphosphetan 1-Oxide.

1). r-1-Benzyl-2,2,trans-3,4,4-pentamethylphosphetan 1-Oxide.

This was prepared by the method of J.R. Corfield, m.p. and mixed m.p. 180-182°.

2). r-1,2,2,trans-3,4,4-Hexamethylphosphetan 1-Oxide.

This was prepared by the method of J.R. Corfield, m.p. and mixed m.p. 169-171°.

r-1-Isopropyl-2,2,trans-3,4,4-pentamethylphosphetan 1-Oxide.

Isopropyl magnesium bromide (0.11mol) in ether (75ml) was added dropwise to a stirred solution of r-1-chloro-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide (19.4g 0.1mol) in ether (100ml). The mixture was refluxed for 18 hours and then cooled in ice while aqueous hydrochloric acid (H/10, 50ml) was cautiously added. The ether was
removed by rotary-evaporation and the precipitate taken up in dichloromethane (100ml). The organic layer was washed with aqueous sodium hydroxide solution (1 M, 2 x 50ml) and saturated sodium chloride solution, and then dried and the solvent removed to yield r-1-isopropyl-2,2-trans-3,4,4-pentamethylphosphetan 1-oxide (18g, 90%), m.p. 136-138° (from cyclohexane), $\nu_{\text{max}}$. 1232, 1179, 1145, 1030, 982, 878, and 691 cm$^{-1}$, m/e 202, 167, 160, 145, 132, and 90, $\tau$ 7.80 (1H, dq, $J$ 7, $J_{\text{PH}}$ 1.5 Hz), 8.72 (6H, dd, $J_{\text{PH}}$ 14 Hz), 8.74 (6H, d, $J_{\text{PH}}$ 15 Hz), 8.76 (6H, d, $J_{\text{PH}}$ 17 Hz), and 9.12 (3H, dd, $J$ 7, $J_{\text{PH}}$ 17 Hz), the isopropyl (CH$_3$) CH signal could not be identified (Found: C, 65.1; H, 11.3; P, 15.0. C$_{12}$H$_{23}$OP requires C, 65.35; H, 11.4; P, 15.35%).

r-1-(p-Bromophenyl)-2,2,trans-3,4,4-Pentamethylphosphetan 1-Oxide.

This was prepared as for r-1-isopropyl-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide; the crude product was chromatographed on basic alumina, and elution with ether-petrol (1:1) yielded r-1-(p-bromophenyl)-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide (66%), m.p. 172-174° (from light petroleum), $\nu_{\text{max}}$. 1576, 1232, 1185, 1070, 1008, 820, and 735 cm$^{-1}$, m/e (quoted for $^{79}\text{Br}$) 3.4, 299, 246, 244, 236, 221, 203, and 196, $\tau$ 1.83-2.50 (4H, m), 7.93 (1H, dq, $J$ 7, $J_{\text{PH}}$ 1.5 Hz), 8.58 (6H, d, $J_{\text{PH}}$ 17 Hz), 8.83 (6H, d, $J_{\text{PH}}$ 20 Hz), and 8.97 (3H, dd, $J$ 7, $J_{\text{PH}}$ 1.5 Hz) (Found: C, 67.35; H, 6.2; P, 9.65. C$_{14}$H$_{20}$BrOP requires C, 67.15; H, 6.35; P, 9.85%).

Reaction of Methylallyl Magnesium Chloride with r-1-Chloro-2,2,trans-3,4,4-Pentamethylphosphetan 1-Oxide.

1). Preparation of the Grignard Reagent.

2-Methylallyl chloride (20g) in ether (250ml) was added dropwise
to a stirred mixture of magnesium (20g) and ether (50ml) over 6
hours at -10° to -15°. The reaction was stirred at room temperature
for 2 hours and then the solids were filtered off to leave the
Grignard reagent (36% by acidimetric titration).

2). Reaction with the Acid chloride.

The Grignard solution (0.07mol) was added dropwise to a stirred
solution of r-1-chloro-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide
(9.7g, 0.05mol) in ether (50ml). The mixture was refluxed for 18 hours
and then cooled in ice while aqueous hydrochloric acid (N/10, 50ml)
was cautiously added. The ether was removed by rotary evaporation
and the precipitated oil taken up in dichloromethane (100ml). The
organic layer was washed with aqueous hydroxide solution (N/10,
2 x 50ml) and saturated sodium chloride solution, and then dried and
the solvent removed by rotary evaporation. Crystallisation of the crude
product from ether-petrol yielded 2,2,trans-3,4,4-pentamethyl-r-1-
(2'-Methylallyl)-phosphetan 1-Oxide (0.8g, 8%), m.p. 127-128°,
(sublimation), v_max. 1639, 1236, 1161, 1160, 1139, 899, and 671cm⁻¹,
(m/e 214, 199, 194, 172, 152, 144, 122, and 06, τ 4.90 (2H, br, s),
7.35 (2H, d, J_PH 11 Hz), 8.02 (3H, br, s), 8.40 (1H, dq, J 7,
J_PH 1.5 Hz), 9.81 (12H, d, J_PH 17 Hz), and 9.14 (3H; dd, J 7,
J_PH 1.5 Hz) (Found: C, 67.2; H, 10.9; P, 14.7. C_{12}H_{23}OP requires
C, 67.3; H, 10.75; P, 14.5%). Recrystallisation of the crude oxide
(from dichloromethane-light petroleum) yielded a new dimeric-phosrhine
oxide, m.p. 167-169°, v_max. 1642, 1230, 1191, 1155, 1136, 891, 821, 688
and 650cm⁻¹, m/e 429, 413, 356, 316, 269, 255, 215, 214, 199, and 159,
\( \tau \, 4.45 \, (0.5H, \text{br. s}), \, 4.90 \, (0.5H, \text{br. s}), \, 7.17 \, (2H, d, J_{PH} \, 10 \, Hz), \)
\( 7.47 \, (3H, s), \, 8.10 \, (2H, d, J_{PH} \, 9 \, Hz), \, 8.42-9.00 \, (24H, m), \, \text{and} \, 9.11 \)
\( (6H, dq, J_7, J_{PH} \, 1 \, Hz); \, \text{The ring} \, 3-H \, \text{signal could not be identified,} \)
\( (\text{Found:} \, C, \, 67.1; \, H, \, 10.8; \, P, \, 14.5). \, \text{Evaporation of the filtrate from the methylallyl} \)
\( \text{phosphine oxide isolation, and chromatography of the residue on basic} \)
\( \text{alumina, (100g) yielded, on elution with ether-light petroleum (1:1),} \)
\( 2,2,\text{trans-3,4,4-pentamethyl-r-1-(2'-methylprop-1'-enyl)phosphetan 1-oxide} \)
\( (2.0g, \, 20\%), \, \text{m.p.} \, 110-112^\circ \, (\text{from light petroleum}), \nu_{\text{max}}. \, 1633, \, 1228, \, 1179, \)
\( 1148, \, 1010, \, 843, \, \text{and} \, 642 \, \text{cm}^{-1}, \, m/e \, 214, \, 169, \, 184, \, 172, \, 144, \, \text{and} \, 129, \)
\( \tau \, 4.47 \, (1H, d, J_{PH} \, 26 \, Hz), \, 7.92 \, (3H, d, J_{PH} \, 12 \, Hz), \, 7.94 \, (3H, d, J_{PH} \, 10 \, Hz), \, 8.47 \, (1H, dq, J_8, J_{PH} \, 18 \, Hz), \, \text{and} \, 9.13 \, (3H, d, J_8 \, Hz) \)
\( (\text{Found:} \, C, \, 67.5; \, H, \, 10.9; \, P, \, 15.05). \, \text{Elution with ether-methanol (100:1) yielded} \)
\( \text{the same (dimeric) phosphine oxide as recrystallisation of the methylallyl phosphine oxide (2.5g, 25%), m.p.} \)
\( \text{and mixed m.p.} \, 168-170^\circ. \)

\text{2,2,trans-3,4,4-Pentamethyl-r-1-t-butylphosphetan 1-Oxide.}

\text{t-Butyl-lithium (2.26N, 10ml) was added dropwise to a stirred} \)
\text{solution of r-1-chloro-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide} \)
\( (4.4g) \, \text{in ether (100ml).} \, \text{The mixture was refluxed for 24 hours and} \)
\text{then cooled while hydrochloric acid (2N, 25ml) was added dropwise.} \)
\text{The ether was removed by rotary-evaporation and the precipitate} \)
\text{taken up in dichloromethane (50ml).} \, \text{The organic layer was washed} \)
\text{with aqueous sodium hydroxide (N/10, 50ml), dried and evaporated to} \)
\text{yield 2,2,trans-3,4,4-pentamethyl-r-1-t-butylphosphetan 1-oxide}
(3.6 g, 76%), m.p. 150-151° (from light petroleum), ν_max. 1230, 1177, 1149, 1053, 1010, 810, 671, and 644 cm⁻¹, m/e 216, 201, 174, 160, 146, 145, and 104, δ (CDCl₃) δ 7.00-8.33 (1H, m), 8.67 (6H, d, 13.5 Hz), and 9.13 (3H, dd, 1.5 Hz). (Found: C, 66.85; H, 11.5; P, 14.15. C₁₂H₂₅OP requires C, 66.65; H, 11.55; P, 14.35%).

**Preparation of Phosphetans.**

1). By reduction of the Phosphetan 1-oxides.

**Reduction of 2,2,3,3-Tetramethyl-1-phenylphosphetan 1-Oxide with Polymethylhydrogensiloxane.**

A mixture of the phosphetan 1-oxide (22 g) and polymethylhydrogensiloxane (22 ml) was slowly heated to 120°, at which temperature the mixture became a polymeric mass. The temperature was held at 120° for 2 hours and then the phosphine was distilled out of the glass under reduced pressure (16.0 g, 80%), b.p. 90-92°/0.5 mm.

**Reduction of 2,2,trans-3,4,5-Pentamethyl-1-(2-Methylprop-1-enyl)phosphetan with Phenylsilane.**

Phenylsilane (0.55 g) was added in 3 portions to the phosphetan 1-oxide (1.00 g) at room temperature. The temperature was raised to 100° over 2 hours and then the phosphine was distilled out of the mixture under reduced pressure to yield the phosphine, (0.85 g, 85%), b.p. 76-78°/2 mm, ν_max. (film) 1616, 1465, 1370, 1150, 1057, 980, 979,
and 763 cm$^{-1}$, $\tau$ (benzene) 3.00 (1H, m), 7.40 (1H, $q$, $J$ 8 Hz), 8.00 (3H, s), 8.13 (3H, s), 8.73 (6H, $d$, $J_{PH}$ 19 Hz), 9.00 (6H, $d$, $J_{PH}$ 6 Hz), and 9.27 (3H, $d$, $J$ 7 Hz), $^{31}$P (benzene) -32.5 p.p.m.

Reduction of 2,2,trans-3,4,4-Pentamethyl-r-1-(2'-methylallyl)-phosphetan with Phenylsilane.

Phenylsilane (0.33g) was added in 3 portions to the phosphetan 1-oxide (0.65g) at room temperature. The temperature was raised to 100° over 2 hours and then the phosphine was distilled out of the reaction mixture under reduced pressure to yield the phosphine (0.30g, 50%), b.p. 64-65°/1.8mm, $\tau$ (neat) 5.10-5.40 (2H, br. s), 7.43 (1H, $q$, $J$ 7 Hz), 7.42-7.65 (2H, br. s), 8.23 (3H, s), 8.08 (6H, $d$, $J_{PH}$ 18 Hz), 9.07 (6H, $d$, $J_{PH}$ 6 Hz), and 9.33 (3H, $d$, $J$ 7 Hz).

Reduction of 2,2,trans-3,4,4-Pentamethyl-r-1-t-butyolphosphetan 1-oxide with Phenylsilane.

Phenylsilane (1.5g) was added in 3 portions to the phosphetan 1-oxide (2.0g) at room temperature. The temperature was raised to 100° over 2 hours and the phosphine was distilled out of the mixture under reduced pressure to yield the phosphetan as a mixture of isomers (1.8g, 97%), b.p. 84-86°/1.0mm, $\nu_{max}$. (film) 1365, 1260, 1173, 1122, 1050, and 833 cm$^{-1}$, $\tau$ (benzene) for the major isomer, 7.43 ($q$, $J$ 7 Hz); for the minor isomer, 7.92 ($dq$, $J$ 6.5, $J_{PH}$ 1.5 Hz), ratio of isomers 3:2.
Reduction of \( r-1-(p\text{-Bromophenyl})-2,2,\text{trans-}3,4,4\text{-pentamethylphosphetan} \) with Phenylsilane.

Phenylsilane (0.45g) was added to the phosphetan 1-oxide (1.25g) in 3 portions at room temperature. The temperature was raised to 100° over 2 hours and the phosphine was distilled out of the mixture under reduced pressure to yield the phosphetan as a mixture of isomers (1.16g, 98%), b.p. 117-118°/0.25mm, \( v_{\text{max}} \) (film) 1566, 1476, 1382, 1369, 1063, 1010, 810, and 773 cm\(^{-1}\), \( \tau \) (benzene) for the major isomer 7.23 (q, \( J = 7 \) Hz); for the minor isomer, 7.68 (dq, \( J = 7, J_{\text{PH}} = 3 \) Hz), ratio of isomers, 3:2.

Reduction of \( r-1-(p\text{-Methoxyphenyl})-2,2,\text{cis-}3,4,4\text{-pentamethylphosphetan} \) with Phenylsilane.

Phenylsilane (0.3g) was added to the phosphetan 1-oxide (0.7g) in 3 portions at room temperature. The temperature was raised to 100° over 2 hours and the phosphine was distilled out of the mixture under reduced pressure to yield the phosphetan as a mixture of isomers (0.4g, 62%), b.p. 117-119°/0.5mm, \( v_{\text{max}} \) (film) 1596, 1482, 1369, 1276, 1246, 1176, 1031, 833, and 822 cm\(^{-1}\), \( \tau \) for the minor isomer, 7.12 (q, \( J = 7 \) Hz); for the major isomer 7.47 (dq, \( J = 7, J_{\text{PH}} = 3 \) Hz), ratio of isomers, 3:4.

Reduction of \( r-1-(\text{Chloro})-2,2,\text{trans-}3,4,4\text{-pentamethylphosphetan 1-Oxide} \) with Phenylsilane; Preparation of 2,2,3,4,4-Pentamethylphosphetan.

Phenylsilane (3.7g) was added in 4 portions to the phosphetan 1-oxide (0.5g) with ice cooling. After 10 minutes the temperature was slowly raised to 100° over 3 hours, after which time gas evolution
had ceased. Distillation of the reaction mixture under reduced pressure yielded 2,2,3,4,4-pentamethylphosphetan (3.7g, 77%), b.p. 80-90°/110mm. Redistillation of the phosphetan using a Buchi 60cm spinning-band column yielded the pure phosphetan, b.p. 89°/80mm, \( \nu_{\text{max}} \) (film) 2260, 1367, 1202, 1055, 917, 887, and 796 cm\(^{-1}\), \( \tau \) (neat) 6.26 (1H, \( \Delta_{\text{PH}} 170 \text{ Hz} \)), 7.33 (1H, q, \( \Delta 7 \text{ Hz} \)), 8.66 (6H, d, \( \Delta_{\text{PH}} 13 \text{ Hz} \)), and 9.17 (3H, d, \( \Delta 7 \text{ Hz} \)), apparently as a single isomer, \( ^{31}\text{P} \) (neat) -23p.p.m.

