ASPECTS OF THE CHEMISTRY OF PHOSPHORUS
YLIDES AND PHOSPHORANES

by

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DEDICATION

This thesis is for my family and also for my first chemistry teacher, Sister Margaret of St. Joseph's Convent, St. Lucia.
Declaration

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted in any previous application for a higher degree.

The thesis describes results of research carried out in the Department of Chemistry, University of Edinburgh, under the supervision of Professor J. I. G. Cadogan since the 1st of October 1974, the date of my admission as a research student.

The following courses were attended during the period of research:-

Lab 10/29 seminars (three years attendance); 'Organophosphorus Reagents in General Organic Synthesis,' 5 lectures by Professor J. I. G. Cadogan and Dr. I. Gosney (University of Edinburgh); 'High Speed Liquid Chromatography,' 5 lectures by Professor J. H. Knox and Dr. J. Done (University of Edinburgh); 'NMR Spectroscopy,' 5 lectures by Dr. R. K. Harris (Varian Associates); 'Organic Sulphur Compounds in General Synthesis,' 5 lectures by Dr. D. Leaver (University of Edinburgh) and 'Petrochemical Research,' 5 lectures by members of the B. P. research group.
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**ABSTRACT**

The room temperature reaction of tervalent phosphorus reagents with 2-azido ketones and 2-azido oximes, in benzene, has been investigated. In some cases the products obtained were the expected iminophosphoranes, but in other instances, attack by oxygen and proton transfer led to the formation of novel amino-oxyphosphoranes. The chemistry of the derived pentaco-ordinate phosphoranes has also been investigated.

Of the several factors found to influence iminophosphorane vis-a-vis $P^V$ formation, the most important appeared to be the small ring effect and the electronic situation at phosphorus. The results indicated that enclosure of the phosphorus moiety in a small ring and the presence of electron-withdrawing groups at phosphorus favoured the formation of a pentaco-ordinate phosphorane.

The reactions of 1-phenyl-2-azidoethan-1-one O-methyl oxime with $P^{III}$ reagents were also investigated. A notable result was the formation of an iminophosphorane dimer, a $P^V$ species, from the reaction with 2-phenyl-1, 3, 2-dioxaphospholan. This appeared to demonstrate the power of the small ring effect since related acyclic and six-membered ring $P^{III}$ reagents yielded only iminophosphoranes.

In related studies, the room temperature reaction of 2-diazo ketones (azibenzils), with $P^{III}$ reagents yielded only the expected phosphinazines. Upon decomposition at high temperature these compounds gave several products including the corresponding phosphine
and phosphine oxide in a 1:2 molar ratio as well as a plethora of non-phosphorus-containing compounds. The nature of the products obtained indicated that a $P^V$ species was not involved in these decompositions. Instead, the phosphinazine apparently underwent an initial dissociation into a phosphine and a diazo ketone which subsequently reacted to give the observed multiplicity of products.
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Note on Nomenclature

A significant proportion of this work is concerned with the formation and characterisation of phosphoranes of general structure as shown below:

The nomenclature used for these compounds in this thesis is based on that recommended for similar systems by the Chemical Society.

These model structures and their accepted names are shown below:

2-methoxy-5-methyl-2,2,4-triphenyl-Δ\(^4\)-1,3,2-oxazaphospholine

1',4-diphenylspiro-[Δ\(^4\)-1,3,2-oxazaphospholine-2,1'-phosphetan]
INTRODUCTION
INTRODUCTION

Preamble

Phosphorus ylides were first prepared in the 1890s when Michaelis and co-workers apparently obtained the stable ylides, \((1a),^1 (1b)^2 \) and \((1c)^2 \) by treatment of the corresponding phosphonium salts with base. However, they assigned 'phosphonium betaine' structures e.g. \((2)\) to the substances and the true ylidic nature of the compounds was not proved until later work by Aksønes\(^3\) and Ramirez\(^4\).

In the 1920s Staudinger and his group\(^5-8\) carried out a series of remarkable pioneering experiments which provided the basis of much of present-day phosphorus ylide chemistry.

Widespread interest in ylides was not incited until the 1950s when Wittig and Geissler\(^9\) in a celebrated experiment, observed that treatment of methyltriphenylphosphonium iodide with phenyl lithium resulted in the formation of an ylide, methylenetriphenylphosphorane, which reacted with benzophenone to give triphenylphosphine oxide and diphenylethylene in 84% yield (Scheme 1). This general reaction of phosphorus ylides with carbonyl compounds had been discovered in the 1920s by...
Staudinger and co-workers. However Wittig's later observation led to the reaction being developed into one of the most versatile syntheses of olefins which has since found extensive use in preparative organic chemistry and is now universally known as the Wittig reaction. The importance of phosphorus ylides is derived mainly from their synthetic utility in a variety of reactions of which the Wittig is probably the most commonly used.

Much of the investigations into phosphorus ylide chemistry has involved the use of the methylenephosphoranes (3a). Their direct nitrogen analogues, the iminophosphoranes (3b), were first discovered in 1919 by Staudinger and Meyer. The iminophosphoranes appear to have similar chemistry to the methylenephosphoranes although, until recently, they had not been extensively investigated. Polymeric iminophosphoranes have become the subject of much study as they are proving increasingly
useful as fire retardants to improve the fire resistance of a number of materials including butadiene rubbers and viscose rayons. The polymers have also found uses as polyelectrolytes and additives for lubricating oils.

The iminophosphoranes and the methylenephosphoranes can be considered as nitrogen and carbon anions, respectively, which are stabilised by the adjacent phosphonium centre. Generally, the reactions of all phosphorus ylides reflect their nucleophilic character and the initial step in most reactions, particularly in polar media, is assumed to be electrophilic attack at ylidic carbon or nitrogen. Thus, the methylenephosphoranes undergo the usual carbanion reactions such as acylation and alkylation.

However, a characteristic feature of the phosphorus ylides arises because the phosphorus atom can become pentaco-ordinated. Thus, the betaines which are formed by initial electrophilic attack on the ylide can undergo subsequent nucleophilic attack at the positive phosphonium centre to form pentaco-ordinate phosphoranes e.g. (5) as intermediates or transition states. In some phosphorus ylide reactions P^V phosphoranes are formed directly without the intermediacy of a betaine. For example, Schlosser and co-workers have reported the results of low temperature
$^3$P n.m.r. spectroscopic studies which indicate that methyl- and ethyl-triphenylphosphoranes react with benzaldehyde and formaldehyde, in non-polar and salt free media, to give 1,2-oxaphosphetans (6) and not betaines (7) as detectable intermediates of the Wittig reaction (Scheme 2).

\[
\begin{align*}
\text{Ph}_3\text{P}^+ - \text{CHR}^1 \\
\text{HR}^1 \\
\text{HR}^2 \\
\text{R}^2 \text{CHO}
\end{align*}
\]

Scheme 2

\[
\begin{align*}
\text{Ph}_3\text{P}^+ - \text{HR}^1 \\
\text{HR}^2
\end{align*}
\]

This ability of phosphorus to expand its valence shell and form $P^V$ species has great significance in phosphorus chemistry. The Wittig reaction is only a particular example of a very general phenomenon in tetrahedral phosphorus chemistry whereby $P^V$ species are involved as intermediates in many reactions. It is generally assumed that substitution reactions at tetrahedral phosphorus proceed via $P^V$ species as outlined in Scheme 3.\(^{19}\) Therefore an understanding of the chemistry of pentaco-ordinate phosphoranes is necessary for mechanistic interpretation of numerous important phosphorus reactions\(^{20}\) including the Wittig.
Michaelis-Arbuzov and the biologically significant hydrolysis of phosphate esters. Indeed a great deal of the interest in P\textsuperscript{V} species arose when they were postulated as intermediates or transient species in such reactions particularly those of biochemical importance as the transformation of redox energy into the energy storehouse, ATP.\textsuperscript{21}

Stable pentaco-ordinate phosphorus compounds containing halogen atoms e.g. phosphorus pentachloride,\textsuperscript{22} PCl\textsubscript{5}, or with aromatic ligands e.g. pentaphenylphosphorane,\textsuperscript{23} Ph\textsubscript{5}P have long been well known. However it is only since the 1960s that it has been possible to prepare phosphoranes with a sufficient variety of ligands to allow detailed studies of their general chemistry. In this respect a significant breakthrough occurred in 1960 when Ramirez developed the reaction of diketones with phosphites and related compounds into a general synthesis of cyclic oxyphosphoranes (Scheme 4).\textsuperscript{24,25,26} Metastable oxyphosphoranes have been postulated as intermediates in the hydrolysis of phosphate esters.\textsuperscript{20} In 1966, Hellwinkel\textsuperscript{27} reported the first synthesis of an optically active
pentaarylphosphorane by the acid-catalysed synthesis of a resolved octahedral ion. At about the same time, Denney and his group developed a synthesis of open-chain oxyphosphoranes by the reaction of phosphorus(III) reagents with peroxides.

\[ \text{Scheme 4} \]

\[
P(\text{OR}^3)_3
\]

\[ \begin{align*}
\text{R}_1 & \quad \text{O} & \quad \text{R}_2 \\
\text{O} & \quad + & \quad \text{OR}^3 \\
\rightarrow & \quad \text{P(OR}^3)_3
\end{align*} \]

\[ \text{p(0R}^3) \]

N. m. r. spectroscopy is proving to be a valuable tool in the study of the chemistry of pentaco-ordinate phosphoranes and their intermediacy in phosphorus reactions. The highly shielded \( P^v \) species resonate at characteristically low frequency and \( \text{P n. m. r.} \) spectroscopy enables the detection of phosphoranes which are either too reactive or of insufficient lifetimes to be isolated. Thus, n. m. r. spectroscopy has been useful in the recent observation, in solution, of the first stable hydroxyphosphorane.

Such phosphoranes had long been postulated as intermediates in many substitutions at four-co-ordinate phosphorus. The recent expansion in the use of \( \text{P n. m. r.} \) spectroscopy has resulted in much valuable information as to the mechanism of reactions such as the Wittig, Michaelis-Arbuzov.