**Reduction of \( \text{r-1-Chloro-2,2,trans-3,4,4-pentamethylphosphetan 1-Oxide} \) with Polymethylhydrogensiloxane:**

**Preparation of 1-Chloro-2,2,3,4-pentamethylphosphetan.**

A mixture of the phosphetan 1-oxide (50g) and polymethylhydrogensiloxane (40ml) was slowly heated with stirring to 120°. The temperature was held at 120° while an acid gas was evolved. After 30 minutes the mixture set into a jelly and then the temperature was raised to 180° over 4 hours. The volatile products were distilled out under reduced pressure (24g), b.p. 68-140°/3mm, shown by the n.m.r. spectrum to be a mixture of the secondary phosphetan and the chlorophosphetan, the ratio of which could be estimated by the signal intensities of the ring-methyl groups. This varied between 1:1 and 100% chlorophosphetan on repeated preparations. A solution of chlorine in 1,2-dichloroethane (1 mole of chlorine per mole of secondary phosphetan) was added to a stirred solution of the mixture of phosphines (24g, 1:1 ratio) in dichloromethane (100ml) at -20° over 15 minutes. The mixture was held at -20° for 30 minutes and then allowed to warm to room temperature. Removal of the solvent and
distillation of the residue under reduced pressure yielded
1-chloro-2,2,3,4,4-pentamethylphosphetan (20g, 45%), b.p. 64-68°/7mm,
\[ \tau \, 7.70 \, (1H, q, J = 3 \text{ Hz}), 8.75 \, (6H, d, J_{pH} = 20 \text{ Hz}), 8.77 \, (6H, d, J_{pH} = 8 \text{ Hz}), \text{ and } 9.23 \, (3H, d, J = 8 \text{ Hz}) \] for the major isomer; the minor isomer showed its presence through shoulders on the low-field parts of the

doublets at \[ \tau \, 8.75 \text{ and } 8.77 \], ratio of isomers, 3:1.

**Preparation of r-1-(Dimethylamino)-2,2,trans-3,4,4-pentamethylphosphetan.**

Dimethylamine (5.4g, 0.12mol) was added dropwise to a stirred
solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan (5.3g, 0.03mol)
in pentane (50ml) at -20° over 5 minutes. After stirring for 24 hours
at room temperature the precipitate was filtered off, the solvent
removed, and the residue distilled under reduced pressure to yield
r-1-(dimethylamino)-2,2,trans-3,4,4-pentamethylphosphetan (3.3g, 66%),
b.p. 71-73°/6mm, \[ \nu_{\text{max}} \, (\text{film}) \, 1660, 1362, 1268, 1172, 1100, 1052, 975, 923, \text{ and } 675 \, \text{cm}^{-1}, \tau \, (\text{benzene}) \, 7.32 \, (6H, d, J_{pH} = 8.5 \text{ Hz}), 8.30-8.60 \]
(1H, m), 8.74 (6H, d, 5 Hz), 8.80 (6H, d, J_{pH} = 20 Hz) and 9.22 (3H, dd,
\[ J = 8, J_{pH} = 1 \text{ Hz} \]), \[ \delta^{1}P \, (\text{neat}) \, -106 \text{p.p.m.} \]

**Oxidation of r-1-(Dimethylamino)-2,2,trans-3,4,4-pentamethylphosphetan.**

Hydrogen peroxide solution (20vol, 20ml) was added dropwise to a
stirred solution of the phosphetan (0.2g) in dichloromethane (40ml).
After 30 minutes the organic layer was dried and evaporated to yield
the crude phosphetan oxide. Distillation under reduced pressure
yielded (the hygroscopic) r-1-(dimethylamino)-2,2,trans-3,4,4-penta-
methylphosphetan 1-oxide (0.1g, 48%), b.p. 90-95°/1.5mm, m.p. 40-50°,
Preparation of \( r-1-(\text{dimethylamino})-2,2,\text{trans}-3,4,4\)-pentamethylphosphetan 1-oxide.

A solution of dimethylamine (4.0g) in hexane (20ml) was added dropwise to a stirred solution of \( r-1\)-chloro-2,2,\text{trans}-3,4,4-pentamethylphosphetan 1-oxide (7.0g) in hexane (25ml) at -20° over 5 minutes. After stirring at this temperature for 24 hours the mixture was filtered and the solvent removed under reduced pressure. The residue was taken up in dichloromethane (40ml) and the required phosphetan oxide extracted with hydrochloric acid (\( \text{H/20, 3 x 25ml} \)). The combined acid extracts were rapidly made basic with aqueous sodium hydroxide and the phosphetan oxide extracted with dichloromethane (3 x 50ml). The combined organic extracts were dried and evaporated, and the residue distilled to yield \( r-1-(\text{dimethylamino})-2,2,\text{trans}-3,4,4\)-pentamethylphosphetan 1-oxide (1.0g, 12%), m.p. 42-47°, b.p. 85-90/1.0mm, n.m.r. and i.r. spectra identical to those of the product from the oxidisation of the dimethylamino-phosphine.

Preparation of \( 2,2,3,4,4\)-Pentamethyl-1-pyrrolidylphosphetan.

Pyrrolidene (2.1g, 0.03mol) in pentane (10ml) was added dropwise to a stirred solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan
(1.8 g, 0.01 mol) in pentane (25 ml) at 0°. After stirring for 24 hours the precipitate was filtered off and the solvent removed under reduced pressure to yield the crude phosphine (2.0 g, 94%), \( \nu_{\text{max}} \) (film) 1469, 1365, 1260, 1115, 1054, 1003, and 907 cm\(^{-1}\), \( \tau \) (neat) 6.50-7.00 (4H, m), 7.33-8.50 (4H, m), 8.70 (6H, d, J\(_{\text{PH}}\) 4 Hz), 8.85 (6H, d, J\(_{\text{PH}}\) 20 Hz), and 9.15 (3H, d, J 0 Hz) for the major isomer; the 3-H signal was obscured by that from the pyrrolidyl N-CH\(_2\) group. Heating a sample of the phosphine at 100° for 3 hours resulted in the equilibration of the isomers, favouring the other isomer, \( \tau \) (neat) 6.60-7.07 (4H, m), 7.30 (1H, q, J 7.5 Hz), 8.03-8.40 (4H, m), 8.91 (6H, d, J\(_{\text{PH}}\) 6 Hz), and 9.27 (3H, d, J 7.5 Hz). Initial ratio of isomers 3:1; equilibrated ratio of isomers, 3:4.

**Oxidation of 2,2,3,4,4-Pentamethyl-1-pyrrolidylphosphetan.**

A solution of the phosphine (0.11 g, ratio of isomers 3:4) in dichloromethane (20 ml) and hydrogen peroxide solution (20 vol, 20 ml) were stirred together for 2 hours. The organic layer was washed, dried, and the solvent removed to yield 2,2,3,4,4-pentamethyl-1-pyrrolidylphosphetan 1-oxide (0.9 g, 80%), b.p. 90-95°/0.5 mm, \( \nu_{\text{max}} \) (film) 1380, 1233, 1179, 1159, 1068, 990, 910, 747, 660, and 633 cm\(^{-1}\), m/e 229, 214, 187, 159, 118, and 91, \( \tau \) (benzene) 6.67-7.20 (4H, m), 8.17-8.67 (4H, m), 8.78 (6H, d, J\(_{\text{PH}}\) 16.5 Hz), 8.88 (6H, d, J\(_{\text{PH}}\) 16.5 Hz), and 9.28 (3H, d, J 7.5 Hz) for the major isomer; the minor isomer had signals 8.74 (6H, d, J\(_{\text{PH}}\) 17 Hz), and 8.93 (6H, d, J\(_{\text{PH}}\) 17 Hz), the 3-H signal could not be identified, ratio of isomers, 3:2, \(^{31}\)P -64 p.p.m. (Found: C, 62.7; H, 18.9; N, 6.95. C\(_{12}\)H\(_{24}\)NO requires C, 62.9; H, 19.7; N, 6.1%).
Preparation of 2,2,3,4,4-Pentamethyl-1-phenoxyphosphetan.

Sodium phenoxydide (2.6g) was added in 4 portions to a stirred solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan (5.5g) in ether (120ml) at room temperature over 20 minutes. After 18 hours the precipitate was filtered off and the solvent removed under reduced pressure to leave 2,2,3,4,4-pentamethyl-1-phenoxyphosphetan (6.9g, 94%), \( \nu_{\text{max}} \) (film) 1600, 1236, 1220, 1165, 1071, 1025, 1000, 866, 755, 720, and 690 cm\(^{-1}\), \( \tau \) (neat) 2.63-3.33 (5H, m), 8.10 (1H, dq, \( J = 7 \), \( J_{\text{ph}} \) 2 Hz), 8.78 (6H, d, \( J_{\text{ph}} \) 13 Hz), 8.90 (6H, d, 11.5 Hz) and 9.19 (3H, d, \( J = 7 \) Hz) for the major isomer; the minor isomer had signals 7.18 (1H, q, \( J = 7 \) Hz), 8.63 (6H, d, \( J_{\text{ph}} \) 13.5 Hz), 8.93 (6H, d, \( J_{\text{ph}} \) 14 Hz), and 9.28 (3H, d, \( J = 7 \) Hz), ratio of isomers, 66:34. Addition of t.m.s. to the phosphine apparently catalysed isomer equilibration, within 2 hours at 35° the isomer ratio had changed to 33:67 with the opposite isomer predominating. In the absence of t.m.s. the equilibration was complete after 6 days at 0°.

Preparation of 2,2,3,4,4-Pentamethyl-1-phenylthiophosphetan.

Sodium thiophenate (4.0g) was added in 4 portions to a stirred solution of 1-chloro-2,2,3,4,4-pentamethylphosphetan (5.5g) in ether (100ml) at room temperature over 20 minutes. After 18 hours the precipitate was filtered off and the solvent removed under reduced pressure. Distillation of the residue yielded 2,2,3,4,4-pentamethyl-1-phenylthiophosphetan (6.0g, 80%), b.p. 108-110°/0.2mm, \( \nu_{\text{max}} \). 1580, 1368, 1155, 1081, 1068, 1024, 740, and 680 cm\(^{-1}\), \( \tau \) (neat) 2.30-3.00 (5H, m), 7.43 (1H, q, \( J = 8 \) Hz), 8.63 (6H, d, \( J_{\text{ph}} \) 8.5 Hz), 8.80 (6H, d, \( J_{\text{ph}} \) 14 Hz), and 9.27 (3H, d, \( J = 8 \) Hz) for the major isomer; the minor


isomer had signals 7.87 (1H, d, \( J_{PH} \) 1.5 Hz), 8.72 (6H, d, \( J_{PH} \) 12.5 Hz), 8.86 (6H, d, \( J_{PH} \) 11 Hz), and 9.17 (3H, d, \( J_{PH} \) 1 Hz), ratio of isomers, 55:45, unchanged by distillation, \(^{31}\text{P}\) (neat) -99 p.p.m.

**Addition of Sulphur to 2,2,3,4,4-Pentamethyl-1-phenylthiophosphetan.**

Sulphur (0.05g), the phosphetan (0.25g), and a small crystal of aluminium chloride were refluxed in benzene (10ml) for 12 hours. The solvent was removed and the residue chromatographed on basic alumina (10g). Elution with pentane yielded 2,2,3,4,4-pentamethyl-1-phenylthiophosphetan 1-sulphide (0.2g, 70%), b.p. 145°/0.5mm, \( \nu_{max} \) (film) 1560, 1440, 1370, 1160, 1022, 743, 710, and 686 cm\(^{-1}\), m/e 284, 269, 252, 242, 214, 175, 172, and 110, \( \tau \) 2.25-2.75 (8H, m), 7.25-7.87 (1H, m), 8.60 (6H, d, \( J_{PH} \) 21 Hz), 8.68 (6H, d, \( J_{PH} \) 22 Hz), and 9.07 (3H, dd, \( J_{PH} \), \( J_{PH} \) 1.5 Hz) for the major isomer; the minor isomer had signals 8.53 (6H, d, \( J_{PH} \) 22 Hz), 8.60 (6H, d, \( J_{PH} \) 21 Hz), and 9.02 (3H, dd, \( J_{PH} \), \( J_{PH} \) 1.5 Hz), ratio of isomers 61:39, \(^{31}\text{P}\) (Chloroform) -118 p.p.m., (Found: C, 59.6; H, 7.45; S, 21.95. \( \text{C}_{14}\text{H}_{21}\text{PS}_{2} \) requires C, 59.15; H, 7.4; S, 22.55%).
Preparation of 1-Benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium Bromide.

Trichlorosilane (47g) in dichloromethane (100ml) was added dropwise to a stirred solution of 2,2,3,3-tetramethyl-1-phenylphosphetan 1-oxide (73g) in dichloromethane (500ml). After stirring for 3 hours benzyl bromide (100g) was added over 2 hours and the mixture set aside for 24 hours. The mixture was cooled in ice while water (500ml) was cautiously added. The phosphetanium salt and silica were filtered off and taken up in boiling chloroform (300ml). The silica was removed by filtration and the chloroform solution combined with the dichloromethane solution. The solution was dried and evaporated, and the residue crystallised to yield 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium bromide (100g, 80%), m.p. and mixed m.p. 257-259° (from chloroform-ethyl acetate).

Separation of Optical Enantiomorphs.

A slurry of silver D(-) dibenzoylhydrogen tartrate (74.2g) in methanol (250ml) was added to a stirred solution of the phosphetanium bromide (74.6g) in methanol (750ml). After 1 hour the precipitate of silver bromide was filtered off and the solvent removed, leaving a colourless glass. This was fractionally crystallised from propanol. The first crop (15.5g) had [α]$_D$$_{MeOH}$ -22°; the second crop (24.5g, 15%) had [α]$_D$$_{MeOH}$ -56.4°, unchanged on further recrystallisation; the third fraction (15g, 9%) had [α]$_D$$_{MeOH}$ -51°. Shutt quoted a value of [α]$_D$$_{MeOH}$ -48.9° as the maximum rotation he achieved by fractional crystallisation.
Metathesis Investigations.

1). Horner's Method to form the Iodide.

A solution of methyl iodide (3.0g) and the phosphetanium tartrate (1.0g) \([\alpha]_{D}^{MeOH} -56.4^\circ\) in anhydrous acetonitrile was refluxed for 12 hours and then anhydrous ether (40ml) was added. The precipitated phosphetanium iodide (0.6g) was filtered off, washed with ether, and dried. The phosphetanium iodide so produced had \([\alpha]_{D}^{MeOH} +15.0^\circ\).