This present study of phosphorus ylides and pentaco-ordinate phosphoranes is an extension of work done by Scott. Cadogan, Gee,
Scott and Gosney\textsuperscript{31, 32} found that certain 1-N-(o-nitroaryl)-1,2,5-triphenylphospholimines (8), on heating in mesitylene at 150-160\textdegree, gave good yields of benzofurazans (10). Evidence from kinetic studies and competitive deoxygenations indicated a first order intramolecular reaction. This is consistent with a mechanism as outlined in Scheme 5 which involves nucleophilic attack by oxygen of the nitro group, on the phosphorus atom, to give the \( P^V \) species (9) as intermediate (Scheme 5).

Since the corresponding \( N\)-2-nitrophenyliminotriphenyolphosphorane, \( \text{Ph}_3^+\NN\text{Ar} \) and triethyl \( N\)-(2-nitrophenyl)phosphorimidate, \( (\text{EtO})_3^+\NN\text{Ar} \),
did not rearrange on heating, the enhanced reactivity of the phosphole imines was attributed, at least in part, to the relief of ring strain on formation of the $P^V$ intermediate (9). Small rings are known to favour pentaco-ordinate phosphorane formation. Also, it has been reported that, in SN2 reactions at carbon, ring strain can be relieved by formation of a five co-ordinate trigonal bipyramidal transition species. As will be discussed later, Westheimer and others, have invoked the 'small ring effect' to explain the difference in reactivity of many cyclic and acyclic phosphorus compounds.

Although trichloro-$N$-(2-nitrophenylimino)phosphorane ($\text{Cl}_3\text{P}-\text{NAr}$) gave low yields of benzofurazan, further studies by Scott indicated that reactivity of the phosphole imine was due mainly to the presence of the small ring. Thus, $N$-(2-nitrophenyl)iminodiethylphenylphosphorane (11) did not rearrange on heating whereas its cyclic analogue,

![PhP=NAr](image)

(11)

the 1-phenylphospholan imine (12) gave the benzofurazan in 36\% yield.

More recently, Taylor has carried out kinetic studies on a series of cyclic and acyclic $N$-(2-nitroaryl)iminophosphoranes using a combination of $^1H$ and $^{31}P$ n.m.r. spectroscopy. The results agree with Scott's and indicate that the rate of decomposition of the iminophosphoranes depended largely on the ring strain present in the phosphorus moiety. Interestingly, in only one case was there a detectable intermediate. Thus, a $^{31}P$ n.m.r. spectroscopic study of the thermolysis of the imino-
phosphorane derived from 2-phenyl-1,3,2-dioxaphospholan revealed
the presence of an intermediate species which absorbed -54 p. p. m.
The signal was assigned to the $P^v$ species (13). This was the first
direct evidence of the involvement of such species in these reactions.

As an extension of Scott's work it was decided to prepare and
investigate the intramolecular rearrangements of a number of bisfunc-
tional iminophosphoranes and, in particular, to attempt to utilise the
small ring effect for the synthesis of stable pentaco-ordinate phosphoranes
via such rearrangements. Since this thesis is concerned mainly with
iminophosphoranes and pentaco-ordinate phosphoranes, the introduction
which follows describes the chemistry of both these classes of compounds.
Particular emphasis is given to the preparation of pentavalent phosphoranes
by means of nucleophilic attack at tetrahedral phosphorus compounds.
A. The Chemistry of Iminophosphoranes

The iminophosphoranes are usually represented as resonance hybrids with two contributing canonical forms (14) and (15), the latter involving $\pi - \pi$ overlap between phosphorus and nitrogen. As with the carbon analogues, the amount of $\pi - \pi$ overlap is not clear and the exact nature of the ylidic bond is a matter of some debate.\(^{36}\)

X-Ray studies indicate an $sp^2$ hybridised nitrogen with a P-N-C bond angle close to 120° and a P-N bond length much closer to the double bond length (1.64\(\AA\)) calculated from covalent radii than the single bond length (1.78\(\AA\)). Thus, N-methyl iminodifluorodiphenylphosphorane (16)\(^{37}\) and N-p-bromophenyliminotriphenylphosphorane (17)\(^{38}\) have been reported to have P-N-C bond angles of 119° and 124° respectively, and P-N bond lengths of 1.64\(\AA\) and 1.57\(\AA\) respectively. The high P-N bond strength of iminophosphoranes compared with aminophosphonium salts has also been interpreted to indicate some delocalisation of charge from nitrogen to phosphorus as in (15).\(^{39}\) However, the dipole moment
of iminophosphoranes suggest that the P-N bond is quite highly polarised but this does not preclude structures such as (15), since the dipole may well derive mainly from $\sigma$-electron displacement.

A.1 Preparation of Iminophosphoranes

The three major methods of preparing iminophosphoranes are by the action of azides on phosphorus(III) reagents, by the reaction of phosphines with substituted amines, and by treatment of dihalophosphoranes with amines.

(a) Iminophosphoranes from Azides and Phosphorus(III) Reagents

By far the most widely used method is the reaction of azides with tervalent phosphorus compounds. This reaction was first used to prepare iminophosphoranes by Staudinger and Meyer in 1919 and is now called the Staudinger reaction. It is generally accepted that the reaction proceeds via a triazine (18), the so-called Staudinger adduct, which subsequently loses nitrogen to give the iminophosphorane (Scheme 6). The

$$R_3P + R^1N_3 \rightarrow R_3P^+\overline{N}(N_2)R^1$$

(18)

$$R_3P^+\overline{NR}^1 + N_2$$

(19)

Scheme 6

reaction provides a very versatile route to iminophosphoranes. Among the phosphorus(III) reagents that have been used in the Staudinger reaction...
are phosphines, phosphites, and chlorophosphines. A wide variety of azides can also be used including \( R_1 \)-alkyl, \( R_2 \) aryl, organophosphorus, and organometallic. For example, the iminophosphoranes (20, \( R_1 \)=OR, \( R_2 \)=Me, Et, Z=O, S, n=0-3) which have been reported to have potential herbicidal and defoilant activity, were prepared by this route. Similarly (21) has been obtained by the reaction of azides with the iminophosphoranes, \( R_1 N-P=NR_2 \).

\[
\begin{align*}
(\text{Et}_2\text{N})_n R_3^1 P &\equiv \text{N} & (\text{P}(\text{NB})_2 R_2 N_2) \\
(20) & & (21)
\end{align*}
\]

The mechanism of the Staudinger reaction appears to involve nucleophilic attack by the phosphorus on the azide. Horner and Gross have reported a \( p \) value of +1.36 for the reaction of triphenylphosphine with a series of substituted phenyl azides. Also various workers have shown that the rate of the reaction increases with increasing nucleophilicity of the phosphorus reactant and increasing electrophilicity of the azide. Thus, the observed reactivities of various phosphines in decreasing order are \( (\text{C}_5\text{H}_{10}\text{N})_3^1 \text{P} > \text{Et}_3\text{P} > \text{Ph}_3\text{P} > (\text{EtO})_3\text{P} > (\text{PhO})_3\text{P} > \text{PCl}_3 \), phosphorus trichloride being non-reactive.

A number of intermediate triazines have been isolated. The results suggest that the linear structure (22a) is common, although in certain cases, e.g. when \( R_1 \) is capable of stabilising structure (22b), the non-linear adduct may be formed. Thus, Bergman and Wolf have isolated the adduct from the reaction of triphenylphosphine and triphenyl-
methyl azide. On heating the adduct lost nitrogen to give the imino-phosphorane which was characterised by the formation of a Schiff base with ketene. Later, Leffler and his co-workers\textsuperscript{52} characterised this adduct as the linear triazine (22a), largely on the evidence that no azide absorption could be observed in its i.r. spectrum although they could not obtain the iminophosphorane. However, on standing in solution, the adduct seemed to dissociate as an azide absorption slowly appeared in the i.r. spectrum. Similarly, Bock and Wiegrass\textsuperscript{53} have isolated a linear adduct with no azide absorption from the reaction of p-toluene sulphonyl azide with triphenylphosphine. In another study, Franz and Osuch\textsuperscript{54} have reported that the crystalline adduct obtained from benzenesulphonyl azide and triphenylphosphine showed an azide absorption in solution but not in the solid state. To explain the spectroscopic data Leffler and Temple\textsuperscript{55} have suggested that reversible triazine formation was occurring.

Leffler and Temple\textsuperscript{55} also investigated the reaction of substituted phenyl azides with substituted triphenylphosphines. The results indicated that the reaction passed through two isomeric transition states and an intermediate complex, all of which had empirical formula $\text{Ar}_3\text{P}.\text{ArN}_3$. E.s.r. studies, radical chain transfer agents or inhibitors gave no evidence of the reaction being a free radical process. On the basis of the kinetic measurements the authors postulated a four-membered transition state (23) for triazine decomposition.

From mass spectroscopic results using $^{15}$N-labelled compounds, Bock and Schmoller\textsuperscript{56} concluded that it is the terminal nitrogens of the azide that are always lost, thereby supporting a mechanism for triazine decomposition as shown in Scheme 7.
The reaction of hexamethyolphosphorus triamide with alkyl and phenyl azides has been investigated. The intermediate triazines (24) were isolated in many cases and the results of kinetic studies of their thermal decomposition have been interpreted to the involvement of a four-centered transition state such as (25).

\[
\begin{align*}
\text{R}_3\text{P} \equiv \text{N} & \equiv \text{N} \equiv \text{NR}^1 \quad \rightarrow \quad \text{R}_3\text{P} \equiv \text{NR}^1 \\
\text{N} & \equiv \text{N} \\
\end{align*}
\]

\[(23)\]

\[
\begin{align*}
\text{R}_3\text{P} \equiv \text{NR}^1 + \text{N}_2
\end{align*}
\]

Scheme 7

Schwiezer and his co-workers have carried out a study of the decomposition of N-tosyltriphenylphosphazide (22; R=Ph, \(R^1 = \text{Tos}\)) and report that the results are in agreement with the mechanism outlined in Scheme 7. Thus at -10-39°C, no triphenylphosphine was observed. At the latter temperature very rapid decomposition of the phosphazide occurred as evidenced by nitrogen evolution and peak enhancement with authentic N-tosyltriphenylphosphinimine (26; \(R^1 = \text{Tos}\)). These results appeared to rule out alternative mechanisms such as the one outlined in Scheme 8.
The linear triazine structure was also confirmed by i.r. spectroscopic data of $^{15}$N-isotopically labelled derivatives, in the tosylazide and triphenylphosphine case. Further chemical evidence for the unbranched phosphazide structure was obtained by Mosby and Silva. They reported that the reaction of 2,3-bisazidonaphthoquinone with triphenylphosphine gave in addition to the expected iminophosphorane a phosphinyl derivative of naphtho(2,3-d)triazole-
dione (27) whose formation can only be explained by a linear phosphazide intermediate.

However, Thayer and West\textsuperscript{47} have characterised the adduct from triphenylsilylazide as the non-linear structure (28) since the compound

\[ \text{Ph}_3\text{P}^+ - \text{N} - \text{SiPh}_3 \quad \text{Ph}_3\text{P} - \mathbf{N\text{SiPh}_3} \]

(28)

exhibited an azide absorption at 2018 cm\textsuperscript{-1} both in solution and as a solid. The adduct decomposed easily on heating to give the iminophosphorane (29). Johnson\textsuperscript{10} has suggested that the formation of the non-linear adduct with triphenylsilyl azide but not with triphenylmethyl azide may be due to extra stability in (28) gained by delocalisation of the lone pair of electrons on nitrogen to the 3d orbitals of both phosphorus and silicon.

The ease of formation of the iminophosphorane from (28) provides some evidence for the non-linear structure. Leffler and his co-workers\textsuperscript{52} have obtained linear phosphazides from triphenylmethyl azide and 9-azido-fluorene which decompose at almost the same temperature as the free azide to give azide decomposition products but not iminophosphoranes. Leffler has suggested that this is because there is too much steric crowding in the linear phosphazides to allow formation of the necessary four membered transition state for nitrogen elimination. It might be expected that in the triphenylsilyl azide case, if (28) were a linear adduct, the bulky groups would similarly prevent iminophosphorane formation.
The triazine (30) from o-azidobenzoic acid and triphenylphosphine has been reported to be surprisingly stable, remaining undecomposed on heating in the solid state to $150^\circ$ but decomposing to the iminophosphorane on heating in toluene under reflux. The i.r. spectrum showed the OH stretching absorption to be shifted to a lower frequency indicating the presence of hydrogen bonding. In view of this it is likely that there is strong interaction between the ortho carboxylic acid group and the triazine nitrogen as in (30).

(b) **Iminophosphoranes from Aminophosphonium salts and Bases**

In a reaction analogous to the 'salt method' for the preparation of methylene phosphoranes, iminophosphoranes have been obtained by the treatment of aminophosphonium salts with a number of bases including ammonia, sodium amide and magnesium hydride. The reaction is reversible, iminophosphoranes reacting with acids to form aminophosphonium salts (Scheme 9).
Aminophosphonium salts can be prepared by nucleophilic displacement by phosphines on substituted amines (Scheme 10). This method has been used with chloroamine and its derivatives (31; \(X=\text{Cl}\)) and hydroxylamine-\(\text{O}\)-sulphonic acid (31; \(X=\text{HSO}_3\), \(R=\text{H}\)). Use of the sodium salts of the chloroamines and dichloroamines in the

\[
\begin{align*}
\text{R}_3\text{P} & \quad + \quad \xrightarrow{\text{base}} \quad \text{R}_3\text{P}^+\text{NHR} \\
\text{X} & - \quad \text{NHR} \\
\text{X}^- \\
(31)
\end{align*}
\]

reactions results in direct formation of the iminophosphorane without the necessity of adding base. Schonberg and Singer have obtained sulphonyliminophosphoranes from the reaction of \(N,N\)-dichlorosulphonamides with triphenylphosphine in the presence of copper powder.

(c) **Iminophosphoranes from Dihalophosphoranes and Amines**

Possibly the most general method of preparing iminophosphoranes is that developed by Horner and Oedingen involving reaction of
primary amines and related compounds with dihalophosphoranes (Scheme 11). The reaction probably involves initial attack by amine on the

\[ \text{R}_3\text{P} \text{X}_2 + \text{H}_2\text{NR}^1 \rightarrow \left[ \text{R}_3\text{P}^+\text{NH}_2\text{R}^1 \right] \text{X}^- \]

\[ \text{R}_3\text{P} \equiv \text{NR}^1 \]

Scheme 11

phosphorane followed by double deprotonations. In the case of the arylamines and dibromotriphenylphosphorane, the reaction is carried out in the presence of two equivalents of triethylamine which removes the acid to give the iminophosphoranes (32; R=Ph, R^1=Ar) in good yields. By contrast the reaction of alkylamines and dibromotriphenylphosphorane in the presence of triethylamine results in the isolation of the phosphonium salt (33; R=Ph, R^1=alkyl). This salt is readily converted to the iminophosphorane by stronger bases such as sodium amide in liquid ammonia. In many cases heating without the presence of base, lead to dehydrohalogenation.

This method is particularly valuable in cases where the azide preparation fails e.g. in the formation of iminophosphoranes derived from phosphorus trichloride which is not sufficiently nucleophilic to attack the azide. Thus, reaction of the alkylamines (34) with pentachlorophosphorane gives good yields of the iminophosphoranes (35) or their dimers.

\[ \text{RNH}_2 + \text{PCl}_5 \rightarrow \text{RN} \equiv \text{PCl}_3 + 2\text{HCl} \]
Reaction of hydrazine with dibromotriphenylphosphorane results in the formation of either the iminophosphorane (36) or, in the presence of excess phosphine dihalide, the bisiminophosphorane (37).

\[
\text{Ph}_3\text{PBr}_2 + \text{N}_2\text{H}_4 \xrightarrow{\text{NaNH}_2} \text{Ph}_3\text{P=NNH}_2
\]  

(36)

\[
2 \text{Ph}_3\text{PBr}_2 + \text{N}_2\text{H}_4 \xrightarrow{\text{NaNH}_2} \text{Ph}_3\text{P=NN=PPPh}_3
\]  

(37)

Gotsmann and Schwarzman have adapted this procedure in the preparation of iminophosphoranes by reaction of phosphine, amine and halogens in a single step.

(d) Other Methods

Apart from these general methods of preparing iminophosphoranes, there are many less widely applicable preparations, some of which will be described below.

There are a number of iminophosphorane preparations involving the use of phosphonium ylides. For example, reaction of the phosphonium ylides (38) with Schiff’s bases give iminophosphoranes (39) possibly via a Wittig type intermediate (40).

\[
\text{Ar}_3\text{P=CHAr}  \quad (38) \quad \xrightarrow{R_1\text{NCHR}} \quad \text{Ar}_3\text{P=NR}_1  \quad (39)
\]

(40)
Similarly phosphonium ylides such as (38) react with nitriles to give iminophosphoranes (Scheme 12). 72, 73

$$\text{PhCN} + \text{ArHC} \rightarrow \text{ArPH}_{3}$$

\[ \text{ArCN} \]

\[(38)\]

**Scheme 12**

The more stable phosphonium ylides react only with activated nitriles such as $\text{CF}_3\text{C}≡\text{N}$ or $\text{CF}_3\text{C}≡\text{N}$.

Aminophosphines react with activated olefins to give iminophosphoranes 74 (Scheme 13).

$$\text{Ph}_2\text{PNHPh} + \text{H}_{2}\text{C}≡\text{CHR}\rightarrow \text{Ph}_2\text{P}_\text{NHPh}$$

**Scheme 13**

In a similar manner the cyclic aminophosphite (41) reacts with activated olefins to yield iminophosphoranes of type (42; $X=\text{CN}$, $\text{CO}_2\text{Me}$). 75
Reaction of aminophosphines with p-nitrobenzaldehyde and benzil affords the iminophosphoranes (43) and (44) respectively, presumably by initial attack of phosphorus on carbonyl oxygen followed by proton transfer.

The acyclic aminophosphite (45) reacts with the activated ketone (46) to give the product of attack at oxygen, the iminophosphorane (47).
Treatment of tetraphenyolphosphonium chloride with sodium amide gives triphenyliminophosphorane (48) which is a useful precursor to

$$\text{Ph}_4\text{P}^+ \text{Cl}^- + \text{KNH}_2 \rightarrow \text{Ph}_4\text{PNH}_2$$

more complex iminophosphoranes (vide infra). Other routes to (48) include the reaction of phosphines with chloroamine or hydroxylamine-O-sulphonic acid, described earlier, and cleavage of N-trimethylsilyliminophosphorane (49) in methanolic sulphuric acid. 79

$$\text{Ph}_3\text{P}==\text{NSiMe}_3$$

Kirsanov and his co-workers 80 have used (48) to prepare N-substituted iminophosphoranes as shown in Scheme 14. The iminophosphorane can also be alkylated 81 and acylated 60 to produce other iminophosphoranes, but the maximum yield of substituted iminophosphorane that can be obtained is 50% since the intermediate phosphonium salt is
Scheme 14

deprotonated by another molecule of the parent iminophosphorane (Scheme 15).

\[ (48) + RX \rightarrow \text{Ph}_3\text{PNHR} \]

\[ \text{Ph}_3\text{PNR} + \rightarrow \text{Ph}_3\text{PNH}_2 \]
N-Sulphinylsulphonamides react with triphenylphosphine, triphenylphosphine oxide or triphenylphosphine sulphide to give $\text{N-tosyl-iminophosphoranes} (50)^{82}$ (Scheme 16).

\[ \text{RSO}_2\text{NSO} \rightarrow \]

\[ \text{Ph}_3\text{PO} \rightarrow \text{Ph}_3\text{PS} \]

\[ (50) + \text{SO}_2 \rightarrow \text{Ph}_3\text{P} \rightarrow (50) + \text{S}_2\text{O} \]

\[ \text{Ph}_3\text{P} = \text{NSO}_2\text{R} + \text{SO} \]

\[ (50) \]

Scheme 16

Treatment of $\text{N}$-chloriminocarboxylic acid derivatives with triphenylphosphine gives iminophosphoranes presumably via the intermediacy of a phosphonium salt (51).$^{83}$ In a related reaction $\text{N}$-chloro-

\[ \text{Ph}_3\text{P} + \text{RC} = \text{NCl} \rightarrow \text{Ph}_3\text{P}^+ \text{N} = \text{CR} \text{Cl}^- \]

\[ \text{OR} \rightarrow \text{OR}^1 \]

$^{83}$

amidines form iminophosphoranes of type (52) on treatment with triphenylphosphine (Scheme 17).$^{84}$
Amides of sulphonic and carboxylic acids and anilines form trichloroiminophosphoranes (53) on reaction with phosphorus pentachloride. Treatment of (53) with alkoxides and Grignard reagents give the phosphorimidates (54) and iminophosphoranes (55), respectively.