The use of reagent grade solvent resulted in the production of phosphetanium iodide, \([\alpha]_{D}^{MeOH} +14.0^\circ\).

2). Horner's Method to form the Bromide.

A solution of ethyl bromide (1.5g) and the phosphetanium tartrate (0.45g) \([\alpha]_{D}^{MeOH} -56.4^\circ\) in anhydrous acetonitrile was refluxed for 24 hours and then anhydrous ether (40ml) was added. The precipitated phosphetanium bromide was filtered off, washed with ether, and dried. The phosphetanium bromide so produced had \([\alpha]_{D}^{MeOH} +18.0^\circ\).

The use of the reagent grade acetonitrile resulted in the production of phosphetanium bromide \([\alpha]_{D}^{MeOH} +13.6^\circ\).

3). Ammonium Iodide in Methanol.

Ammonium iodide (0.50g) was added to a stirred solution of the phosphetanium tartrate (0.86g) \([\alpha]_{D}^{MeOH} -56.4^\circ\), in anhydrous methanol (25ml). After 15 minutes ethyl acetate (25ml) was added and the mixture stirred for a further 10 minutes. The precipitated phosphetanium iodide was filtered off, washed with ether, and dried. The phosphetanium iodide so produced had \([\alpha]_{D}^{MeOH} +18.0^\circ\).
Alkaline Hydrolysis of 1-Benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium Halides.

The following hydrolysis was typical.

Aqueous sodium hydroxide (N/10, 25ml) was added to a stirred solution of the phosphetanium halide (1mmol) in methanol (15ml) at 0°. After 2 hours the solution was diluted with water (50ml) and extracted with dichloromethane (5 x 30ml). The combined organic extracts were dried and evaporated to yield the crystalline 2,2,3,3-tetramethyl-1-phenylphosphetan 1-oxide (90-100%).

Wittig Olefin Synthesis on 1-Benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium Bromide.

The phosphetanium bromide (0.75g) \([\alpha]_{D}^{18.0°} +18.0°\) was stirred with butyl-lithium (2.0M, 1.0ml) in anhydrous tetrahydrofuran (75ml) at room temperature for 15 minutes. Benzaldehyde (1ml) was added and the solution was stirred for a further 12 hours. The solvent was removed and residue partitioned between water (50ml) and dichloromethane (50ml). The organic layer was dried and evaporated and the residue chromatographed on basic alumina (10g). Elution with ether-methanol (200:3) yielded 2,2,3,3-tetramethyl-1-phenylphosphetan 1-oxide \(\,[\alpha]_{D}^{34.0°}, (temperature = 12.5°)\).

589 +34.0, 578 +34.5, 546 +38.6, 463 +71.0, 365 +130.0

Wittig Olefin Synthesis on 1-Benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium Iodide.

The phosphetanium iodide (0.59g) \([\alpha]_{D}^{22.0°} +22.0°\) was stirred with butyl-lithium (1.84M, 0.75ml) in anhydrous tetrahydrofuran (25ml).

589 +34.0, 578 +34.5, 546 +38.6, 463 +71.0, 365 +130.0
After 12 minutes benzaldehyde (1ml) was added and the solution stirred for a further 12 hours. The solvent was removed and the residue partitioned between water (25ml) and dichloromethane (25ml). The organic layer was dried and evaporated and the residue chromatographed on basic alumina (15g). Elution with ether-methanol (100:1) yielded 2,2,3,3-tetramethyl-1-phenylphosphetan 1-oxide, $[\alpha]_{D}^{\text{MeOH}} +37.1^\circ$, (temperature = 16°).

538 +37.1, 578 +37.5, 546 +42.1, 436 +72.0, 363 +150.0.

**Optical Stability of 2,2,3,3-Tetramethyl-1-phenylphosphetan 1-Oxide.**

Aqueous sodium hydroxide (1M, 20ml) was added to a solution of the phosphetan oxide (0.05g) $[\alpha]_{D}^{\text{MeOH}} +24.8^\circ$ in methanol (15ml) and the mixture stirred for 24 hours. Water (20ml) was then added and the aqueous solution extracted with dichloromethane (4 x 20ml). The combined organic extracts were dried and evaporated to leave the phosphetan oxide (0.045g, 90% recovery) $[\alpha]_{D}^{\text{MeOH}} +24.75^\circ$.

**Preparation of 3,4,-Dimethyl-1-(2'-methylallyl)-1-phenyl-3-phospholenium Chloride.**

2-ethylallyl chloride (3g) was refluxed with a solution of 3,4-dimethyl-1-phenyl-3-phospholen (3.2g) in benzene for 2 hours. The precipitate was filtered off and recrystallised to yield the phospholenium salt (3.4g, 71%), m.p. 187-188° (from chloroform-ethyl acetate), $v_{\text{max}}$. 1403, 1243, 1221, 1120, 1003, 920, 892, 741, and 687 cm$^{-1}$, $\tau$ 1.50-2.50 (5H, m), 4.67-5.00 (2H, m), 5.90 (2H, $J_{PH} 17$ Hz), 6.00-6.92 (4H, m), 8.17 (6H, s), and
2.17-8.42 (3H, s), (Found: C, 68.25; H, 7.95; P, 10.7. 
C₁₆H₁₂ClP requires C, 68.45; H, 7.85; P, 11.05%).

Hydrolysis of 3,4-Dimethyl-1-(2'-methylallyl)-1-phenyl-3-
phospholenium Chloride.

Aqueous sodium hydroxide (1 N, 60 ml) was added to a stirred solution of the phosphonium salt (2.8 g) in methanol (60 ml) at 0°. An immediate effervescence occurred which subsided after 2 hours. The system was then flushed with nitrogen for 30 minutes and the exhaust gas passed through a solution of bromine in dichloromethane at -20°. The hydrolysis solution was rotary-evaporated to half its original volume and the precipitated oil taken up in dichloromethane (40 ml). The organic layer was separated, washed with dilute hydrochloric acid (1 N/10), and water, dried, and evaporated to yield 3,4-dimethyl-1-phenyl-3-phospholen 1-oxide (2.0 g, 95%), b.p. 150-155°/0.3 mm, n.m.r. and i.r. spectra identical to those of an authentic sample. The bromine solution was evaporated and the residue distilled under reduced pressure to yield 1,2-dibromo-2-methylpropane (1.8 g, 80%), b.p. 157-159°, n.m.r. and i.r. spectra identical to those of an authentic sample.

Preparation of 1,3,4,4-Tetramethyl-1-phenyl-2-phospholenium Iodide.

Methyl iodide (2.8 g) was added to a solution of 3,4,4-tetramethyl-1-phenyl-2-phospholen (2.0 g) in benzene (20 ml). The mixture was refluxed for 12 hours and the precipitated phospholenium salt filtered off (3.4 g, 98%), m.p. 146-147° (from chloroform-ethyl acetate)
Hydrolysis of 1,3,4,4-Tetramethyl-1-phenyl-2-phospholenium Iodide.

The phospholenium iodide (1.15g) in methanol (20ml) was refluxed with aqueous sodium hydroxide (1M, 20ml) for 3 hours. The solution was rotary-evaporated to half its original volume and the precipitated oil taken up in chloroform (40ml). The organic layer was dried and evaporated, and the residue chromatographed on basic alumina (30g). Elution with ether-ethyl acetate (3:1) yielded (methyl)phenyl(2,2,3-trimethylbut-3-enyl)phosphine oxide, m.p. and mixed m.p. 40-43°, n.m.r. and i.r. spectra identical to those of an authentic sample. Elution with ether-methanol (25:1) yielded 1,3,4,4-tetramethyl-2-phospholen 1-oxide, b.p. 120-122°/0.1 mm, \( \nu_{\text{max}} \). (film) 1602, 1460, 1299, 1178, 1133, 899, and 810 cm\(^{-1} \), m/e 158, 143, 118, and 76, \( \tau \) 4.10 (1H, d, \( J_{\text{PH}} \) 23 Hz), 7.03-0.33 (2H, m), 7.33-8.17 (3H, m), 0.30 (3H, d, \( J_{\text{PH}} \) 17 Hz), 8.72 (3H, s), and 8.33 (3H, s), (Found: C, 60.3; H, 9.7; P, 19.35. \( \text{C}_{6}\text{H}_{15}\text{OP} \) requires C, 60.75; H, 9.5; P, 19.6%). The n.m.r. spectrum of the crude mixture gave the ratio of ring-open:ring-intact products as 79:21.

Preparation of 3-Methyl-1-(2-Methylallyl)-1-phenyl-2-phospholenium Chloride.

2-Methylallyl chloride (1.8g) was refluxed with a solution of
3-methyl-1-phenyl-2-phospholen in benzene (50ml) for two hours. The precipitated salt was filtered off and recrystallised to yield 3-methyl-1-(2'-methylallyl)-1-phenyl-2-phospholenium chloride (1.6g, 90%), m.p. 150-152° (from chloroform-ethyl acetate), νₘₐₓ 1610, 1220, 1000, 925, 740, and 694 cm⁻¹, τ 1.50-2.50 (5H, m), 3.45 (1H, d, Jₚₜₚ 29 Hz), 4.60-5.00 (2H, m), 4.28 (2H, d, Jₚₜₚ 10 Hz), 6.00-7.50 (4H, m), 7.33 (3H, s), and 0.10-8.33 (3H, n), (Found: C, 67.3; H, 7.65; P, 11.4. C₁₅H₂₀C₁P requires C, 67.55; H, 7.5; P, 11.65%).

Ylide Isomerisation of 3-Methyl-1-(2'-methylallyl)-1-phenyl-2-phospholenium Chloride.

Butyl-lithium (2.1M, 2.4ml) was added dropwise to a stirred suspension of the phospholenium salt (1.33g) in tetrahydrofuran (30ml). The ylide solution was stirred for 15 minutes and then aqueous sodium hydroxide (1M, 30ml) was added cautiously. The organic solvent was removed under reduced pressure and the precipitated oil taken up in dichloromethane (30ml). The organic layer was washed and evaporated to yield 3-methyl-1-phenyl-2-phospholen 1-oxide (0.8g, 83%), b.p. 150-155°/2mm, n.m.r. and i.r. spectra identical to those of an authentic sample.

Hydrolysis of 3-Methyl-1-(2'-methylallyl)-1-phenyl-2-phospholenium Chloride.

Aqueous sodium hydroxide (1M, 30ml) was added to a stirred solution of the phosphonium salt (1.33g) in methanol at 0°. When the effervescence had ceased (30 minutes) the solution was rotary-evaporated to half of its original volume and the precipitated oil
taken up in dichloromethane (40mL). The organic layer was dried and evaporated to yield 3-methyl-1-phenyl-2-phospholen 1-oxide (1.73g, 90%), n.m.r. and i.r. spectra identical to those of an authentic sample.
Reaction of Potassium Cyanide with 1,2,2,3,3-Pentamethyl-1-phenylphosphetanium Iodide.

The phosphetanium salt (5.3g, 0.15mol) and potassium cyanide (0.05g, 0.015mol) in methanol (75ml) were refluxed for 24 hours. The solution was cooled in ice while hydrogen peroxide solution (20vol, 40mol) was added dropwise. After stirring for 2 hours the solvent was removed under reduced pressure and the residue partitioned between chloroform and water. The organic layer was washed, dried, and evaporated, and the residue chromatographed on basic alumina (100g). Elution with ether-methanol (100:1) yielded (3-hydroxy-2,2,3-trimethylbutyl)methyl(phenyl)phosphine oxide (2.0g, 80%), as a viscous liquid, \( \nu_{\text{max}} \) (film) 3200, 1300, 1163, 1115, 953, 894, 767, 475, and 697 cm\(^{-1}\), m/e (no molecular ion) 230, 221, 195, 180, 165, 153, 130, and 125, \( \tau \) 1.00-2.67 (5H, m), 4.70 (1H, br. s, which collapsed on the addition of 1 drop of D\(_2\)O), 7.87 (2H, d, \( \Delta_{\phi} \) 12 Hz), 0.93 (3H, d, \( \Delta_{\phi} \) 13 Hz), 8.70 (3H, s), 8.73 (3H, s), 8.36 (3H, d, \( \Delta_{\phi} \) 1.5 Hz), and 9.09 (3H, d, \( \Delta_{\phi} \) 1 Hz), (Found: C, 65.9; H, 9.1; P, 12.3. \( \text{C}_{14}\text{H}_{25}\text{O}_{2}\text{P} \) requires C, 66.15; H, 9.05; P, 12.2%).

A solution of the above alcohol (0.52g, 2mmol) and toluene-\( \mu\)-sulphonic acid monohydrate (0.2g, 1mmol) in benzene was boiled under reflux for 6 hours with azeotropic separation of water (Dean Stark). The solution was cooled and washed with saturated sodium carbonate solution and with water. The dried benzene extract was evaporated and the residue chromatographed on basic alumina (15g). Elution with ether-ethyl acetate (2:1) yielded (methyl)phenyl(2,2,3-trimethylbut-3-enyl)phosphine oxide (0.24g, 50%), m.p. 41-44° (from
Reaction of Cyanogen Bromide with 2,2,3,3-Tetramethyl-1-phenylphosphetan.

1). A solution of cyanogen bromide (1.1g, 0.01mol) and the phosphetan (2.0g, 0.01mol) in benzene (30ml) was refluxed for 24 hours and then cooled in ice while aqueous sodium hydroxide (0.2, 50ml) and hydrogen peroxide solution (20vol, 50ml) were added. After stirring for 30 minutes the organic layer was dried and evaporated to yield 3,4,4,5,5-tetramethyl-1-phenyl-2-phospholene-1-oxide (1.4g, 65%), m.p. 85.5-87° (from benzene), \( \nu_{\text{max}} \) 1605, 1395, 1200, 1166, 1119, 1076, 852, 725, 748, and 703 cm\(^{-1}\), m/e 220, 205, 190, 164, 149, and 124, \( \tau \) 1.97-2.67 (5H, m), 4.15 (1H, d, \( J_{\text{PH}} \) 22 Hz), 7.68 (1H, d, \( J_{\text{PH}} \) 14 Hz), 7.91 (1H, d, \( J_{\text{PH}} \) 11 Hz), 7.98 (3H, s), 8.02 (3H, s), and 8.77 (3H, s), (Found: C, 72.55; H, 7.9; P, 13.5. \( \text{C}_{13}\text{H}_{17}\text{OP} \) requires C, 71.2; H, 8.9; P, 13.15%).