Stegman and Bauer have obtained cyclic iminophosphoranes (57) by thermal cyclisation of the 2-hydroxyiminophosphoranes (56). These compounds were also prepared in 52-68% yield by a modification of Horner and Oediger's method followed by loss of hydrogen chloride.

Schmidpeter and Zeiss have prepared cyclic iminophosphoranes by the 1,3-dipolar cycloaddition of methyleneaminophosphines to electrophilic olefins and acetylene dicarboxylates as shown in Scheme 18.
Scheme 18
A.2 Reactions of Iminophosphoranes

The reactions of iminophosphoranes are similar in many respects to those of the isoelectronic methylenephosphoranes and an important factor in the reactions is the nucleophilicity of nitrogen. As with their carbon analogues, a characteristic feature of iminophosphorane reactions is the ready tendency to form compounds containing the strong phosphorus-oxygen double bond. The phosphorus-oxygen double bond has been calculated to have a bond energy of 535 kJ mol\(^{-1}\) in triphenylphosphine oxide, the phosphoryl compound usually involved in these reactions. The general aspects of the reactions of iminophosphoranes are described below under the following headings: basicity and hydrolysis, acylation and alkylation, Wittig-type reactions with aldehydes and ketones, reaction with other multiple bonds, reactions with 1,3-dipoles and finally other reactions.

(a) Basicity and Hydrolysis

Like their carbon analogues, iminophosphoranes are basic and form aminophosphonium salts on treatment with acid. As might be expected the basicity of the iminophosphoranes can be correlated with the degree of charge resident of a nitrogen e.g. the presence of electron-withdrawing substituents on nitrogen reduces the basicity of the iminophosphorane.

The basicity of ylides is an important factor in their hydrolysis, the first step of which is usually assumed to be protonation of nitrogen to form an aminophosphonium salt. 5,46,60,61,91,92 The latter then undergoes nucleophilic attack by water to form a pentaco-ordinate
phosphorane which finally collapses to give a phosphine oxide and amine. The reactivity towards hydrolysis depends on the basicity of the iminophosphorane. Thus, the parent iminophosphorane and the N-alkyliminophosphoranes are hydrolysed rapidly by exposure to moist air \(^{60, 67}\) whereas \(^{24, 56}\) the less basic N-aryliminotriphenylphosphoranes are stable on exposure to the atmosphere and in aqueous solution but are hydrolysed rapidly in dilute acid media. \(^{5}\) Similarly N-(triphenylsilyl) iminotriphenylphosphorane is hydrolysed only in the presence of strong acid.

Some evidence for the intermediacy of pentaco-ordinate phosphoranes in the hydrolysis of iminophosphoranes has come from studies by Horner and Winkler \(^{92}\) of the hydrolysis of the optically active N-(p-nitrophenyl) iminomethylphenylpropylphosphoranes. The reaction proceeds mainly but not exclusively, with inversion at phosphorus indicating the occurrence of a mechanism as outlined in Scheme 19.

\(_N\)-Trimethylsilyl)iminotriphenylphosphorane has been reported to undergo cleavage of the Si-N bond in methanolic sulphuric acid to form methoxytrimethylsilane and iminotriphenylphosphorane (Scheme 20). \(^{41}\) It has been suggested \(^{10}\) that in this case the intermediate aminophosphonium salt is probably best represented by structure (58).
Scheme 19

\[ \text{Ph}_3\text{P} \equiv \text{NSiMe}_3 + \text{H}_2\text{SO}_4 \xrightarrow{\text{MeOH}} \left[ \text{Ph}_3\text{P} \equiv \text{NHSiMe}_3 \right] \quad (58) \]

Scheme 20

\[ \text{Ph}_3\text{P} \equiv \text{NH} + \text{MeOSiMe}_3 \]
Phosphorimidates\textsuperscript{93} and trichloroiminophosphoranes\textsuperscript{87} on hydrolysis undergo nucleophilic displacement of the O-alkyl or O-aryl and chloride groups to give phosphoramidates (59) and aminodichlorophosphine oxides (60), respectively.

\begin{align*}
\text{(59)} & \quad (\text{RO})_2P-NHR^1 \\
\text{(60)} & \quad Cl_2P-NHR^1
\end{align*}

Stegman and co-workers\textsuperscript{94, 95} have observed the intramolecular addition of O-H to the $\hat{P}-\hat{\Lambda}$ group of certain iminophosphoranes.

\begin{align*}
\text{(61)} & \quad \text{X-} \quad \text{N=PR}_3 \\
\text{(62)} & \quad \text{X-} \quad \text{NHR}^1 \quad \text{PR}_3
\end{align*}

Thus, the iminophosphoranes (61), easily prepared by the Staudinger reaction of 2-azidophenols with phosphorus(III) reagents, are found to exist in equilibrium with the pentaco-ordinate phosphorane (62). As will be discussed later, the position of the equilibrium depends on the substituents attached to the phosphorus atom and to the aromatic ring, and on the temperature and solvent used. The authors stated that the reaction conditions can be varied to produce either iminophosphorane or pentavalent phosphorane. More recently other workers have reported similar intramolecular additions.\textsuperscript{96, 97, 98}
(b) **Acylation and Alkylation**

Iminophosphoranes can be acylated and alkylated in a similar manner to their carbon analogues (Scheme 21).

\[
R_3P=NR^1 + R^2X \rightarrow [R_3^+P-NR^1 R^2] X^-
\]

Scheme 21

As discussed previously, use of the parent iminophosphorane (63; \( R^1 = H \)) results in the preparation of acylated and alkylated iminophosphoranes. The substituted iminophosphoranes (63; \( R^1 \neq H \)) form \( N, N \)-dialkyl and \( N \)-alkylacyl-aminophosphonium salts on treatment with alkylating and acylating agents respectively.

Zbiral\(^9\) has prepared oxazolosteroids by the treatment of \( \alpha \)-azidosteroidketones with triphenylphosphine and acylating agents as shown in Scheme 22.
Zbiral and Bauer\textsuperscript{100} have obtained imidoyl halides (64) by treatment of $N$-alkyl- and $N$-aryl-iminophosphoranes with acyl halides. Kricheldorf\textsuperscript{101} has reported that reaction of $N$-(trimethylsilyl)iminophosphoranes with both acid anhydrides and acyl halides gives $N$-acylated iminophosphoranes (65).

\[
R^1N\equiv CXR^2 + \text{Ph}_3\text{P} \equiv \text{O} \\
R^1 = \text{aryl or alkyl} \\
\text{Ph}_3\text{P} \equiv \text{NR}^1 + R^2\text{COX} \\
R^1 = \text{SiMe}_3 \\
X = \text{Cl} \\
\text{Ph}_3\text{P} \equiv \text{NCO}R^2 + \text{Me}_3\text{SiCl} \\
(65)
\]

(c) \textbf{Wittig-type Reactions with Aldehydes and Ketones}

Iminophosphoranes undergo Wittig-type reactions with carbonyl compounds, eliminating the phosphorus moiety as its oxide,\textsuperscript{5, 60a, 70, 102-104} to give products containing the imine bond (Scheme 23).

\[
\text{R}_3\text{P} \equiv \text{NR}^1 + \text{R}^2\text{R}^3\text{C} \equiv \text{O} \rightarrow \text{R}_3\text{P} \equiv \text{O} + \text{R}^2\text{R}^3\text{C} \equiv \text{NR}^1 \\
(66) \\
\text{Scheme 23.}
\]
Johnson and Wong\textsuperscript{105} have investigated the reaction of a number of N-aryltriphenylphosphinimines (66), \( R = \text{Ph}, \quad R^1 = \text{Ar} \) with aromatic aldehydes and postulated that the reaction proceeds via the intermediacy of a betaine (67). In the series of N-phenyliminophosphoranes: (a) \( p \)-\( \text{NO}_2 \), (b) \( m \)-\( \text{NO}_2 \), (c) \( m \)-Cl, (d) \( p \)-Br, (e) \( H \), (f) \( p \)-Me, (g) \( p \)-\( \text{OMe} \) it was found that a Hammett plot showed straight-line behaviour for (a)-(e) whereas (e)-(g) gave a plot of opposite sign. The authors concluded that, in the reaction of aromatic aldehydes with iminophosphoranes, \( \text{Ph}_3\text{P}^+\text{N}^\cdot\text{C}_6\text{H}_4\text{X} \), the rate determining step changes from betaine formation to betaine decomposition as \( \text{X} \) changes from electron-withdrawing to electron donating. However, it was found that substitution of the phenyl groups attached to phosphorus by alkyl groups caused a rate increase of \( 3 \times 10^3 \). It would have been expected that the replacement of the phenyl groups by the electron donating alkyl groups should cause betaine decomposition to be the rate determining step and result in a similar lowering of the rate as observed for \( e \)-withdrawing groups in the substituted N-phenyl-triphenylininophosphoranes.

In contrast, Frøyen\textsuperscript{106} has studied the reaction between \( p \)-nitrobenzaldehyde and a series of N-phenyliminophosphoranes in benzene, acetone, DMF, and DMSO and interpreted the results to indicate the
direct formation of a 4-centred intermediate (68) rather than a betaine. Thus the rates were first order in imine and aldehyde and were also almost independent of the polarity of the solvent. Moreover, in H-bonding solvents, the rate of reaction increased which was assumed to be due to stabilisation of the transition state. Further support for oxazaphosphetan formation being rate determining was the observation of a ring effect in the reaction. Thus inclusion of the phosphorus in a ring as in \( \text{N-} \text{(phenyl)} \text{- imino-1-phenylphospholan} \) (69) caused a rate enhancement viz a viz the acyclic analogue, \( \text{N-} \text{(phenyl)} \text{- iminodiethylphenylphosphine} \) presumably due to a relief of angle strain in the former on going from the tetrahedral phosphorus to the five co-ordinate phosphorus intermediate.