The basic aqueous layer was acidified with hydrochloric acid (2N) and extracted with chloroform (3 x 50ml). The combined organic layers were dried and evaporated to yield a viscous oil. Chromatography on silica (20g) and elution with ether-light petroleum (9:1) yielded 4,4,5,5-tetramethyl-2-phenyl-1,2-oxaphospholane-2-oxide (0.35g, 13%), m.p. 66-67° (from pentane), \( \nu_{\text{max}} \) 1220, 1193, 1134, 1117, 952, 909, 835, 798, 749, 713, and 695 cm\(^{-1}\), m/e 233, 223, 196, 180, 155, and 140,
1) A solution of chlorine (2.1g, 0.03mol) in 1,2-dichloromethane (20ml) was added dropwise to a stirred solution of the phosphetan (7.2g, 0.03mol) in 1,2-dichloromethane (20ml) at -20°. The solution was allowed to warm to room temperature over 1 hour and the solvent removed under reduced pressure. Distillation of the liquid yielded (chloro)phenyl(2,2,3-trimethylbut-3-eny1)phosphine (4.1g, 50%).

2). A solution of cyanogen bromide (6.4g, 0.06mol) and the phosphetan (6.2g, 0.03mol) were refluxed in benzene for 24 hours. Workup as for the previous experiment yielded 3,4,4-trimethyl-2-phospholen-1-oxide (4.8g, 72%) from the organic layer. Chromatography of the acidic products on silica and elution with ether-light petroleum (4:1) yielded (4-bromo-2,2,3-trimethylbut-3-enyl)phenylphosphinic acid (1.2g, 13%), n.p. 120-121° (from ether-light petroleum), \( \nu_{\text{max}}. \) 2250br., 1620, 1164, 1138, 1050, 961, 810, 772, 744, 716, and 693 cm\(^{-1}\), m/e (for ions containing bromine only the peaks due to \(^{79}\)Br are quoted) 316, 237, 223, 197, 181, 156, and 141, \( \tau =0.33 \) (1H, s, which collapsed on the addition of one drop of D\(_2\)O), 2.02-2.03 (5H, m), 4.03 (s, 1H), 7.07 (2H, d, \( \nu_{\text{ppm}} \) 10 Hz), 8.52 (3H, s), and 8.35 (6H, s), (Found: C, 49.25; H, 5.8; Br, 25.5. \( \text{C}_{13}\text{H}_{14}\text{BrO}_2\text{P} \) requires C, 49.2; H, 5.7; Br, 24.25%). Elution with ether yielded 4,4,5,5-tetramethyl-2-phenyl-1,2-oxaphospholan-2-oxide (0.4g, 6%), m.p. and mixed m.p. 65-66.5°.
b.p. 80°/0.05mm-82°/0.075mm, ν 2.00-2.77 (5H, m), 5.20 (2H, br. s), 7.67 (2H, s), 8.38 (3H, s), and 8.83 (6H, s).

2). A solution of chlorine (2.8g, 0.04mol) in 1,2-dichloroethane (20ml) was added dropwise to a stirred solution of the phosphetan (4.1g, 0.02mol) in 1,2-dichloroethane (30ml) at -20°. The solution was allowed to warm to room temperature over 1 hour and the solvent removed under reduced pressure. Distillation of the residue yielded 3,4,4-trimethyl-1-phenyl-2-phospholen (3.1g, 76%), b.p. 104-118°/0.1mm, n.m.r. spectrum identical to that of an authentic sample.

Reaction of Phosgene with 2,2,3,3-Tetramethyl-1-phenylphosphetan.

A solution of phosgene (4.0g, 0.04mol) in dichloromethane (20ml) was added dropwise to a stirred solution of the phosphetan (0.2g, 0.04mol) in dichloromethane (40ml) at -20°. The solution was allowed to warm to room temperature over 1 hour and the solvent removed under reduced pressure. Distillation of the residue yielded (chloro)phenyl(2,2,3-trimethylbut-3-enyl)phosphine (7.2g, 75%), b.p. 98-99°/0.1mm, the n.m.r. spectrum was identical to that of the product from the reaction of chlorine with the phosphetan.

Redistillation of the phosphine at a pressure of 1.4mm yielded 3,4,4-trimethyl-1-phenyl-2-phospholen (95%), b.p. 140-150°/1.4mm, the n.m.r. spectrum was identical to that of an authentic sample.

Reaction of Bromine with 2,2,3,3-Tetramethyl-1-phenylphosphetan.

Bromine (4.8g, 0.03mol) in dichloromethane (10ml) was added
dropwise to a stirred solution of the phosphetan (6.2g, 0.03mol) in dichloromethane (50ml) at -20°. The solution was allowed to warm to room temperature and then the solvent was removed under reduced pressure. Distillation of the residue under reduced pressure yielded the 2-phospholen hydrobromide (7.3g, 85%), b.p. 108-110°/0.4mm, v\text{max} (\text{CHCl}_3) 2440, 2250, 1589, 1438, and 1117 cm\textsuperscript{-1}, 0.40 (1H, br. d, \text{J}_\text{PH} 540 Hz), 1.50-2.50 (5H, m), 3.66 (1H, d, \text{J}_\text{PH} 27 Hz), 6.27-7.50 (2H, m), 7.70 (3H, d, \text{J}_\text{PH} 1.5 Hz), 8.60 (3H, s), and 8.63 (3H, s).

A solution of the hydrobromide (2.2g) in chloroform (20ml) was added to 50 ml of N/10 sodium hydroxide solution, and the excess sodium hydroxide back-titrated with N/10 hydrochloric acid using phenolphthalein as indicator. The volume needed was 37.3ml; a 1:1 adduct of the phosphine and hydrogen bromide would require 35.5ml. Hydrogen peroxide solution (20vol, 50ml) was added and the mixture stirred for 1 hour. The organic layer was washed, dried, and evaporated to yield 3,4,4-trimethyl-1-phenyl-2-phospholen 1-oxide (1.5g, 93%), m.p. and mixed m.p. 34-35°, i.r. and n.m.r. spectra identical to those of an authentic sample.

Preparation of 3,4,4-Trimethyl-1-phenyl-2-phospholen Hydrobromide.

Phenylsilane (0.54g) was added in 4 portions to 3,4,4-trimethyl-1-phenyl-2-phospholen 1-oxide (1.1g) and then the mixture was heated to 100° over 2 hours. Distillation of the mixture under reduced pressure yielded 3,4,4-trimethyl-1-phenyl-2-phospholen (0.92g, 90%), b.p. 83-91°/0.2mm, \text{J} 2.17-2.83 (5H, m), 4.25 (1H, d, \text{J}_\text{PH} 38 Hz), 7.33-3.08 (2H, m), 8.12 (3H, s), and 8.97 (3H, s).
Hydrogen bromide was passed into a solution of the phospholen (0.62g) in benzene (10ml) to give the crystalline hydrobromide. Removal of the solvent and distillation under reduced pressure yielded the hydrobromide (1.07g, 90%), b.p. 115-120°/0.5mm, i.r. and n.m.r. spectra identical to those of the product from the reaction of bromine with 2,2,3,3-tetramethyl-1-phenylphosphetan. An analysis was not obtained due to the hygroscopic nature of the compound.

Reactions of (Chlorophenyl(2,2,3-trimethylbut-3-onyl)phosphine.

1). Thermal Cyclisation.

A sample of the chlorophosphine was heated in an n.m.r. tube to 170°, at which temperature an acid gas was evolved. The evolution became rapid at 180° and ceased after 2 hours at 180°. The n.m.r. spectrum of the product was found to be identical to that of an authentic sample of 3,4,4-trimethyl-1-phenyl-2-phospholen. No signals not attributed to the phospholen were observed.

2). Chlorine-Catalysed Cyclisation.

A solution of chlorine (0.17g) in 1,2-dichloroethane (5ml) was added to a stirred solution of the chlorophosphine (0.60g) in 1,2-dichloroethane (20ml) at 0°. The solution was refluxed for 24 hours and then treated with aqueous sodium hydroxide (N/2, 20ml) and hydrogen peroxide solution (20vol, 10ml). After stirring for 1 hour the organic layer was washed with saturated sodium chloride solution, dried, and evaporated to yield 3,4,4-trimethyl-1-phenyl-2-phospholen 1-oxide (0.44g, 80%), m.p. and mixed m.p. 84-86°, n.m.r. and i.r. spectra identical to those of an authentic sample.
3). **Aluminium Chloride-Catalysed Cyclisation.**

A solution of aluminium chloride (0.27g, 2mmol) and the chlorophosphine (0.48g, 2mmol) in 1,2-dichloroethane (10ml) was stirred for 24 hours and then treated with aqueous sodium hydroxide (N/2, 20ml) and hydrogen peroxide solution (20vol, 10ml). After 2 hours the organic layer was separated off and the aqueous layer extracted with dichloromethane (3 x 10ml). The combined organic layers were dried and evaporated and the residue chromatographed on basic alumina (15g). Elution with ether yielded 2,2,3,3-tetramethyl-1-phenylphosphetan 1-oxide (0.17g, 39%), m.p. and mixed m.p. 82-83°. Elution with ether-methanol (50:1) yielded 3,4,4-trimethyl-1-phenyl-2-phosphen 1-oxide (0.15g, 35%), m.p. and mixed m.p. 84-86°. The products were further characterised by comparison of their n.m.r. and i.r. spectra with those of authentic samples.

4). **Attempted Cyclisation with Hydrogen Chloride.**

Hydrogen chloride was passed continuously through a refluxing solution of the chlorophosphine (0.5g) in 1,2-dichloroethane (20ml) for 24 hours. Aqueous sodium hydroxide (N/5, 10ml) and hydrogen peroxide solution (20vol, 10ml) were added and the mixture stirred for 2 hours. The organic layer was washed, dried, and evaporated to yield a small quantity of tarry material (0.05g), whose n.m.r. spectrum showed the absence of the phospholen and phosphetan oxides. Acidification of the basic extract yielded phenyl(2,2,3-trimethylbut-3-enyl) phosphinic acid (0.43g, 86%) as a viscous syrup, \( \tau = -0.75 \) (1H, br. s, which collapsed on the addition of one drop of D_2O), 1.83-2.92 (5H, m), 5.35 (2H, d), 7.96 (2H, d, J = 15 Hz), 3.40 (3H, s), and 0.86 (6H, s).
Chromatography of the products on silica (20g) and elution with ether yielded 4,4,5,5-tetramethyl-2-phenyl-1,2-oxaphospholan 2-oxide (0.30g, 88%), m.p. and mixed m.p. 64-66°, n.m.r. and i.r. spectra identical to those of an authentic sample.

5). Alkaline Hydrolysis.

Aqueous sodium hydroxide (1H, 20nl) and hydrogen peroxide solution (20vol, 10ml) were added to a stirred solution of the chlorophosphine (1g) in dichloromethane (30ml) at 0°. After 4 hours the aqueous layer was separated off, acidified, and extracted with dichloromethane (4 x 30ml). The combined extracts were dried and evaporated to yield phenyl(2,2,3-trimethylbut-3-enyl)phosphinic acid (0.74g, 74%), n.m.r. identical to that described above. Chromatography on silica (10g) and elution with ether-methanol (200:1) yielded 4,4,5,5-tetramethyl-2-phenyl-1,2-oxaphospholan 2-oxide (0.5g, 67%), m.p. and mixed m.p. 64-66°.

Preparation of But-3-enyl(diethylaminophenylphosphine). But-3-enyl magnesium bromide (0.067mol) in ether (100ml) was added dropwise to a stirred solution of chloro(diethylamino)phenylphosphine (14.3g, 0.066mol) in ether (100ml). After 18 hours the precipitate was filtered off, the solvent evaporated, and the residue distilled to yield but-3-enyl(diethylamino)phenylphosphine (11.5g, 74%), b.p. 116-118°/9.6mm, \( \nu_{\text{max}} \) (film) 1636, 1370, 1180, 1020, 910, 703, 735, and 690 cm\(^{-1} \), \( \delta \) (neat) 2.17-2.07 (5H, m), 3.43-4.17 (2H, m), 4.50-4.67 (2H, m), 6.78 (4H, dq, J 7, JPH 6.5 Hz), 7.17-8.17 (4H, m), and 6.73 (6H, t, J 7 Hz).
Preparation of But-3-enyl(Chloro)phenylphosphine.

Hydrogen chloride (3.5g) was passed into a stirred solution of but-3-enyl(diethylamino)phenylphosphine (11.5g) in hexane (200ml) at 0° over 1 hour. The reaction was stirred for a further 2 hours and then the precipitate was filtered off, the solvent evaporated, and the residue distilled to yield but-3-enyl(chloro)phenylphosphine (8.3g, 85%), b.p. 104-105°/0.5mm, ν_max. (film) 1640, 1435, 1093, 934, 913, 741, and 690 cm⁻¹, τ (neat) 1.63-2.67 (5H, m), 3.67-4.33 (1H, m), 4.58-5.00 (2H, m), and 7.33-8.00 (4H, m).

Reactions of But-3-enyl(Chloro)phenylphosphine.

1). Attempted Thermal Cyclisation.

A sample of the chlorophosphine was slowly heated in an n.m.r. tube. At temperatures up to 230° the chlorophosphine was unaffected; at 240° charring of the sample occurred.

2). Attempted Chlorine-Catalysed Cyclisation.

A solution of chlorine (0.7g, 0.01mol) in 1,2-dichloroethane (10ml) was added to a stirred solution of the chlorophosphine (2.0g, 0.01mol) in 1,2-dichloroethane (10ml) at 0°. The mixture was refluxed for 24 hours and then treated with aqueous sodium hydroxide (1N, 40ml) and hydrogen peroxide solution (20vol, 40ml). The organic layer was dried and evaporated to yield a small quantity of tarry material (0.05g). Acidification of the basic extract, extraction with chloroform (4 x 40ml), and evaporation of the dried chloroform yielded but-3-enylphenylphosphinic acid (1.0g, 96%), m.p. 67-68° (from ether-light petroleum), ν_max. 2270 br.
1638, 1508, 1435, 1166, 1125, and 957 cm⁻¹, m/e 196, 179, 169, 156, 141, and 124, ν 1.93-2.65 (6H, m), 4.27-4.60 (1H, m), 4.83-5.33 (2H, m), and 7.50-8.33 (4H, m), (Found: C, 61.75; H, 6.3; P, 14.8. C₁₀H₁₃O₂P requires C, 61.2; H, 6.55; P, 15.3%).

3). Attempted Bromine-Catalysed Cyclisation.

A solution of bromine (1.6g, 0.01mol) in 1,2-dichloroethane (15ml) was added dropwise to a stirred solution of the chlorophosphine (2.0g, 0.01mol) in 1,2-dichloroethane (20ml) at -20°C. The mixture was refluxed for 24 hours (during which time a dense white precipitate formed) and then cooled in ice while aqueous sodium hydroxide (1M, 40ml) and hydrogen peroxide solution (20vol, 40ml) were added. The organic layer was washed, dried, and evaporated to yield a small quantity of tarry material (0.07g). Acidification and chloroform extraction (4 x 40ml) of the basic layer yielded but-3-enylphenylphosphinic acid (1.5g, 76%), m.p. and mixed m.p. 64-66°C, n.m.r. and i.r. spectra identical to those of an authentic sample. Chromatography on silica failed to induce cyclisation to 5-methyl-2-phenyl-1,2-oxaphospholan 2-oxide; the phosphinic acid was recovered unchanged.

4). Aluminium Chloride-Catalysed Cyclisation.

A solution of aluminium chloride (1.35g, 0.01mol) and the chlorophosphine (2.0g, 0.01mol) in 1,2-dichloroethane was stirred for 24 hours and then treated with aqueous sodium hydroxide (1M, 50ml) and hydrogen peroxide solution (20vol, 50ml). After 2 hours the organic layer was separated and the aqueous layer extracted with chloroform (3 x 25ml). The combined organic layers were dried and evaporated and the residue chromatographed on basic alumina (100g). Elution
with ether-methanol (50:1) yielded 1-phenyl-2-phosphenyl 1-oxide (1.0g, 56%), m.p. 56-60°, n.m.r. and i.r. spectra identical to those of an authentic sample.

5). Alkaline Hydrolysis.

Aqueous sodium hydroxide (1M, 50ml) and hydrogen peroxide solution (20vol, 30ml) were added to a stirred solution of the chlorophosphine (2.0g) in dichloromethane (50ml). After 24 hours the alkaline layer was separated, acidified, and extracted with dichloromethane (4 x 50ml). The combined extracts were dried and evaporated to yield but-3-enylphenyl phosphoric acid (1.6g, 30%), m.p. and mixed m.p. 64-65°, n.m.r. and i.r. spectra identical to those of an authentic sample.

Preparation of Chloro(pent-4-enyl)phenylphosphine.

Pent-4-enyl magnesium bromide (0.1mol) in ether (75ml) was added dropwise to a stirred solution of chloro(diethylamino)phenylphosphine (21.5g, 0.1mol) in ether (50ml). After stirring for 12 hours the mixture was cooled in ice while hydrogen chloride was bubbled through the solvent. When the precipitates formed a coagulent mass in the bottom of the flask the ether solution was decanted off, the solvent removed, and the residue distilled under reduced pressure to yield chloro(pent-4-enyl)phenylphosphine (5.3g, 25%), b.p. 120-130°/0.3mm, v_max. (film) 1639, 1436, 1090, 995, 911, 740, and 690 cm⁻¹, τ 2.00-2.03 (5H, m), 3.80-4.67 (1H, m), 4.83-5.27 (2H, m), and 7.67-8.03 (6H, m).
Reactions of Chloro(pent-4-enyl)phenylphosphine.

1. Reaction with Aluminium Chloride.

A solution of aluminium chloride (2.0g, 0.015mol) and the chlorophosphine (3.2g, 0.015mol) in 1,2-dichloroethane (50ml) was stirred for 24 hours and then treated with aqueous sodium hydroxide (1N, 50ml) and hydrogen peroxide solution (20vol, 50ml). After two hours the organic layer was separated and the aqueous layer extracted with chloroform (3 x 30ml). The combined organic layers were dried, evaporated, and the residue chromatographed on basic alumina (60g). Elution with ether-methanol (40:1) yielded 1-phenyl-2-hexynorinophosphin-1-oxide (0.26g, 9%), b.p. 134-136°/0.05mm, ν\text{max} (film) 1600, 1433, 1163, 1110, 910, 803, 746, 724, and 701 cm\textsuperscript{-1}, m/e 192, 166, 164, 149, 125, and 108, τ 1.67-2.67 (5.5H, m), 2.68-4.33 (1.5H, m), and 7.00-8.33 (3H, m), (Found: C, 69.0; H, 6.75; P, 16.0. C\textsubscript{11}H\textsubscript{15}OP requires C, 68.8; H, 6.75; P, 16.15%). Elution with ether-methanol (10:1) yielded a polymeric gum (0.94g), ν\text{max}, 1638, 1590, 1252, 1170, 1116, 813, 747, and 696 cm\textsuperscript{-1}, τ 1.03-2.58 (m), 4.87 (br. s), 5.07 (br. s), and 6.83-9.17 (m). This compound could not be obtained in an analytically pure state.

Alkaline Hydrolysis.

Aqueous sodium hydroxide (1N, 50ml) and hydrogen peroxide solution (20vol, 30ml) were added to a stirred solution of the chlorophosphine (2.0g) in dichloromethane (50ml). After 24 hours the alkaline layer was separated off, acidified, and extracted with dichloromethane (4 x 50ml). The combined extracts were dried and
evaporated to yield pent-4-enylphenyl-phosphinic acid, as a glass
(1.5g, 70%). $v_{max}$. 2600 br., 2250 br., 1640, 1592, 1430, 1170, 1125,
965, 913, and 693 cm$^{-1}$, m/e 219, 193, 192, 137, 125, and 108, $\tau$.
-3.10 (1H, br. s, which collapsed on the addition of one drop of $D_2O$),
1.70-2.67 (5H, m), 3.77-4.53 (1H, m), 4.70-5.17 (2H, m), and 7.67-7.83
(6H, m), (Found: C, 62.95; H, 7.05; P, 14.75. $C_{11}H_{15}O_2P$ requires
C, 62.9; H, 7.15; P, 14.75%).

Preparation of Chloro-(2-methylallyl)phenylphosphate.

2-Methylallyl magnesium chloride (0.2mol) in ether (500ml) was
added dropwise to a stirred solution of chloro-diethy lamino)phenyl-
phosphine (43g, 0.2mol) in ether (500ml). The mixture was refluxed
for 3 hours and then cooled in ice while hydrogen chloride was bubbled
through the stirred mixture. When the precipitates formed a coagulent
mass in the bottom of the flask the ether solution was decanted off,
the solvent removed and the residue distilled under reduced pressure to
yield chloro(2-methylallyl)phenylphosphine (10g, 50%), b.p. 110-112°/
3.0mm, $v_{max}$. (film) 1641, 1434, 1375, 1279, 1090, 801, 740, and 690 cm$^{-1}$,
$\tau$ (neat) 1.83-2.67 (5H, m), 4.83-5.17 (2H, m), 6.67-7.17 (2H, m), and
6.07 (3H, s).

Reactions of Chloro(2-methylallyl)phenylphosphine.


The chlorophosphine (2.0g) was slowly heated to 200° at which
temperature a slow evolution of an acid gas occurred. After 2 hours
the reaction was cooled in ice while aqueous sodium hydroxide ($N/2$, 50ml)
and hydrogen peroxide solution (20vol, 20ml) were added dropwise. After 24 hours the organic layer was dried and evaporated to yield a viscous tarry material (0.6g). This was chromatographed on basic alumina (20g) but elution with a variety of solvents of polarity up to ether-methanol (10:1) yielded only small quantities of a variety of unidentified products (less than 0.04g). Acidification of the basic extract yielded (2-methylallyl)phenylphosphinic acid as a glass (1.2g, 60%), m.p. 70-85°, $v_{\text{max.}}$ 2250 br., 1610 br., 1592, 1170, 1122, 950, 725, and 638 cm$^{-1}$, m/e 196, 179, 155, 141, and 124, $\tau$ 1.52 (1H, br. s, which collapsed on the addition of one drop of D$_2$O), 2.00-2.88 (5H, m), 5.00-5.43 (2H, m), 7.15 (1H, d, $J_{HH}$ 15 Hz), 7.18 (1H, d, $J_{HH}$ 12 Hz), and 8.17-8.30 (3H, m). A satisfactory analysis could not be obtained for this compound.

**Action of Aluminium Chloride**

A solution of aluminium chloride (1.35g, 0.01mol) and the chlorophosphine (1.85g, 0.01mol) in 1,2-dichloroethane (40ml) was stirred for 24 hours and then treated with hydrogen peroxide solution (20vol, 20ml). The organic layer was separated, washed with saturated sodium carbonate solution, dried, and the solvent evaporated to leave a tar (0.40g). Chromatography on basic alumina and elution with ether-methanol yielded a small quantity of polymeric material (0.1g), $v_{\text{max.}}$ (film) 1630, 1593, 1440, 1175, 1122, 948, 737, and 696 cm$^{-1}$, the mass spectrum showed a mass of peaks throughout the range up to m/e 603 mass units. No other products could be isolated in quantities greater than 0.03g.
Reaction of 2,2,3,3-Tetramethyl-1-phenylphosphetane with Benzylidene Acetylacetone.

Benzylidene acetylacetone (4.0g) in dichloromethane (10ml) was added dropwise to a stirred solution of the phosphetane (4.3g) in dichloromethane (10ml). The solution was then refluxed for 2 hours. Removal of the solvent yielded a yellow oil, crystallising on standing to give the 1:1-adduct (6.5g, 79%), m.p. 134-135° (from ethyl acetate), \( \nu_{\text{max}} \): 1630, 1130, 1095, 942, 802, 640, 706, 693, and 650 cm\(^{-1}\), m/e 324, 206, 205, and 191, \( \tau \): 2.7-3.3 (5H, m), 8.53 (1H, d, \( \Delta_{\text{PH}} \) 12 Hz), 7.52 (3H, s), 7.2-8.0 (2H, m), 8.17 (3H, s), 8.55 (3H, d, \( \Delta_{\text{PH}} \) 23 Hz), 0.70 (3H, d, \( \Delta_{\text{PH}} \) 22 Hz), 6.95 (3H, s), and 9.47 (3H, s), for the major isomer; the other isomer had \( \tau \): 6.30 (d, \( \Delta_{\text{PH}} \) 12 Hz), \( ^{31}\text{P} \) + 30.2 p.p.m., (Found: C, 76.4; H, 7.7; P, 7.5. \( \text{C}_{28}\text{H}_{26}\text{O}_{2}\text{P} \) requires C, 76.15; H, 7.65; P, 7.85%).

Reaction of 2,2,3,3-Tetramethyl-1-phenylphosphetane with 9,10-Phenantraquinone.

9,10-Phenantraquinone (6g) in dichloromethane (15ml) was added dropwise to a stirred solution of the phosphetane (6g) in dichloromethane (25ml) at 0°. After the exothermic reaction had subsided the solution was refluxed for 2 hours. The solvent was evaporated leaving the crystalline yellow 1:1-adduct (11g, 88%), m.p. 230-239° (from ethyl acetate), \( \nu_{\text{max}} \): 1635, 1340, 1115, 1093, 1048, 1022, 945, 722, and 748 cm\(^{-1}\), m/e 414, 331, 316, and 239, \( \tau \): 1.42-2.92 (13H, m), 6.32 (1H, d, \( \Delta_{\text{PH}} \) 16 Hz), 6.07 (1H, d, \( \Delta_{\text{PH}} \) 13 Hz), 5.40 (3H, d, \( \Delta_{\text{PH}} \) 18.5 Hz), 8.57 (3H, d, \( \Delta_{\text{PH}} \) 22 Hz), 8.95 (3H, s), and 9.37 (3H, d, \( \Delta_{\text{PH}} \) 1.5 Hz), \( ^{31}\text{P} \) + 4.5 p.p.m. (Found: C, 70.1; H, 6.7; P, 7.25. \( \text{C}_{27}\text{H}_{27}\text{O}_{2}\text{P} \) requires C, 78.25; H, 6.5; P, 7.5%).
Reaction of 2,2,3,3-Tetramethyl-1-phenylphosphetan with Biacetyl.

Biacetyl (5g) in dichloromethane (10mL) was added dropwise to a solution of the phosphetan (5.1g) in dichloromethane (10mL) at 0°. The solution was then refluxed for 12 hours. The solvent and excess biacetyl were removed under reduced pressure and the residue distilled to yield the 1:1-adduct (5.8g, 80%), b.p. 112-114°/0.5mm, m.p. 54-58° (from pentane), ν_max. 1240, 1153, 1116, 994, and 790 cm⁻¹, τ 1.75-2.25 (5H, m), 7.07 (2H, d, J_PH 14 Hz), 8.35 (6H, s), 8.50 (3H, d, J_PH 18 Hz), 8.83 (3H, d, J_PH 22 Hz), 9.00 (3H, s), and 9.52 (3H, d, J_PH 1.5 Hz), 31P(CHCl₃) + 16.1 p.p.m. An analysis was not obtained due to the hygroscopic nature of the compound.

Hydrolysis of the Biacetyl Adduct.

A solution of the adduct (1.5g) in dichloromethane (10mL) was stirred with water (10mL) for 2 hours and the organic layer dried and evaporated under reduced pressure to yield 2,2,3,3-tetramethyl-1-phenylphosphetan 1-oxide (0.95g), m.p. and mixed m.p. 82-84°. The n.m.r. and i.r. spectra were identical to those of an authentic sample.

Reaction of 2,2,3,3-Tetramethyl-1-phenylphosphetan with Hexafluoroacetone.

Hexafluoroacetone (15mL) was condensed into a stirred solution of the phosphetan (7.3g) in pentane (50mL) at -78°. The mixture was kept at -78° for 30 minutes and then allowed to warm to 0°. Removal of the solvent under reduced pressure yielded the 1,4,2-dioxaphospholan adduct (18g, 94%), m.p. 64-68°, ν_max. 1306, 1270, 1226, 1165, 1147,
1097, 1053, 970, 732, and 653 cm\(^{-1}\), \(\tau\) 1.62-2.65 (5H, m), 6.70 (2H, d, \(\delta_{PH}\) 20 Hz), 8.42 (3H, d, \(\delta_{PH}\) 21 Hz), 8.83 (3H, d, \(\delta_{PH}\) 20 Hz), 9.03 (3H, s), and 9.60 (3H, s), \(^{19}\)F (CHCl\(_3\)) +1.47 (3F, m), +2.60 (3F, m), +14.57 (3F, m), and +17.58 (3F, m), p.p.m.

**Thermal Rearrangement of the 1,4,2-Dioxaphospholan Adduct.**

A solution of the adduct (5.4g) in benzene (100ml) was refluxed for 30 minutes. The solvent was removed under reduced pressure and the residue chromatographed on basic alumina (180g). Elution with pentane yielded the 1,3,2-dioxaphospholan adduct (3.9g, 72%), m.p. 61-65\(^\circ\) (from methanol), \(\nu_{max}\). 1258, 1236, 1205, 1101, 951, and 875 cm\(^{-1}\), m/e 538, 519, 469, 454, and 205, \(\tau\) 1.75-2.67 (5H, d, \(\delta_{PH}\) 20 Hz), 6.82 (1H, d, \(\delta_{PH}\) 19 Hz), 8.58 (3H, d, \(\delta_{PH}\) 19 Hz), 8.82 (3H, d, \(\delta_{PH}\) 20 Hz), 9.05 (3H, s), and 9.57 (3H, d, \(\delta_{PH}\) 2 Hz), \(^{19}\)F (chloroform) +3.85 (6F, m), 5.57 (3F, m), and 6.49 (3F, m), p.p.m., \(^{31}\)P (benzene) +0.2 p.p.m.; (Found: C, 42.15; H, 3.35; F, 42.45. \(\text{C}_{19}\text{H}_{19}\text{F}_{12}\text{O}_{2}\text{P}\) requires C, 42.35; H, 3.55; F, 42.35%). Elution with ether-petrol (1:9) yielded hexafluoroisopropyl phenyl(1,1,2,2-tetramethyl-5,5,5-trifluoro-4-trifluoromethylpent-3-enyl)phosphinate (1.0g, 18%), b.p. 100-105\(^\circ\)0.05mm, \(\nu_{max}\). 1650, 1305, 1290, 1228, 1157, 1110, 899, 866, and 833 cm\(^{-1}\), m/e 538, 519, 500, 355, 291, 247, and 141, \(\tau\) 1.88-2.67 (5H, m), 2.83 (1H, s), 4.82 (1H, m, \(\delta_{HF}\) 5 Hz), 8.62 (3H, d, \(\delta_{PH}\) 21 Hz), 8.63 (3H, d, \(\delta_{PH}\) 19 Hz), 8.63 (3H, s), and 8.70 (3H, s), \(^{19}\)F(chloroform) -9.47 (3F, q, \(\delta_{8}\) Hz), +0.49 (3F, q, \(\delta_{8}\) Hz), and +9.93 (6F, d, \(\delta_{HF}\) 5 Hz) p.p.m. (Found: C, 42.55; H, 3.65; F, 42.55. \(\text{C}_{19}\text{H}_{19}\text{F}_{12}\text{O}_{2}\text{P}\) requires C, 42.35; H, 3.55; F, 42.35%).
General Procedure for the Preparation of Single Isomers of the Hexafluoroacetone adducts of 1-Alkyl-, and 1-Aryl-2,2,3,4,4-pentamethylphosphetans.