Johnson and Wong\(^{107}\) have reported additional examples of the change in the rate determining step from betaine formation to betaine decomposition in the reactions of substituted \( \text{N-phenyltriphenylimino-phosphoran} \)es with substituted benzaldehydes. The reaction was found to be first order in both imine and aldehyde with a low energy of activation (8.46 kcal mol) and a large negative entropy of activation. The authors reported that \( \alpha \rho \)-value of 2.1 was obtained for variation of the substituent in the benzaldehydes and interpreted this to indicate that the rate constant for betaine decomposition is greater than that for betaine formation.

In the case of the Wittig reaction of carbon ylides, \(^{31}\)P n.m.r.
spectroscopy has provided direct evidence of oxaphosphetan formation in salt-free non-polar media. This confirms the results of several kinetic studies. However in the presence of lithium salts lithiated adducts of intermediate betaines, which are isolable in some cases, are formed. The presence of strongly-electron-withdrawing groups in the carbonyl compounds has also been found to favour betaine vs oxaphosphetan formation presumably by delocalising the negative charge.

Recently, direct evidence for oxazaphosphetan formation in the reaction of iminophosphoranes and carbonyl compounds has been obtained by Schmidpeter and von Griegern in a study of the reactions of the cyclic iminophosphoranes (70) with a number of ketones (Scheme 24). In this instance, stable, crystalline [2+2] cycloadducts (72) which displayed no tendency to go to the betaine (73), were obtained although some of the cycloadducts did decompose to the starting components in solution. High temperature and dilution were reported to favour this dissociation but generally, the stability of the adducts appeared to depend on the acceptor strength of the ketone (71a) < (71b) < (71c) < (71d) and the donor strength of the iminophosphorane (70a) > (70b). The authors concluded that the Wittig analogue of iminophosphoranes is more likely to involve a four-membered intermediate than a betaine. Concurrent with these studies, the reaction of the cyclic iminophosphoranes with a series of aldehydes (71; \( R^1 = H, \ R^2 = CCl_3, \ R^2 = C_6H_4NO_2, \ C_6H_5 \)) was also investigated but in no case was a detectable intermediate observed, a finding confirmed by independent study of the reaction of \( N \)-phenyliminophosphoranes and benzaldehyde in these laboratories.
Intramolecular Wittig-type reactions of iminophosphoranes have proved valuable in a number of syntheses.

Nitriles are obtained on heating N-acyliminophosphoranes and their thio analogues by intramolecular elimination of phosphine oxide or sulphide, respectively (Scheme 25).\(^{46, 54, 83, 103, 111-113}\)

\[
\begin{align*}
R_3P^+ &-N^- \quad \text{(heat)} \quad R_3PX \quad + \quad R^1C \equiv N \\
X &= \text{O or S}
\end{align*}
\]
Niclas and Martin \(^{114}\) have reported the formation of alkylisocyanates and alkylisocyanurates in yields of 20-62 and 15-26\% respectively, by thermolysis of \(N\)-alkoxycarbonyliminophosphoranes and \(N\)-alkoxycarbonyl phosphorimidates (Scheme 26).

\[
\text{ROC—N} = \text{PX}_3 \quad \xrightarrow{120-280^\circ} \quad \text{ROCN} \quad + \quad \text{X}_3\text{PO}
\]

\(X = \text{Ar, Bu}, \text{Bu}^n, \text{EtO}, \text{or PhO}\)

Scheme 26

Zbiral and Stroh \(^{115}\) have prepared tetrazoles from acylated iminophosphoranes as shown in Scheme 27. The acylations were carried

\[
\text{R}_3\text{PNR}^1 \quad + \quad \xrightarrow{X = \text{Cl}} \quad \text{R}_3^+\text{PNR}^1\text{COR}^2 \quad \xrightarrow{X = \text{N}_3} \quad \text{R}^1\text{N} \equiv \text{CR}^2 \quad + \quad \text{R}_3\text{PO}
\]

Scheme 27
out in the normal manner using acyl halides and also, in some cases, using acyl azides. Similarly iminonitriles (74) can be formed by acylation with acyl cyanides. 115

\[
\begin{align*}
R^2C\equiv NR^1 \\
C\equiv N
\end{align*}
\]

(74)

Zbiral and Stroh\textsuperscript{116} have also synthesised pyrazines by the reaction of triphenylphosphine with 2-azidoketones, presumably via the intermediacy of the iminophosphorane (Scheme 28).

\[
\begin{align*}
R^1\text{CHCOR}^2 + \text{Ph}_3\text{P} &\rightarrow \text{Ph}_3\text{P} \equiv \text{NCHR}^1\text{COR}^2 \\
\end{align*}
\]

Scheme 28

Pailer and Haslinger\textsuperscript{117} have used the intramolecular Wittig reaction to prepare the alkaloid nigrifactine as shown in Scheme 29.
In a similar manner Saunders and co-workers have prepared benzoxazoles\textsuperscript{118} and 2-substituted quinolines,\textsuperscript{119} by reaction of triethyl phosphite with 2-azidophenyl esters and 2-azidocinnamates respectively (Schemes 30 and 31). By contrast, the corresponding reaction of 2-azidophenyl benzoate with hexamethylphosphorus triamide has been reported to give the 2,2-di-(dimethylamino)-1,3,2-benzoazaphosphole (76) in good yield.\textsuperscript{97} This difference in behaviour of the phosphorus reagents could be due to the high nucleophilicity of the nitrogen end of the P-N dipole in (75), favouring a reaction as shown in Scheme 30.
Scheme 30
(d) **Reaction with other Multiple Bonds**

The Wittig reaction can be considered as an example of the general reaction of phosphorus ylides with multiple bonds which are activated by strongly electron-withdrawing substituents or are between atoms of different electronegativities. The products of these reactions can usually be rationalised by assuming addition of the ylide anion to the positive end of the dipole to give a betaine such as (77a) which can subsequently rearrange or decompose. Pentaco-ordinate phosphoranes such as

\[
R_3P\equiv NR^1 + A\equiv B \rightarrow R_3P^+\equiv N\equiv A-\equiv B
\]  

(77a)
There is some evidence that in some reactions such as those of cyclic iminophosphoranes with isocyanates and ketones, discussed earlier in Section A.2.c that these pentaco-ordinate phosphoranes can be formed directly from the addition of the ylide to the multiple bond.

The generality of Wittig-type reactions involving the formation of new doubly bonded compounds by elimination of phosphine oxide or sulphide is illustrated by the examples below

\[
\begin{align*}
R_3P—NR^1 & \xrightarrow{\text{CO}_2} R_3PO + R^3N\equiv C\equiv O \\
& \xrightarrow{\text{CS}_2} R_3PS + R^3N\equiv C\equiv S \\
& \xrightarrow{R^1N\equiv C\equiv O} R_3PO + R^3N\equiv C\equiv NR^1 \\
& \xrightarrow{R^2C\equiv C\equiv O} R_3PO + R^3N\equiv C\equiv CR^2_1 \\
& \xrightarrow{R^1N\equiv C\equiv S} R_3PS + R^3N\equiv C\equiv NR^1 \\
\end{align*}
\]

Zimmer and Singh\(^{124}\) have reported that treatment of \(N\)-phenyliminotriphenylphosphorane with nitrosyl chloride at \(-70^\circ\) gave triphenylphosphine oxide and phenyldiazonium chloride, the latter was subsequently identified by trapping with 2-naphthol. The proposed mechanism involved an intermediate \(N\)-nitrosoaminophosphonium salt as outlined in Scheme 33. Evidence for this mechanism was supplied by Horner.
and Winkler\textsuperscript{92} who reported that the reaction proceeded with retention of configuration at phosphorus.

Campbell\textsuperscript{125} has proposed that iminophosphoranes are involved in the phospholen oxide catalysed conversion of isocyanates into carbodiimides via a mechanism as shown in Scheme 34. More recently, Hall and Smith\textsuperscript{126} have provided further evidence for this mechanism by the isolation of iminophosphoranes from the reaction of phosphetan oxides with toluene-\textit{p}-sulphonyl isocyanate (Scheme 34).

Brown and co-workers\textsuperscript{127} have shown that dimethyl acetylene-dicarboxylate reacts with iminophosphoranes to form 1:1 adducts provided that electron-withdrawing groups such as benzoyl, \textit{2,4}-dinitrophenyl are not attached to the nitrogen. X-Ray studies of the adduct obtained from \textit{N}-\textit{(p}-bromophenyl)iminotriphenylphosphorane showed the compound was a phosphorus-carbon ylide. The proposed mechanism involves nucleophilic attack by nitrogen on the
\[ R_3P=O + R^1NCO \rightleftharpoons R_3P-O \]

\[ R^1N-C=O + CO_2 \]

\[ R_3P=NR^1 + R^1NCO \rightleftharpoons R_3P-NR^1 \]

\[ O-C=NR^1 \]

\[ R_3PO + R^1N=C=NR^1 \]

Diagram:

```
Me Me2 P Ph O Me2 P Ph TsNCO
```

Scheme 34
acetylene to give a betaine which rearranges via a 4-centred Wittig-type intermediate to give the product (Scheme 35). A similar reaction has been observed for phosphole imines. The carbon analogues also react with acetylenes to give rearranged ylides. Activated nitriles react with iminophosphoranes to form rearranged iminophosphoranes (Scheme 36).
Zbiral\textsuperscript{130} has obtained iminophosphoranes containing the 1,3-thiazole (78; X=S) and naphtho-1,3-selenazole groups (78; X=Se) by the intramolecular addition of \( \ddagger \text{P-N} \) to \( \equiv \text{N} \) of 1-thio and 1-selenocyanato-2-triphenyliminylnaphthalene respectively (Scheme 37).

\begin{center}
\begin{tikzpicture}
\node (N) at (0,0) [shape=circle, draw] {\( \equiv \text{N} \)};
\node (X) at (-0.5,0) [shape=circle, draw] {\( \ddagger \text{P-N} \)};
\node (C) at (-1,0) [shape=circle, draw] {\( \text{C} \equiv \text{N} \)};
\draw [->] (C) -- (X);
\draw [->] (X) -- (N);
\end{tikzpicture}
\end{center}

\textbf{Scheme 37}

\textbf{(e) Reaction with 1,3-Dipoles}

Although iminophosphoranes are generally not as reactive towards 1,3-dipoles as their carbon analogues and do not form isolable cycloadducts, there are a number of reactions whose products are best rationalised by formation of an intermediate pentavalent phosphorane which subsequently decomposes.\textsuperscript{131,132}

For example, Huisgen and Wulf\textsuperscript{132} have shown that benzonitrile oxide reacts with iminophosphoranes to form carbodiimides and phosphine oxides, presumably via the pentaco-ordinate phosphorane (79) (Scheme 38).
It has also been shown that exchange of organic groups between the carbodiimide and iminophosphorane can occur via the cycloadduct.