Trichlorosilane (2.0g, 0.015mol) in toluene (10ml) was added dropwise to a stirred solution of triethylamine (1.5g, 0.015mol) and the phosphetan 1-oxide (0.015mol) in toluene (50ml) at 0°. After 30 minutes aqueous sodium hydroxide (5N, 30ml) was added dropwise. The organic layer was separated, washed with saturated sodium chloride and dried over magnesium sulphate. The solution was then cooled to -73° while excess hexafluoroacetone (10ml) was condensed into the solution. After 30 minutes at -78° the solution was allowed to warm to 0° and the solvent removed under reduced pressure. Chromatography of the crude product on basic alumina (100g) and elution with pentane yielded the 2:1-adduct.

Reaction of 2,2,trans-3,4,4-Pentamethyl-r-1-phenylphosphetan with Hexafluoroacetone.

The trans-oxide was reduced and the phosphine solution reacted with hexafluoroacetone as above to yield the 2:1-adduct (95%), m.p. 95-97° (from methanol, ν max. 1265, 1238, 1207, 1109, 953, and 883 cm⁻¹, m/e 552, 534, 482, 440, 401.66 (m*), 371, and 312.82 (m*), τ 1.83-2.83 (5H, m), 8.60 (6H, d, J PH 17 Hz), 8.65 (6H, d, J PH 19 Hz), and 9.28 (3H, dd, J 7, J PH 1.5 Hz), the signal from the 3-H proton was obscured by those of the ring methyl groups, ¹⁹F (chloroform) +2.89 (6F, m), and +5.65 (6F, m) p.p.m., ³¹P (benzene) -3.4 p.p.m. (Found: C, 43.45; H, 3.7; F, 41.0. C₂₀H₂₁F₁₂O₂P requires C, 43.5; H, 3.8; F, 41.3%).
Reaction of 2,2,cis-3,4,4-Pentamethyl-r-l-phenylphosphetan with Hexafluoroacetone.

The cis-oxide was reduced and the phosphine solution reacted with hexafluoroacetone as above to yield the 2:1-adduct (85%) m.p. 45-50° (from methanol-water), ν max. 1264, 1240, 1207, 1110, 951, and 883 cm⁻¹, m/e 552, 534, 482, 440, and 371, τ 1.83-2.67 (5H, m), 7.78 (1H, q, J 8 Hz), 8.33 (6H, d, JPh 17 Hz), 8.63 (6H, d, JPh 19 Hz), and 9.43 (3H, d, J 8 Hz), 19F (chloroform) +3.20 (6F, m), +5.79 (6F, m), p.p.m., 31P (benzene) -7.7 p.p.m., (Found: C, 43.3; H, 3.8; F, 41.1. C20H21F12O2P requires C, 43.5; H, 3.8; F, 41.3%).

Reaction of r-1,2,2-trans-3,4,4-Hexamethylphosphetan with Hexafluoroacetone.

The trans-oxide was reduced and the phosphine solution reacted with hexafluoroacetone as above to yield the liquid 2:1-adduct (62%), b.p. 89-95°/0.5mm, ν max. (film) 1240, 1207, 1154, 1118, 960, 908, 880, and 749 cm⁻¹, τ 7.45 (1H, q, J 7 Hz), 8.27 (3H, d, JPh 9 Hz), 8.70 (6H, d, JPh 19 Hz), 8.80 (6H, d, JPh 21 Hz), and 9.22 (3H, d, J 7 Hz), 19F (1-bromonaphthalene) +3.69 (6F, m), and +6.70 (6F, m), p.p.m., 31P (neat) -6.2 p.p.m. (Found: C, 36.45; H, 3.9; F, 47.8. C15H19F12O2P requires C, 36.75; H, 3.9; F, 46.5%). Elution with pentane-ether (20:1) yielded r-1-(3',3',3'-trifluoro-2'-hydroxy-2'-trifluoromethylpropyl)-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide (12%), m.p. 125-127° (from light petroleum), ν max. 3120, 1470, 1230, 1210, 1187, 1155, 1010, 950, and 770 cm⁻¹, m/e 340, 325, 321, 271, and 270, τ (carbon tetrachloride) 1.93 (1H, s, which collapsed on the addition of one drop of D₂O), 7.67 (2H, d, JPh 9 Hz), 8.37 (1H, dq, J 7, JPh 2 Hz), 8.55 (6H, d,
Reaction of $r$-1-Isopropyl-2,2,trans-3,4,4-pentamethylphosphetan with Hexafluoroacetone.

The trans oxide was reduced and the phosphine solution reacted with hexafluoroacetone as above to yield the 2:1-adduct (84%) m.p. 76-76.5°C (from methanol), $\nu_{\text{max}}$. 1260, 1235, 1204, 1143, 1109, 941, and 880 cm$^{-1}$, m/e 518, 499, 476, 449, 448, 406, and 363, $\tau$ 7.50-8.00 (2H, m), 8.78 (6H, d, $\delta_{\text{PH}}$ 17.5 Hz), 8.80 (6H, dd, $\delta_{\text{PH}}$ 7 Hz), 8.89 (6H, d, $\delta_{\text{PH}}$ 19 Hz), and 9.43 (3H, dd, $\delta_{\text{PH}}$ 6.5 Hz), $^{19}$F (benzene) +3.00 (6F, m), and +4.47 (6F, m), p.p.m., $\delta$P (benzene) -19.5 p.p.m. (Found: C, 39.35; H, 4.45; F, 44.4. C$_{17}$H$_{23}$F$_{12}$O$_2$P requires C, 39.4; H, 4.45; F, 44.0%).

Reaction of $r$-1-Benzyl-2,2,trans-3,4,4-pentamethylphosphetan with Hexafluoroacetone.

The trans oxide was reduced and the phosphine solution reacted with hexafluoroacetone as above. The initial mass of crystals disappeared within 10 minutes at -78°C. Chromatography on basic alumina and elution with pentane yielded the 1,2-oxaphosphetan (266) (the "Wittig intermediate"), as a colourless liquid (68%), $\nu_{\text{max}}$. (film) 1373, 1295, 1210, 1193, 1146, 1130, 1101, 1086, 969, 896, 873, and 683 cm$^{-1}$, m/e as for the thermolysis products, $\tau$ 2.50-2.83 (5H, br. s), 4.13 (1H, d, $\delta_{\text{PH}}$ 14 Hz), 5.00-5.67 (1H, m), 7.75 (1H, q, $\delta$ 8 Hz),
8.38 (3H, d, J\textsubscript{PH} 24 Hz), 8.66 (3H, d, J\textsubscript{PH} 20 Hz), 8.78 (3H, d, J\textsubscript{PH} 22 Hz), 8.88 (3H, d, J\textsubscript{PH} 20 Hz), and 9.05 (3H, d, J 8 Hz), 19F (benzene) +7.67 (3F, q, J 9 Hz), +9.52 (3F, m), +10.3 (3F, m), and +12.2 (3F, q, J 9 Hz) p.p.m., 31P (benzene) -10.2 p.p.m.

Thermolysis of the "Kittig Intermediate".

A solution of the adduct (2.9g) in benzene (50ml) was refluxed for 30 minutes and the solvent removed under reduced pressure (10mm,0°), The liquid residue was distilled (Kügel-Rohr) under reduced pressure to yield r-1-(hexafluoroisopropoxy)-2,2,cis-3,4,4-pentamethyloospethan 1-oxide (1.5g, 92%), b.p. 85-87°/0.1mm, m.p. 63-66°, v\textsubscript{max}. 1291, 1250, 1216, 1108, 900, 862, 844, and 682 cm\textsuperscript{-1}, m/e 326, 307, 256, 176, 175, 159, and 108, J 4.63 (1H, sept., J\textsubscript{FH} 6 Hz), 8.18 (1H, dq, J 7, J\textsubscript{PH} 2 Hz), 8.67 (6H, d, J\textsubscript{PH} 21 Hz), 8.80 (6H, d, J\textsubscript{PH} 20 Hz), and 9.02 (3H, dd, J 7, J\textsubscript{PH} 1.5 Hz), 19F (benzene) +11.0 (d, J\textsubscript{HF} 6 Hz) p.p.m. (Found: C, 40.55; H, 5.15; F, 34.85. C\textsubscript{11}H\textsubscript{17}F\textsubscript{8}O\textsubscript{2}P requires C, 40.5; H, 5.2; F, 34.95%). A solid carbon dioxide trap connected to the distillation apparatus contained 1,1,1-trifluoro-3-phenyl-2-trifluoromethylprop-2-ene, v\textsubscript{max}. (film) 1662, 1402, 1300, 1282, 1238, 1187, 1155, 978, 837, 747, 714, and 690 cm\textsuperscript{-1}, m/e 240, 221, 171, 160, 151, 90, and 69, J 2.35 (1H, br. s), and 2.62 (5H, s), 19F (benzene) -3.0 (3F, q, J 7 Hz), and +0.50 (3F, q, J 7 Hz) p.p.m.

Hydrolysis of the "Wittig Intermediate".

The adduct (1.45g) and water (50ml) containing 5 drops of hydrochloric acid (2N) were warmed to 80° over 2 hours. The resulting oil was taken up in dichloromethane (50ml) and the organic layer
separated, dried, and evaporated to yield a yellow oil. Distillation
(Kügel-Rohr) under reduced pressure removed the ester (formed by
thermolysis) and left as the distillation residue, \(-\text{I}-(3,3',3''-
trifluoro-2'-hydroxy-1'-phenyl-2'-trifluoromethylpropyl)\)-2,2,trans-3,
\(4,4\text{-pentamethylphosphetan 1-oxide}\) \((0.26\text{g, 25\%})\), m.p. 144-147° (from
petrol), \(v_{\text{max}}\) 2720, 1180, 1222, 1205, 1187, 1146, 1137, 1045, 948,
722 and 703 cm\(^{-1}\), m/e 416, 401, 397, 398, 347, 346, 250, 235, and 160,
\(\tau\) 2.07 (1H, which collapsed on the addition of one drop of \(\text{D}_2\text{O}\)), 2.33
-2.83 (5H, m), 6.27 (1H, d, \(\text{J}_{\text{PH}}\) 3 Hz), 7.93 (1H, q, \(\text{J}\) 7.5 Hz), 8.47 (3H,
d, \(\text{J}_{\text{PH}}\) 19.5 Hz), 8.73 (3H, d, \(\text{J}_{\text{PH}}\) 18 Hz), 9.05 (3H, d, \(\text{J}_{\text{PH}}\) 18 Hz),
9.06 (3H, d, \(\text{J}\) 7.5 Hz), and 9.57 (3H, d, \(\text{J}_{\text{PH}}\) 17.5 Hz), \(19\text{F}\) (benzene)
+8.74 (3F, q, \(\text{J}\) 12 Hz), and +12.6 (3F, dq, \(\text{J}\) 12, \(\text{J}_{\text{PF}}\) 5 Hz), p.p.m.
(Found: C, 51.7; H, 5.7; F, 34.2. \(\text{C}_{18}\text{H}_{23}\text{F}_6\text{O}_2\text{P}\) requires C, 51.95;
H, 5.55; F, 34.5%).

Reaction of 2,2,3,4,4-Pentamethyl-1-t-butylphosphetan with
Hexafluoroacetone.

Hexafluoroacetone \((5\text{ml})\) was condensed into a stirred solution
of the phosphetan \((1.5\text{g})\) in pentane \((25\text{ml})\) at -78°. After 30
minutes the solution was warmed to 0° and the solvent removed under
reduced pressure. Chromatography of the crude product on basic
alumina \((40\text{g})\) and elution with pentane yielded the 2:1-adduct \((1.0\text{g},
25\%)\), m.p. 60-75° decomp. (from pentane) \(v_{\text{max}}\) 1255, 1236, 1202, 1110,
935, and 880 cm\(^{-1}\), m/e 532, 490, 475, 463, 462, 433, 420, 405, and 200,
\(\tau\) 8.25 (1H, dq, \(\text{J}\) 7, \(\text{J}_{\text{PH}}\) 2 Hz), 8.52 (9H, d, \(\text{J}_{\text{PH}}\) 14.5 Hz), 8.63 (6H, d,
\(\text{J}_{\text{PH}}\) 19 Hz), 8.67 (6H, d, \(\text{J}_{\text{PH}}\) 17 Hz), and 9.63 (3H, dd, \(\text{J}\) 7, \(\text{J}_{\text{PH}}\) 22 Hz);
and for the other isomer \(\tau\) 8.47 (6H, d, \(\text{J}_{\text{PH}}\) 21 Hz), 8.63 (6H, d, \(\text{J}_{\text{PH}}\)
19 Hz), and 8.68 (9H, d, J_{PH} = 14.5 Hz) the signal from the 3-H proton of the minor isomer could not be identified; ratio of isomers 5:2 approx. \(^{19}\)F (dichloromethane) +1.33 (6F, m), and +3.04 (6F, m) p.p.m., \(^{31}\)P (dichloromethane) -5p.p.m. this compound was too unstable to be obtained analytically pure. Elution with ether yielded the phosphetan oxide (0.93g, 60%) as a mixture of isomers, ratio 5:2, trans:cis, i.r. and m.s. identical to those of the trans isomer, the cis-isomer had signals \(\tau\) (benzene) 8.53 (1H, dq, J = 7, 2 Hz), 8.85 (6H, d, J_{PH} 19 Hz), 8.93 (9H, d, J_{PH} 14 Hz), 9.08 (6H, d, J_{PH} 17 Hz), and 9.42 (3H, dd, J = 7, J_{PH} 2 Hz).