Huisgen and Wu\textsuperscript{132} have also found that nitrile imines interact with iminophosphoranes to form stable betaines (80) which, in certain cases, undergo proton transfer to form iminophosphoranes

Iminophosphoranes react only with reactive nitrones. Thus, Huisgen and Wu\textsuperscript{132} have obtained $N,N$-diphenyl-$N$-benzoylformamidine from the reaction of $N$-phenyl-$C$-benzoylnitroine with $N$-phenylimino-
triethylphosphorane apparently via the unstable pentavalent phosphorane (81).

Mitsch\textsuperscript{133} has shown that N-cyanoiminophosphoranes interact with hydrazoic acid to undergo 1,3-dipolar addition at the C-N triple bond forming N-(5-tetrazoyl)iminophosphoranes (Scheme 39).
Iminophosphoranes interact with a variety of Lewis acids. For example, co-ordination compounds have been reported to be formed by reaction with metal carbonyls, $^{134,135}$ Cu (I), Co (I) and Ni (I) halides, $^{136}$ and mercury and cadmium iodides. $^{137}$ Adducts are also produced, with halides and trialkyls of the third-row metals (Scheme 40). $^{132,138}$

The parent iminophosphorane reacts with the alkyls of lithium, cadmium, gallium, indium and aluminium to form organometallic iminophosphoranes as shown in Scheme 41. $^{139,140}$ The $^N$-(organo-
metaloid) iminophosphoranes exist as dimers in some cases. The N-
lithioiminophosphoranes have proved useful in a number of syntheses
of N-substituted iminophosphoranes e.g. treatment with chloro and
dichloro-silanes gives a series of disilanyl substituted iminophosphoranes
(82) and reaction with dimethylphosphinous chloride gives (83).

Iminophosphoranes react with halogens in a similar manner as
their carbon analogues. N-Bromotriphenylphenylphosphorane (84),
formed by interaction of the parent iminophosphorane and bromine,
undergoes ready substitution at nitrogen to give new iminophosphoranes
as for example (85).
A number of iminophosphoranes have been reported to be susceptible to photolytic fragmentation. Thus, irradiation of some $N$-alkyl-aminotriphenylphosphoranes leads to rearrangement of the $N$-alkyl substituent analogous to that observed during irradiation of corresponding azides by comparison. The irradiation of $N$-arylaminophosphoranes in inert solvents leads to efficient production of triphenylphosphine and diaryl azo compounds derived from the $N$-aryl substituent. Since all attempts to trap nitrene intermediates failed the reaction was considered to proceed via excited ylide intermediates. Triphenylaminophosphoranes in which the nitrogen substituents are strongly electron withdrawing, e.g. benzoyl, are photostable but photolysis of $N$-t-butylaminotriphenylphosphorane results in cleavage of both $P=N$ and $C-N$ bonds.

The chemistry of iminophosphoranes has been reviewed in several publications.
B. The Chemistry of Pentaco-ordinate, Quinquecovalent Phosphoranes

General Aspects

(a) Structure and Bonding

The title compounds, which will be referred to as phosphoranes, contain five ligands covalently bonded to a central phosphorus atom. Compounds in this category have the general formula, $L_5P$, and known examples of $L$ include aryl, alkyl, amino, alkoxy and thio groups.\textsuperscript{11,149,150}

Both valence shell electron pair repulsion theory\textsuperscript{151} and molecular orbital theory\textsuperscript{152} predict two likely geometries for five co-ordinate species. These are the trigonal bipyramid, t.b.p. for short, (85), which contains three equatorial ligands at 120° to each other and

\begin{align*}
\text{(85)} \quad \text{at right angles to the two collinear apical ligands, and the square} \\
\text{pyramid (86), s.p. for short, which has one apical ligand at 104° to the} \\
\text{four basal ligands which are themselves separated by angles of 88°.} \\
\text{X-Ray diffraction data on phosphoranes have revealed geometries}
\end{align*}
varying between both these ideal geometries. Moreover, it is possible to derive the square pyramid from the t.b.p by a simple bond-bending process which will be described later. Also, theoretical calculations indicate that although the t.b.p. form is generally favoured over the s.p form, the energy difference is usually slight, 1.56 k cal/mol. However, the evidence to date, from a variety of sources including X-ray measurements, electron diffraction studies, n.m.r., and i.r. data, and theoretical calculations, suggest that the preferred geometry of the majority of simple phosphoranes is the trigonal bipyramid. The data also indicates that distortion towards the square pyramid form is favoured by the presence of bidentate, electronegative ligands.

It has been observed that the apical bonds of a t.b.p. phosphorane are usually longer and weaker than the equatorial bonds. This agrees with the predictions regarding such geometries. If the bonds of a t.b.p. are assumed equal, the 90° apical-equatorial (a,e) interactions are obviously greater than the 120° equatorial-equatorial (e,e) interactions. Each apical ligand has three 90° nearest neighbours whereas each equatorial ligand has only two such neighbours. Hence, it is expected that there will be greater steric compression at the apical positions than at the equatorial position of a t.b.p. As the system will have a tendency to reach an energy equilibrium by minimising the different interactions, it can be predicted that, as observed, the apical bonds will be longer and hence weaker than the equatorial bonds. Also, calculations using the CNDO/2 approximation to the SCF-LCAO-MO method indicate that phosphoranes increase their stability by minimising
the polarity difference between the central phosphorus atom and its ligand set. This is done by back-donation of electron density into phosphorus from the filled π orbitals of the ligand into the empty d-orbitals of phosphorus. The calculations also show that an atom in the apical position of a t.b.p. has a lower capability of donating electrons to the central phosphorus atom than the same atom placed in an equatorial position. Moreover, the lengthening of the apical bonds due to the increased steric compression, results in reduced 3d orbital participation towards these positions and hence there is less back-bonding from the apical position of the t.b.p. than from the equatorial position. This lessened back bonding from the apical position results in reduced double bond character at the apical position and it follows that the apical bonds will be longer and weaker than the equatorial bonds.

(b) **Pseudorotation**

Although ligand reorganisation can occur by irregular processes involving bond breaking and six-co-ordinate species one of the characteristic features of these pentaco-ordinate phosphoranes is their ability to undergo permutational isomerisation by regular processes which do not involve bond rupturing (cf. their carbon analogues). For example, the $^{19}$F n.m.r. spectrum of phosphorus pentafluoride, PF$_5$, shows only a single fluorine resonance even at -100° although it is known that the apical position of a t.b.p. is different from the equatorial position and hence should give rise to different signals. By contrast, the i.r. spectrum of the compound showed the bands of a
This was confirmed by electron diffraction studies which showed a t.b.p. structure with two axial bonds longer than the three equatorial bonds. These spectroscopic results imply that a process exists by which the apical and equatorial fluorine atoms interchange and that this process is fast compared to the n.m.r. time scale but slow compared to the i.r. time scale.

It is generally accepted that this ligand reorganisation involves the pairwise, simultaneous interchange of two apical and two equatorial ligands. Evidence for this was provided by Whitesides and Mitchell's study of the variable temperature $^{19}$F n.m.r. spectrum of $N,N$-dimethylaminotetrafluorophosphorane (87). Below -100°C two fluorine signals of equal intensity are present, indicating a frozen t.b.p. structure as shown in (87). Above -50°C, the fluorine atoms are equivalent indicating rapid positional exchange. In the temperature range -100°C to -50°C, mathematical analysis of the spectrum shows that the apical and equatorial fluorine atoms interchange position in a pairwise, concerted manner. So far, two mechanisms have been postulated which
are in agreement with these results.

The first plausible mechanism was proposed by Berry\textsuperscript{163} in 1960, before the Whitesides and Mitchell\textsuperscript{162} experiment, and is commonly called Berry pseudorotation or BPR for short. The 'regular' intramolecular ligand positional exchange of pentaco-ordinate species are usually referred to as pseudorotation although Ugi, Ramirez and co-workers\textsuperscript{21,165} later proposed another mechanism, Turnstile rotation or TR for short.

The BPR process demonstrates neatly the close relationship of the t.b.p. and s.p. structures. As shown in Scheme 42, the process involves bending the two equatorial and two axial ligands of the t.b.p. with one equatorial ligand ($L_3$) acting as pivot, to form a square pyramid (88) as intermediate which by further bond bending with $L_3$ as pivot forms the new t.b.p. (89). In the case of PF$_5$, multiple BPR processes would lead to the observed fluorine equivalence.

The Turnstile Rotation\textsuperscript{21,165} process is outlined in Scheme 43 and involves an internal rotation of a pair of ligands ($L_3, L_4$ in Scheme)
Scheme 42

BPR

\[ \L^3 \text{ as pivot} \]

(88)

BPR

\[ \L^3 \text{ as pivot} \]

(89)
towards a set of three ligands ($L_1, L_2, L_5$) to give a new t.b.P. A complex series of twists and turns are involved. The trio ligands in the schematic TR move like a turnstile which is entered by pushing the trio-equatorial ligand which will remain equatorial.