**Reaction of 2,2,trans-3,4,4-Pentamethyl-1-(2'-Methylprop-1'-enyl)phosphetan with Hexafluoroacetone.**

Hexafluoroacetone (2ml) was condensed into a stirred solution of the phosphetan (0.70g) in pentane (30ml) at -78°. After 30 minutes' the reaction was allowed to warm to 0° and the solvent removed under reduced pressure. Chromatography of the crude product and elution with pentane yielded the 2:1-adduct (1.05g, 52%), m.p. 80-82° (from methanol), \(\nu_{max}\) 1620, 1259, 1230, 1205, 1106, 993, 955, and 879 cm\(^{-1}\), m/e 530, 461, 442, 403, and 178, \(\tau\) (benzene) 4.25 (1H, d, J_{PH} 25 Hz), 8.20 (3H, s), 8.32 (3H, s), 8.72 (6H, d, J_{PH} 18 Hz), 8.92 (6H, d, J_{PH} 20 Hz), and 9.45 (3H, dd, J = 6, J_{PH} 1.5 Hz), \(^{19}\)F (benzene) +2.29 (6F, m), and +6.40 (6F, m), p.p.m., \(^{31}\)P (benzene) +0.5 p.p.m. (Found: C, 41.15; H, 4.45; F, 42.3. \(C_{16}H_{23}F_{12}O_{2}P\) requires C, 40.75; H, 4.35; F, 43.0%).

**Reaction of 1-(p-Bromophenyl)-2,2,3,4,4-pentamethylphosphetan with Hexafluoroacetone.**

Hexafluoroacetone (5ml) was condensed into a stirred solution
of the phosphetan (1.5g), in pentane (40ml) at -78°. After 30 minutes the solution was allowed to warm to 0° and the solvent removed under reduced pressure. Chromatography of the crude product on basic alumina and elution with pentane yielded the 2:1-adduct (3.0g, 95%), m.p. 85-95° (from methanol-water), \( \nu_{\text{max}} \). \( \nu \) 1579, 1262, 1235, 1205, 1110, 950, and 834 cm\(^{-1} \), m/e (for \(^{79}\)Br) 630, 615, 611, 561, 560, 518, and 298, \( \tau \) 1.9-2.6 (4H, m), 7.57-8.10 (1H, m), 8.55 (6H, d, \( J_{PH} \) 18 Hz), 8.60 (6H, d, \( J_{PH} \) 19.5 Hz), and 9.23 (3H, dq, \( J \) 7, \( J_{PH} \) 2 Hz) for the major isomer (trans) isomer; the minor (cis) isomer had \( \tau \) 8.37 (6H, d, \( J_{PH} \) 17 Hz), 8.67 (6H, d, \( J_{PH} \) 20 Hz), and 9.42 (3H, d, \( J \) 7.5 Hz), ratio of isomers 72:28, \(^{19}\)F (benzene) +3.41 (6F, m), and +6.23 (6F, m) p.p.m. \(^{31}\)P (benzene) -3.7 p.p.m. for the major (trans) isomer, and -6.3 p.p.m. for the minor (cis) isomer. (Found: C, 38.25; H, 3.3; F, 35.95. \( \text{C}_{19}\text{H}_{21}\text{BrF}_{12}\text{O}_{2} \) requires C, 38.05; H, 3.15; F, 36.15%).

**Reaction of 1-(p-Methoxyphenyl)-2,2,3,4,4-pentamethylphosphetan with Hexafluoroacetone.**

Hexafluoroacetone (2ml) was condensed into a stirred solution of the phosphetan (0.50g) in pentane (25ml) at -78°. After 30 minutes the reaction was allowed to warm up to 0° and the solvent removed under reduced pressure. Chromatography of the crude product on basic alumina (40g) and elution with pentane yielded the 2:1-adduct (0.12g, 10%), m.p. 43-61° (from methanol-water), \( \nu_{\text{max}} \). \( \nu \) 1601, 1570, 1257, 1236, 1204, 1107, 950, and 833 cm\(^{-1} \), m/e 582, 563, 513, 470, and 250, \( \tau \) (benzene) 1.83-3.17 (4H, m), 6.40 (3H, s), 7.70 (1H, dq, \( J \) 7, \( J_{PH} \) 1.5 Hz), 8.45 (6H, d, \( J_{PH} \) 20 Hz), 8.83 (6H, d, \( J_{PH} \) 21 Hz), and 9.47 (3H, dd, \( J \) 7, \( J_{PH} \) 1.5 Hz) for the major isomer; the minor isomer had signals 6.38 (3H, s), 8.60
(6H, d, $\delta$H 18 Hz), and 8.80 (6H, d, $\delta$H 21 Hz), the other signals from the minor isomer were obscured by those from the major isomer; ratio of isomers 3:2, $\delta^{19}$F (benzene) $\pm$3.07 (6F, m), and 5.88 (6F, m), p.p.m., $\delta^{31}$P (benzene) -5 p.p.m., (Found: C, 43.1; H, 3.6; F, 39.0. C$_{21}$H$_{23}$F$_{12}$O$_{3}$P requires C, 43.3; H, 3.95; F, 39.15%). Elution with ether yielded 1-(p-methoxyphenyl)-2,2,3,4,4-pentamethylphosphetan 1-oxide as a mixture of isomers (0.4g, 75%), i.r. and n.m.r. spectra identical to those of an authentic sample.

Reaction of $\tau$-1-(2'-Methylallyl)-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide with Hexafluorooacetone.

Hexafluorooacetone (2ml) was condensed into a stirred solution of the phosphine (0.30g) in pentane (25ml) at -78°. After 30 minutes the solution was allowed to warm to 0° and the solvent removed under reduced pressure (100mm). The residue (0.7g, 90%) was found by $\delta$H and $\delta^{19}$F n.m.r. to be a mixture of the 1-(hexafluoroisopropoxy)phosphetan 1-oxide and 5,5,5-trifluoro-2-methyl-4-trifluoromethyl-1,3-pentadiene. Chromatography on basic alumina and elution with pentane yielded the diene (0.1g, 30%), v$_{max}$. (film) 1687, 1637, 1460, 1330, 1265, 1240, 1209, 1112, 962, 886, and 753 cm$^{-1}$, m/e 204, 189, 185, 163, 135, and 41, r 2.50 (1H, q, $\delta$HF 7 Hz), 4.90 (1H, s), 5.03 (1H, s), and 6.23 (3H, s), $\delta^{19}$F -3.71 (3F, dq, $\delta$ 7, $\delta$HF 7 Hz), and $\pm$0.83 (3F, q, $\delta$ 7 Hz) p.p.m. The diene could not be obtained analytically pure. Elution with ether-pentane (1:20) yielded 1-(hexafluoroisopropoxy)-2,2,trans-3,4,4-pentamethylphosphetan 1-oxide (0.30g, 60%), m.p. and mixed m.p. 62-64°, n.m.r. and i.r. spectra identical to those of an authentic sample.
**Reaction of \( r-l-(\text{Dimethylamino})-2,2,\text{trans}-3,4,4\)-pentamethylphosphetan with Hexafluoroacetone.**

Hexafluoroacetone (5ml) was condensed into a stirred solution, of the phosphetan (1.9g) in pentane (40ml) at \(-78^\circ\). After 4 hours the solution was allowed to warm to 0° and the solvent removed under reduced pressure. Chromatography of the crude product on basic alumina (100g) and elution with pentane yielded the 2:1-adduct (2.6g, 50%), m.p. 65-75° (from pentane), b.p. 90-95°/0.5mm, \( \nu_{\text{max}} \) 1260, 1235, 1204, 1109, 1085, 943, and 880 cm\(^{-1}\), m/e 519, 500, 450, 419, 407, and 406, \( \tau \) (benzene) 7.48 (1H, q, \( J \) 7 Hz), 7.50 (6H, d, \( J_{PH} \) 11 Hz), 8.58 (6H, d, \( J_{PH} \) 20 Hz), 8.92 (6H, d, \( J_{PH} \) 20.5 Hz), and 9.40 (3H, d, \( J \) 7 Hz), \(^{19}\text{F} \) (dichloromethane) +4.50 (6F, m), and +6.14 (6F, m) p.p.m., \(^{31}\text{P} \) (benzene) -15.5 p.p.m. (Found: C, 37.15; H, 4.3; F, 43.2.

\( \text{C}_{16}\text{H}_{22}\text{F}_{12}\text{NOP} \) requires C, 37.0; H, 4.6; F, 43.9%).

**Reaction of the Hexafluoroacetone Adduct of \( r-l-(\text{Dimethylamino})-2,2,\text{trans}-3,4,4\)-pentamethylphosphetan with 1,1,1,3,3,3-Hexafluoroisopropanol.**

Hexafluoroisopropanol (0.34g, 2mmol) and the adduct (0.26g, 0.5mmol) were stirred together for 5 minutes at 0° and then the excess hexafluoroisopropanol was removed under reduced pressure to yield the 2:1-hexafluoroacetone adduct of \( l-(\text{hexafluoroisopropoxy})-2,2,3,4,4\)-pentamethylphosphetan (0.36g) m.p. 37-40°. The n.m.r. spectrum in a variety of solvents showed the presence of one isomer only, \( \nu_{\text{max}} \) 1257, 1233, 1213, 1196, 1123, 1106, 1095, 945, and 870 cm\(^{-1}\), m/e 642, 623, 573, 310, 251, 250, and 159, \( \tau \) (benzene) 4.60 (1H, sept, \( J_{HF} \) 6 Hz), 8.20 (1H, dq, \( J \) 7, \( J_{PH} \) 1Hz), 8.83 (6H, d, \( J_{PH} \) 23 Hz), 8.88 (6H, d, \( J_{PH} \) 23 Hz), and
9.47 (3H, dd, \( J_{PH} = 1 \) Hz), \(^{19}\text{F} \) (dichloromethane) +5.06 (12F, s), and +9.76 (6F, d, \( J_{HF} = 6 \) Hz), p.p.m. \( ^{31}\text{P} \) n.m.r. (benzene) -15.3 p.p.m. 

(Found: C, 31.9; H, 2.7; F, 53.45. \( \text{C}_{17}\text{H}_{17}\text{F}_{16}\text{O}_{2}\text{P} \) requires C, 31.8; H, 2.65; F, 53.25%).

**Reaction of 2,2,3,4,4-Pentamethyl-l-pyrroldylphosphetan with Hexafluoroacetone.**

Hexafluoroacetone (5ml) was condensed into a stirred solution of the phosphetan (1.6g) in pentane (25ml) at -78°. After 30 minutes the solution was allowed to warm to 0° and the solvent removed under reduced pressure to yield the 2:1-adduct (3.0g, 74%), m.p. 108-118° (from pentane), \( \nu_{\text{max}} \) 1262, 1238, 1204, 1111, 949, 882, and 748 cm\(^{-1}\), m/e 545, 530, 526, 475, 475, and 433, \( \tau \) 6.33-6.83 (4H, m), 8.00-8.33 (4H, m), 8.63 (6H, d, \( J_{PH} = 21 \) Hz), 8.68 (6H, d, \( J_{PH} = 22 \) Hz), and 9.13 (3H, dd, \( J_{PH} = 21 \) Hz), for the major isomer; the minor isomer had signals \( \tau \) 8.49 (6H, d, \( J_{PH} = 19.5 \) Hz), 8.72 (6H, d, \( J_{PH} = 20 \) Hz), and 9.23 (3H, dd, \( J_{PH} = 1.5 \) Hz), the ring 3-H signal could not be identified for either isomer, ratio of isomers 2:1 after purification, \(^{19}\text{F} \) (benzene) +6.08 (6F, m), and +7.00 (6F, m) p.p.m., \(^{31}\text{P} \) (benzene) -11.2 p.p.m. (Found: C, 39.5; H, 4.25; F, 41.6. \( \text{C}_{18}\text{H}_{24}\text{F}_{12}\text{NO}_{2}\text{P} \) requires C, 39.65; H, 4.4; F, 41.85%).

**Reaction of 2,2,3,4,4-Pentamethylphosphetan with Hexafluoroacetone.**

Hexafluoroacetone (25g) was condensed into a stirred solution of the secondary phosphetan (4.1g) in pentane (40ml) at -78°. After 30 minutes the temperature of the solution was allowed to rise to -20° while the excess hexafluoroacetone was collected in a solid carbon
dioxide trap. The quantity recovered was 15.2g, corresponding to 2 moles of hexafluoroacetone consumed per mole of phosphine (theoretical quantity used 9.4g, actual quantity 9.8g). Removal of the solvent under reduced pressure yielded a white solid (12.0g, 89%), m.p. 25-35° (decomp), νmax. 2244 cm⁻¹, τ 4.97 (0.5H, br. s), 7.63-8.17 (1H, m), 8.77 (12H, d, JPH 21 Hz), and 9.11 (3H, d, J 7 Hz), 19F (dichloromethane) +9.04 (s) and +9.34 (s) p.p.m., ratio 3:4. No 31P signal could be detected. An analysis could not be obtained owing to the unstable nature of the compound.

Thermolysis of the Hexafluoroacetone Adduct of 2,2,3,4,4-Pentamethylphosphetan.

A solution of the adduct (9.5g, 0.02mol) in benzene (100ml) was refluxed for 2 hours. Hexafluoroacetone (3.0g, 0.01mol) collected in a solid carbon dioxide trap connected to the reflux vessel. Removal of the solvent under reduced pressure yielded crude 1-hexafluoroisopropoxy-2,2,3,4,4-pentamethylphosphetan (5.0g, 81%), νmax. (film) 1456, 1374, 1289, 1265, 1218, 1196, 1105, 900, 870, 794, and 695 cm⁻¹, τ (benzene) 5.72 (IH, dsept., JHF 7, JPH 6 Hz), 8.18 (IH, dq, J 7, JPH 2 Hz), 8.92 (6H, d, JPH 12 Hz), 9.03 (6H, d, JPH 18 Hz), 9.42 (3H, d, J 7 Hz), for the major isomer and 5.72 (IH, dsept., JHF 7, JPH 6 Hz), 7.33 (1H, q, J 7, Hz), 8.90 (6H, d, JPH 20 Hz), 9.10 (6H, d, JPH 17 Hz), and 9.42 (3H, d, J 7 Hz) for the minor isomer, ratio of isomers 4:3 by integration of the 3-H signals, 19F (neat) +11.14 p.p.m., (dd, JHF 7, JPH 6 Hz) for the major isomer and +11.71 p.p.m. (dd, JHF 7, JPH 6 Hz) for the minor isomer; ratio of isomers 55:45, by integration of the 19F signals.
Addition of Sulphur to 1-Hexafluoroisopropoxy-2,2,3,4,4-pentamethylphosphetan.