Both the TR and BPR fulfill the criterion necessitated by the Whitesides and Mitchell experiment i.e. the processes involve a pairwise, synchronous exchange of two apical with two equatorial ligands. It has been shown that each BPR process is equivalent to four different TR processes. However there are fundamental differences
between the two processes which arise from the fact that TR is a process which involves an internal rotation about an axis that passes through the central atom, whereas BPR involves no such rotation and, in fact, the term pseudorotation is misleading. As a result of this, the two mechanistic pathways proceed via sets of state which have different geometries, symmetries and potential energies. It has been suggested that as one BPR process is equivalent to four TR processes, TR is the more likely of the two processes. However, both mechanisms appear to account equally well for the regular ligand reorganisations of simple t.b.p. phosphoranes containing unidentate ligands. Thus, CNDO/2 calculations do not allow discrimination between the BPR and TR models for the observed fluorine equivalence in PF$_5$. The BPR barrier is of the order of 4kcal/mol$^{-1}$ and the TR barrier is approximately 9 kcal/mol$^{-1}$. This 5 kcal difference is probably within the calculated error and, also, may be negated by an opposite difference in zero point energies. Ugi, Ramirez and co-workers have suggested that t.b.p. phosphoranes with four and five membered rings in the apical/equatorial position are far more likely to rearrange by a TR process rather than by the Berry mechanism. It is well established that such rings preferentially occupy the a,e rather than the e,e position of a t.b.p. Hence, the observed rapid positional exchange of the ligands in some caged polycyclic phosphoranes such as the adamantoid compound (90) has been cited as evidence that such structures undergo ligand rearrangement via a TR rather than a BPR process, since, assuming ideal t.b.p. geometry for the molecule, the BPR mechanism would involve high energy
intermediates with diequatorial rings. In contrast, a TR mechanism with the two ligands of the five membered ring as the pair and the three ligands of the cage as the trio satisfactorily explains the observed n.m.r. data, again if ideal t.b.p. geometry is assumed. However, more recent evidence seems to support the Berry mechanism. Thus, it has been shown that such cyclic oxyphosphoranes are distorted away from t.b.p. geometry and that these distortions are towards the square pyramidal form which is along the pathway followed in BPR.

In this thesis, the regular ligand reorganisation of phosphoranes will be referred to as pseudorotations, following the established procedure, but no attempt will be made to distinguish between the two mechanisms.
Apicophilicity - factors determining pseudorotation and ligand position in a t. b. p.

The energy of activation of pseudorotation depends on the nature of the ligands involved and, in particular, on their apicophilicity which is defined as the tendency of the ligand to reside in the apical position. The relative apicophilicity of two ligands is the change in energy when these groups exchange apical and equatorial positions in a t. b. p.¹⁹ A great deal of information concerning relative apicophilicities and pseudorotation barriers has been obtained mainly from the results of dynamic n. m. r. studies.¹⁹ X-Ray diffraction data and computer simulated studies have also provided information regarding relative apicophilicities.¹⁵⁴,¹⁵⁷,¹⁶⁸ Several factors appear to influence the relative apicophilicities and hence pseudorotation and the preferred stereoisomer of a phosphorane.¹⁹,¹⁵⁷,¹⁶⁵

Generally, the more electronegative the ligand the greater the tendency to occupy the apical position.¹⁹,²¹,¹⁴⁹,¹⁵⁴,¹⁵⁷,¹⁶⁵-¹⁶⁸ This is the so-called polarity rule. For example the electron diffraction studies of tetrafluoromethylphosphorane and trifluoridi methylphosphorane showed that the apical positions were occupied by the more electronegative fluorine atoms whereas the more electropositive alkyl groups were always equatorial. Meuterties and Schmultzer,¹⁶⁶ in their studies of the ¹⁹F n. m. r. data of a series of alkylfluorophosphoranes, RₙPFₙ₋₅', observed a similar effect. Rapid pseudorotation, using the alkyl group as pivot, occurred in the mono-substituted case. However, pseudorotation was inhibited in the di- and tri-substituted cases indicating the preference of the alkyl groups for the equatorial position.
since any pseudorotation would have resulted in an alkyl group in the unfavourable apical position and a fluorine atom being in the unfavourable equatorial position.

Although, as shown by the above examples, electronegativity is important in determining relative apicophilicities, experimental evidence and theoretical calculations indicate that it is not the only factor determining apicophilicities and, in fact, can be overridden by other factors. Thus, binding energy data of pentaco-ordinate phosphorus compounds calculated using the CNDO/2 approximation showed that use of only one ligand property e.g. electronegativity can provide at best only a rough guide as to the relative stabilities of the various geometric isomers. Similarly, Debruijn et al. have obtained, from a study of the alkaline hydrolysis of a series of cis and trans-2,2,3,4,4-pentamethylphosphetanium salts, the following order of apicophilicity: \( \text{Me}_2\text{N} < \text{OMe OEt OPr}^+ < \text{S Me Cl} \) which does not agree with the polarity rule as stated above.

It has been noted that the back-bonding ability of the ligand appears to be an important factor in determining apicophilicity. Thus, the above-mentioned order of apicophilicity reported by Debruijn et al. is in agreement with other observations that increase in the back-bonding ability of the ligand leads to increased equatorial tendencies.

The observed effects of the electronegativity and back-bonding abilities of a ligand on its apicophilicity have been rationalised by a consideration of the nature of the geometry of the t. b. p. The greater interactions of the apical ligands compared with the equatorial ligands result in there being less space at the apical position. Hence the larger bonding orbitals which have relatively low electron density i.e. those
with maximum $s$ character, tend to occupy the less hindered equatorial position. Conversely, those bonding orbitals which are smaller but longer and more directed and have relatively high electron density will preferentially occupy the apical position: in the ideal case these are $pd$ orbitals. It has also been shown that there is less back-bonding towards the central phosphorus atom from the apical than from the equatorial position. $^{21,165}$ Both the reduced back-bonding ability and the reduced $s$ character in the apical position result in an increase of electron density at the apical position of a t.b.p. $^{149,165}$ Hence, the more electronegative groups will be preferentially sited at the apex where they are capable of supporting more negative charge. By contrast, those groups with greater ability to back-bond to the central phosphorus atom will preferentially occupy the equatorial position where there is greater possibility of back-bonding.

Another consequence of the increased steric hindering at the apical position of the t.b.p. is that, electronegativity permitting, the bulkier ligands preferentially occupy the equatorial sites. $^{19}$ Thus Trippett $^{19}$ has reported a steadily increasing barrier to the pseudorotation shown in Scheme 44 as the alkyl groups increase in bulk the barrier to pseudorotation increased in the order $Me < Et < Pr^1 < Bu^t$. Trippett and co-workers $^{170}$ have also demonstrated that the greater compression at the apical as opposed to the equatorial positions in t.b.p. phosphoranes is an important factor in determining the relative apicophilicities of alkyl and aryl groups in some phosphoranes.
Small ring effect: ring strain

Studies by several groups indicate that ring strain can play an important part in determining the preferred orientations of ligands in a phosphorane containing one or more bidentate ligands. 19, 26, 149, 165, 171 Generally, four and five membered rings preferentially occupy the axial-equatorial positions of the t.b.p. skeleton as in (90). For example

\[(90)\]
as has been noted by Ramirez and Ugi, X-ray data indicates that four and five membered rings occur only in the apical-equatorial (a, e) position of the t. b. p. The four membered ring appears to be able to accommodate the 90° a, e angle without strain. Ugi, Ramirez and co-workers have also noted that CNDO/2 calculations on a model oxyphosphorane containing a five-membered ring showed that the isomer with a diequatorial five-membered ring is less stable than the isomer with the apical-equatorial ring. When the diequatorial CPO bond angle is small (approximately 90°), the angle strain is large although the strain in the remainder of the ring is low but if the angle is enlarged (to approximately 114°) to lessen the angle strain, the strain in the rest of the ring becomes great. However, models show that the envelope form of the five membered ring can accommodate the 90° a, e angle without any appreciable strain. It has been calculated that the energy required to change the phospholan ring in (91) from the a, e to the e, e position is of the order of 9 kcal mol⁻¹. One consequence of this 'small ring effect' is that pseudorotatory processes involving t. b. p. intermediates with diequatorial rings usually require
more energy than those involving t.b.p. intermediates with a, e rings.\(^{19}\)

There are some interesting cases where the small ring effect competes with the polarity rule.\(^{166, 173}\) An example of this was provided by Muettlerties and Schmutzler's\(^{166}\) investigation of the stereochemistry of the cyclic phosphoranes (92) and (93). The \(^{19}\)F n.m.r. data, at \(-70^\circ\)C, indicates that no BPR is occurring and that

\[
\begin{array}{c}
\text{(92a)} \\
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{P} \\
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{(92b)} \\
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{P} \\
\end{array}
\end{array}
\]

the compound exhibits the typical \(R_2PF_3\) structure with equatorial alkyl groups as shown in 92b. However, the room temperature spectrum of 92 contains a single fluorine signal indicating that pseudorotation is unhindered at this temperature.

\[
\begin{array}{c}
\text{F} \\
\text{F} \\
\text{F} \\
\text{F} \\
\text{P} \\
\end{array}
\]

\(\text{(93)}\)

This room temperature pseudorotatory process involves species such as (92b) which violate the polarity rule but allow the ring to be in the favourable a,e position. The different behaviour of the acyclic and cyclic compounds must arise from the gain in stability by release of
ring strain when a five membered ring in a t. b. p. phosphorane such as (92) changes from the unfavourable e, e to the 'strain-free' a, e position. The six-membered ring compound (93) which would be expected to be better able to accommodate the $120^\circ$ e, e angle behaves like the acyclic counterparts. Thus, the $^{19}$F spectrum of (93) does not vary with temperature and indicates a structure as shown in (93) with a diequatorial ring. 166

Other factors

The preferred orientation of lone pairs on equatorially bonded atoms in a t. b. p. phosphorane seems to be important in determining the geometry of phosphoranes containing small rings which contain a heteroatom directly bonded to the central phosphorus. It has been shown that such lone pairs preferentially occupy the equatorial plane. 19, 166, 174

The lone pair effect has been calculated to be approximately 10 kcal mol$^{-1}$ in the case of nitrogen and sulphur, and perhaps 5 kcal mol$^{-1}$ in the case of oxygen. 175

The lone pair effect is presumably related to the effect on apicophilicity of the back bonding abilities of ligands which contain p$\pi$ orbitals has been discussed earlier since it is only in the equatorial position that the ligand can back bond to the central phosphorus atom. Trippett 19 has pointed out that when a small ring e.g. (94) occupies the e, e position in a t. b. p. the lone pairs occupying p-orbitals on the heteroatoms X and Y are in an unfavourable apical plane. Trippett 19 has deduced that the energy difference between the isomeric phosphoranes (94a) and (94b) is composed of three basic terms: (1) the angle strain
factor due to increase in the bond angle at phosphorus; (2) the energy required to rotate the lone pair on X from the equatorial to the axial plane; and (3) the difference in apicophilicity between R and Y, when the lone pair on equatorial Y is constrained to an apical position. The last term is the normal relative apicophilicity R and Y as in the acyclic systems when the lone pair on Y is free to take up the preferred equatorial position, plus the energy required to rotate the lone pair on Y from the e to the a plane. On this basis, Trippett\textsuperscript{19} has devised an equation to derive the energy differences between structures such as (94a) and (94b). The author\textsuperscript{19} has reported that, provided steric effects do not predominate, good results are obtained. X-Ray data provides evidence for this lone pair effect. Models show that the lone pairs on heteroatoms in the six-membered ring of phosphoranes such as (95) are in an unfavourable e,e plane when the strain-free conformations occupy either the a,e or the e,e positions.\textsuperscript{19}
However with an a,e boat conformation the lone pair on the equatorial substituent $X$ can be in the equatorial plane. In support of this Trippett and co-workers$^{175}$ have reported that X-ray data on the phosphorane (96; $X = \text{CF}_3$) shows that the six-membered ring does exist in the boat conformation necessary for the lone pair on the nitrogen to occupy the favoured equatorial plane.