Sulphur (0.35g), the phosphetan (3.10g), and a small crystal of aluminium chloride were refluxed in benzene for 12 hours. The solvent was removed and the residue chromatographed on basic alumina (100g). Elution with pentane yielded 1-hexafluoroisopropoxy-2,2,3,4,4-pentamethylphosphetan 1-sulphide as a mixture of geometrical isomers (3.2g, 94%), b.p. 73-75°/1.5mm, ν_max. 1452, 1289, 1261, 1229, 1195, 1108, 870, 819, 762, 734, and 685 cm⁻¹, m/e 342, 327, 323, 300, 273, 272, 191, 121, and 105, τ (benzene) for the major isomer; 4.28 (1H, dsept., J_HF 6, J_PH 4 Hz), 8.70 (6H, d, J_PH 24 Hz), 8.93 (6H, d, J_PH 22 Hz), and 9.37 (3H, dd, J 7, J_PH 3 Hz), the 3-H signal could not be identified, τ for the minor isomer; 4.28 (1H, dsept., J_HF 6, J_PH 4 Hz), 7.78 (1H, q, J 7 Hz), 8.92 (6H, d, J_PH 22 Hz), and 9.38 (3H, d, J 7, Hz), ratio of isomers 7:5 from the ring methyl signals, ¹⁹F (benzene) +10.7 (d, J_HF 6 Hz) p.p.m. for the minor isomer and +11.2 (d, J_HF 6 Hz) p.p.m. for the major isomer, ratio of isomers 46:54 by integration of the ¹⁹F signals, (Found: C, 38.15; H, 4.9; F, 33.1. C₁₁H₁₇F₆O₂PS requires C, 38.6; H, 4.95; F, 33.35%).

Reaction of 1-Hexafluoroisopropoxy-2,2,3,4,4-pentamethylphosphetan with Hexafluoroacetone.

Hexafluoroacetone (8g) was condensed into a stirred solution of the phosphetan (4.6g) in pentane (50ml) at -78°. After 1 hour the major quantity of the hexafluoroacetone remained unreacted. The solution was allowed to warm to 20° while the hexafluoroacetone refluxed under a solid carbon dioxide condenser; most of the hexafluoroacetone was consumed.
within 30 minutes. The solution was allowed to warm to 0° and the excess hexafluoroacetone was collected in a solid carbon dioxide trap (quantity consumed 5g, 2 moles per mole of phosphetan). The solvent was removed under reduced pressure to yield a glassy solid, m.p. slightly below ambient. $^{19}$F n.m.r. showed the presence of the adduct from the secondary phosphetan as the major impurity; this was removed by refluxing a solution of the crude adduct in dichloromethane (50ml) and removing the resulting 1-hexafluoroisopropoxy phosphetan under high vacuum (0.1mm) at room temperature together with the solvent. Two recrystallisations from pentane at -78° yielded the 2:1-adduct of 1-hexafluoroisopropoxy-2,2,3,4,4-pentamethylphosphetan (4g, 42%), m.p. 33-38°, $\nu_{\text{max}}$. 1295, 1258, 1233, 1104, 944, 870 cm$^{-1}$, m/e 642, 623, 573, 310, 25(196x135), 250, and 159, $\tau$ (benzene) 4.60 (1H, sept., $J_{\text{HF}}$ 6 Hz), 8.82 (6H, d, $J_{\text{PH}}$ 23.5 Hz), 8.88 (6H, d, $J_{\text{PH}}$ 23.5 Hz), the 3-H signal could not be identified, $^{19}$F (dichloromethane) +5.06 (12F, s), and +9.76 (6F, d, $J_{\text{HF}}$ 6 Hz) p.p.m., $^{31}$P (benzene) -15 p.p.m.

Reaction of 2,2,3,4,4-Pentamethyl-l-phenoxyphosphetan with Hexafluoroacetone.

Hexafluoroacetone (3ml) was condensed into a stirred solution of the phosphetan (1.18g, equilibrium mixture of isomers) in pentane (25ml) at -78°. The solution was warmed to -25° and held at this temperature for 2 hours. Removal of the solvent under reduced pressure yielded a slurry of the crude adduct (2.7g, 95%), m.p. 40-40° (after distillation), b.p. 125/0.5mm, $\nu_{\text{max}}$. 1595, 1589, 1490, 1238, 1209, 1097, 959, 860, and 747 cm$^{-1}$, m/e 568, 549, 499, 498, 475, 456, and 237, $\tau$ (benzene) 2.50-3.00 (5H, m), 8.72 (6H, d, $J_{\text{PH}}$ 22.5 Hz), 8.92 (6H, d, $J_{\text{PH}}$ 22 Hz), and
9.39 (3H, d, $J_{PH}$ 7 Hz) for the major isomer; the minor isomer had signals 8.50 (6H, d, $J_{PH}$ 21 Hz), 8.92 (6H, d, $J_{PH}$ 22 Hz); the 3-H signals could not be detected for either isomer, ratio of isomers 33:67, $^{19}$F (dichloromethane) +4.9 p.p.m. (s), $^{31}$P (benzene) -16 p.p.m. (Found: C, 42.55; H, 3.85; F, 40.2. C$_{20}$H$_{21}$F$_{12}$O$_3$P requires C, 42.25; H, 3.7; F, 40.15%).

Reaction of 1-Chloro-2,2,3,4,4-pentamethylphosphetan with Hexafluoroacetone.

Hexafluoroacetone (10ml) was condensed into a stirred solution of the chlorophosphetan (3.6g) in pentane (50ml) at -78°. The solution was allowed to warm to -25° and held at the temperature for 3 hours. On recooling to -78° the adduct crystallised out as long prisms (3.8g, 49%), m.p. slightly above ambient, $v_{\text{max}}$ (dichloromethane) 1295, 1190, 1150, 1094, 1015, 965, 870, and 840 cm$^{-1}$, $\tau$ (CFCI$_3$) 7.08 (1H, dq, $J$ 7.5, $J_{PP}$ 1 Hz), 8.45 (6H, d, $J_{PH}$ 31 Hz), 8.60 (6H, d, $J_{PH}$ 28 Hz), and 9.11 (3H, d, $J_{PH}$ 7 Hz), $^{19}$F (CH$_2$Cl$_2$) +17.4 (6F, m), p.p.m. No analysis could be obtained owing to the unstable nature of the compound.

Decomposition of the Hexafluoroacetone Adduct of 1-Chloro-2,2,3,4,4-pentamethylphosphetan.

A solution of the adduct (5.0g) in dichloromethane (40ml) was refluxed for 4 hours. The $^{19}$F spectrum of the solution showed the absence of any fluorine-containing species, while a solid carbon dioxide trap attached to the system was found to contain hexafluoroacetone (2.0g, 51% recovery). Removal of the solvent under reduced pressure yielded 1-chloro-2,2,3,4,4-pentamethylphosphetan (1.7g,
81% recovery), of identical isomer ratio to the chlorophosphetan starting material.

Reaction of 2,2,3,4,4-Pentamethyl-1-phenylthiophosphetan with Hexafluoroacetone.

1). Under Normal Reaction Conditions.

Attempted reaction of the phosphetan with hexafluoroacetone for 4 hours at -78°, and 12 hours at -25°, resulted in the quantitative recovery of the phosphetan.

2). Under 'Forcing' Reaction Conditions.

Hexafluoroacetone (5ml) and the phosphetan (2.0g) were sealed into a thick-walled ampoule and set aside for 10 days. After this time the ampoule was opened and the white precipitate recrystallised from pentane to yield diphenyl disulphide (0.4g, 46%), m.p. and mixed m.p. 56-58°, i.r. spectrum identical to that of an authentic sample.

Preparation of o-Methoxyphenyldimethylphosphine Sulphide.

o-Methoxyphenyl magnesium bromide (0.05mol) in ether (25ml) was added dropwise to a solution of dimethylphosphinothioic chloride (6.4g, 0.05mol) in ether (50ml). The mixture was refluxed for 24 hours and then added slowly to ice-water (250g). The organic layer was washed with aqueous sodium hydroxide (1N. 5 x 50ml), dried, and evaporated and the residue chromatographed on basic alumina (250g). Elution with ether-light petroleum (1:20) yielded o-methoxyphenyldimethylphosphine sulphide (5.6g, 56%), m.p. 90-91° (from dichloromethane-light petroleum), \( \nu_{\text{max}} \) 1590, 1572, 1273, 1165, 1138, 1021, 919, 771, and 735 cm\(^{-1}\),
m/e 200, 185, 184, 168, 138, 107, 91 and 78, \( \tau \) 1.42-3.17 (4H, m), 6.05 (3H, s), and 7.98 (6H, d, \( \Delta_{pp} \) 14 Hz) (Found: C, 54.05; H, 6.55; P, 15.3. \( \text{C}_6\text{H}_{13}\text{OPS} \) requires C, 54.0; H, 6.5; P, 15.5%).

**Preparation of Difluoro(o-methoxyphenyl)dimethylphosphorane.**

An intimate mixture of o-methoxyphenyldimethylphosphine sulphide (4.5g) and antimony trifluoride (3.5g) was slowly heated to 100° over 4 hours at a pressure of 10mm. The temperature was held at 100° for a further 2 hours and then the volatile products were removed by distillation to yield the difluorophosphorane (2.9g, 62%), b.p. 126-128°/1.5mm, \( \nu_{max} \). (film) 1592, 1580, 1276, 1252, 1141, 1098, 1022, 975, 920, 758, 730, and 685 cm\(^{-1}\), \( \tau \) (\( \text{CH}_2\text{Cl}_2 \)) 2.27-3.33 (4H, m), 6.27 (3H s), and 8.03 (6H, d, \( \Delta_{pp} \) 17.5 Hz), \(^{19}\text{F} (\text{CFCI}_3) \) at +30°, +14.2 p.p.m. (br. s); at -50°, +7.7 p.p.m. (d, \( \Delta_{pp} \) 560 Hz) (rel. \( \text{CFCI}_3 \)), \(^{31}\text{P} + 16.5 \) p.p.m. An analysis was not obtained owing to the hygroscopic nature of the compound.

**Preparation of Dimethyl(1-napthyl)phosphine Sulphide.**

1-Napthyl magnesium bromide (0.1mol) in ether (100ml) was added dropwise to a stirred solution of dimethylphosphinothioic chloride (12.8g, 0.1mol) in ether (50ml). After refluxing for 24 hours the reaction mixture was added slowly to ice-water (250g). The organic layer was washed with aqueous sodium hydroxide (1N, 5 x 50ml), dried, and evaporated and the residue chromatographed on basic alumina (500g). Elution with ether-light petroleum (1:10) yielded dimethyl(1-napthyl) phosphine sulphide (15g, 62%), m.p. 101-102° (from chloroform-light petroleum), \( \nu_{max} \). 1590, 1289, 1148, 986, 951, 921, 801, 779, 742, 730
and 665 cm\(^{-1}\), m/e 220, 219, 205, 189, 171, 157, 128, and 127, 
\(\tau\) 1.83-2.67 (7H, m), and 7.97 (6H, d, \(J_{PH} 13\) Hz) (Found: C, 65.45; H, 5.75; P, 13.85. \(\text{C}_{12}\)H\(_{15}\)PS requires C, 65.5; H, 5.9; P, 14.1%).

**Preparation of Difluorodimethyl(1-napthyl)phosphorane.**

An intimate mixture of dimethyl(1-napthyl)phosphine sulphide (3.2g) and antimony trifluoride (2.7g) was slowly heated to 100° over 4 hours at a pressure of 1mm. The temperature was held at 100° for a further 2 hours and then the volatile products were removed by distillation to yield the difluorophosphorane (1.6g, 49%), b.p. 127-132°/0.3mm, m.p. 80-90°, \(v_{\text{max}}\) 1146, 1021, 990, 964, 920, 870, 850, 793, 768, and 701 cm\(^{-1}\), \(\tau\) (CFC\(_3\)) 1.50-2.83 (7H, m), and 7.88 (6H, d, \(J_{PH} 21\) Hz), \(^{19}\)F (CFC\(_3\)) +5.6 p.p.m. (d, \(J_{PF} 697\) Hz), (rel. CFC\(_3\)), \(^{31}\)P +17 p.p.m. An analysis was not obtained owing to the hygroscopic nature of the compound.

**Reaction of the 1,2-Oxaphosphetan Adduct with Hexafluoroisopropanol.**

A solution of the adduct (266) (0.55g, 1 mmol) in deuteriochloroform (1 ml) was treated with hexafluoroisopropanol (0.17g; 1 mmol). After 18 hours the \(^1\)H n.m.r. spectrum indicated the presence of two isomers, \(\tau\) (for the 'new' isomer) 2.78 (5H, s), 4.10 (1H, d, \(J_{PH} 8\) Hz), and 4.66 (1H, dsept, \(J_{FH} 6.5, J_{PH} 7\) Hz), the remainder of the spectrum was too complex for ready analysis, i.r. and mass spectrum as for the original isomer.

The adduct solution was heated to 60° over 24 hours to yield a solution of the isomers of 1-hexafluoroisopropoxy-2,2,3,4,4-pentamethylphosphetan 1-oxide, \(\tau\) (for the 'new' isomer) 4.73 (1H,sept,\(J_{FH} 6\) Hz), 3.73 (6H, d, \(J_{PH} 21\) Hz 8.75 (6H,d,\(J_{PH} 19\) Hz), and 9.05 (3H,d,\(J_{PH} 8\) Hz), i.r. and mass spectrum as for the cis isomer.
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SUMMARY

The alkaline hydrolysis of optically active 1-benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium iodide is shown to proceed with predominant retention of configuration. Pseudorotation of intermediate phosphoranes is suggested to explain the partial inversion observed during hydrolysis and the base-catalysed racemisation of this salt. The alkaline hydrolyses of 2- and 3-phospholenium salts are studied and the role of pseudorotation in determining the product distribution is discussed.

The ring opening of 1,2,2,3,3-pentamethyl-1-phenylphosphetanium iodide by the cyanide ion is suggested to involve a carbonium ion intermediate. A similar process may be involved in the reaction of chlorine with 2,2,3,3-tetramethyl-1-phenylphosphetan to give chloro-(2,2,3-trimethylbut-3-enyl)phenylphosphine. Cyclisation of this phosphine occurred on heating or on treatment with chlorine to give 2,2,3-trimethyl-1-phenyl-2-phospholen 1-oxide, while treatment with aluminium chloride gave a mixture of phospholen and phosphetan 1-oxides. The generality of these cyclisation reactions are investigated.

A variety of cyclic oxyphosphoranes of the phosphetans were prepared and a study made of the high energy pseudorotations available to these adducts. The process whereby the five-membered ring was placed diequatorial in these phosphoranes was not observed, however the equivalent process for the phosphetan ring was found to occur at temperatures accessible for study by n.m.r. spectroscopy. The energetic data so obtained is suggested to provide a limited scale of relative apicophilicities of the substituents on phosphorus
in phosphoranes. Deviations from the ordering expected on the basis of the electronegativities of the substituents are explained in terms of preferential equatorial π-bonding between ligand π-orbitals and the phosphorus d-orbitals. Applications of an apicophilicity scale are discussed. Attempts are made to observe an enhanced phosphorus-ligand bond rotational barrier due to the suggested π-bonding from aryl substituents and to modify this π-bonding by substituent effects.

Possible mechanisms for two reactions of the phosphetan oxyphosphoranes are discussed, nucleophilic substitution being favoured.