From the above discussion, it is apparent that several factors appear to determine the relative apicophilicities of ligands in a t.b.p. phosphorane and hence the preferred geometric arrangement of the ligands and also the energy required for a particular pseudorotatory process. In some cases, these factors contradict each other and different relative apicophilicities have been obtained depending on the nature of the set of ligands in the particular phosphorane. There are also steric effects which can cancel small differences in apicophilicities. Westheimer and co-workers$^{176}$ have shown that in some cases e.g. (97; $\text{Ar} = 2,6$-dimethylphenyl), intense steric crowding can slow ligand reorganisation.
Thus, on the basis of the published data, the factors affecting the relative apicophilicities of two groups and the preferred arrangement of ligands in a t.b.p. phosphorane can be summarized as (1) electronegativity as the preference of a ligand for the apical site increases as its electronegativity increases; (2) the lone pair effect since the presence on the atom or group directly bonded to phosphorus, of a lone pair results in increased equatorial tendencies as does increase in the back-bonding ability of the ligand; (3) the presence on the ligand of a vacant low-lying orbital as this increases the tendency to occupy an apical site; and (4) the presence of small ring bidentate ligands as these preferentially occupy an a,e site. Trippett has drawn up a tentative apicophilicity scale as shown in Scheme 45. The scale is derived from the published data and the author claims that although it must be used with caution, it agrees with much of the experimental results in the literature.
More recently, Holmes has developed a new model based on the pseudorotatory hypothesis, which allows the estimation of the relative stabilities of the various t. b. p. and s. p. isomers of a given pentaco-ordinate phosphorane. The model uses the known activational energies of the ligand exchange processes of various simple acyclic phosphoranes and also the results of theoretical and spectroscopic studies concerning t. b. p. and s. p. energy differences. The assumption is made that the apicophilicity scales of the t. b. p. and s. p. isomers should have the same range and should correlate linearly with electronegativity. Using this basis, apicophilicity scales of both the t. b. p. and s. p. structures are drawn up. The resultant model incorporates apicophilicity scales spanning 10 kcal mol$^{-1}$ and terms dealing with steric factors such as the a, e interactions in the t. b. p. and also the apical-basal and basal-basal cis ligand interactions in the s. p. The model also has terms dealing with ring strain, where applicable. The model can be used to predict the free energies of activation for B. P. R.'s and should prove useful in predicting the likely pentaco-ordinate intermediates and transition states in phosphorus reaction mechanisms.
results of the model are in good agreement with the experimental
data on a wide range of cyclic and acyclic phosphoranes.

B. Preparation and Reactions of Phosphoranes

B.1 Phosphoranes from the Addition of Tervalent Phosphorus
Reagents to 1,3-Unsaturated Systems.

The title reaction, which is outlined in Scheme 46, has proved
to be one of the most versatile methods of preparing phosphoranes of
general structure (98), and will be discussed below in some detail.

\[
\begin{array}{c}
\text{W} \quad \text{Y} \\
\text{X} \quad \text{Z}
\end{array}
\quad + \quad \text{PR}_3 
\quad \rightarrow 
\begin{array}{c}
\text{W} \quad \text{Y} \\
\text{X} \quad \text{Z} \quad \text{PR}_3
\end{array}
\]

Scheme 46

(a) From Dicarbonyl Compounds

The now well established reaction of tervalent phosphorus
compounds with 1,2-diketones and related compounds is probably the
most extensively used method for preparing phosphoranes containing
the 1,3,2-dioxaphospholen ring (Scheme 4).26 Thus, addition of
acyclic and cyclic phosphites, phosphonites, phosphinites and their amino
and thio analogues to a variety of dicarbonyl compounds leads to the
formation of the so-called Ramirez adducts. For example, Pudovik and co-workers have prepared the phosphoranes (99) by the reaction of diketones with suitable tervalent phosphorus compounds.

\[ \begin{align*}
A, B &= O, NMe_2, \text{or } S \\
X &= NMe_2 \text{or } OMe \\
Z &= CH_2CH_2, CMe_2CM_2, \text{or } CO
\end{align*} \]

The phosphorus moiety can also be included in a diazaphosphetidine ring e.g. (100; \( R^1 = Me_3Si, R^2 = NMe_2 \)) which on reaction with biacetyl at low temperatures affords the spirophosphoranes (101) and (102). Among the other dicarbonyl compounds that have been used in the preparation of Ramirez adducts are benzil, o-quinones, cycloheptane-1,2-dione and cyclo-octane-1,2-dione.

Two mechanisms have been postulated for the 1,4-addition reaction of dicarbonyls and \( P(\text{III}) \) reagents. On one hand, kinetic studies
of the reaction of benzil with trialkyl phosphites support a mechanism involving nucleophilic attack of the phosphorus atom on the carbonyl group as shown in Scheme 47. However, there is also strong e.s.r. evidence that radical intermediates are involved in the reaction of PIII compounds with activated dicarbonyl compounds including 1, 2-diketones, o-quinones and α,β-unsaturated ketones. A possible mechanism is outlined in Scheme 48.

There have been several structural investigations of these oxyphosphoranes and much is known about their geometry. For example, an X-ray diffraction study of the adduct of phenanthrene quinone and tri-isopropyl phosphite (103) has revealed a slightly distorted t.b.p. structure with the ring spanning the a,e position (Table 1). The apical P-O bonds are longer than the equatorial ones as expected. The bond angle at phosphorus in the ring is 89.3° which is very close to the 90° angle predicted for ideal t.b.p. geometry. The X-ray diffraction

![Diagram](image)

**Table 1**

<table>
<thead>
<tr>
<th>Bond Length, Å</th>
<th>Bond Angle, deg</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-O1</td>
<td>1.735</td>
</tr>
<tr>
<td>P-O2</td>
<td>1.649</td>
</tr>
<tr>
<td>P-O3</td>
<td>1.641</td>
</tr>
<tr>
<td>P-O4</td>
<td>1.601</td>
</tr>
<tr>
<td>O1-C1</td>
<td>1.386</td>
</tr>
<tr>
<td>O2-C1</td>
<td>1.347</td>
</tr>
<tr>
<td>O3-C1</td>
<td>1.433</td>
</tr>
<tr>
<td>O4-C1</td>
<td>1.463</td>
</tr>
</tbody>
</table>
data have also shown that the trigonal bipyramid is crowded due to several short non-bonded distances e.g. the apical oxygen of the ring, $O_1$ is very close (2.63 Å) to the carbon attached to the equatorial oxygen, $C_4$, and the apical oxygen of the alkoxy group is very close (2.70 Å) to the carbon attached to the other equatorial oxygen, $C_5$. Ramirez\(^{25,26}\) has attributed the observed greater stability of the five-membered cyclic penta-oxyphosphoranes when compared to their acyclic analogues to the extreme crowding in the t.b.p. structure. The presence of bidentate ligands partly reduces the crowding in the structure.

The $^1$H n.m.r. spectra of many of the adducts of trimethylphosphite indicate t.b.p. structures with rapid positional exchange of the apical and equatorial methoxy groups since only one methoxy signal is present even at low temperatures.\(^{26,149}\)

In some cases, the phosphoranes exist in equilibrium with the ring opened form e.g. (104) and (105). Ramirez and co-workers\(^{159}\) have reported that the reaction of hexamethylyphosphorus amide with

\[
\begin{align*}
\text{(104)} & \quad \text{(105)} \\
\text{colourless} & \quad \text{yellow} \\
31^P\delta \quad -30.2 \text{ (hexane)} & \quad -13.1 \text{ (CH}_2\text{Cl}_2) \\
\nu_{\text{max}} \text{ (hexane)} 1684 - 1645 & \quad \text{(enolate C=O)} \\
\text{(C=O)} &
\end{align*}
\]
benzil produces an insoluble deep yellow adduct, formulated as the betaine (105), which slowly dissolves in n-hexane to give the colourless phosphorane (104). Solutions of each form contain the same molecular species in equilibrium. As expected, more polar solvents such as dichloromethane shift the equilibrium towards the betaine.

A number of factors appear to influence the betaine/phosphorane equilibrium in the adducts. An important factor is the electronegativity of the phosphorus ligands, increase of which leads to increasing tendencies to form the phosphorane. Thus, the adducts of phosphites exist in the $P^V$ form whereas those of the acyclic phosphamides form equilibrium mixtures. Another factor is the small ring effect which favours $P^V$ rather than $P^{IV}$ formation. For example, the adduct of benzil and the cyclic phosphorus compound (106) does not ring open to give the dipolar species (cf the acyclic analogue, 104/105). Also the dipolar form is favoured by the possibility of charge delocalisation.

\[ \text{(106)} \]

\[ \text{(107)} \]

e.g. the adducts (107, $R^1 = \text{Ph}$, $R^2 = \text{CO}_{2}\text{Ph}$ and $R^1 = \text{OEt}$, $R^2 = \text{CO}_{2}\text{Et}$) exist only as the dipolar form; however, conjugation of the double bond with aryl groups favours the ring closed form (cf. 105).

A number of reactions of these oxyphosphoranes have been investigated and they have proved useful synthetic intermediates. The condensation of the oxyphosphoranes with a wide range of carbonyl...
compounds provides a useful synthetic route to new phosphoranes containing the dioxaphospholan ring (Scheme 49). As a rule, the reactivity of the carbonyl compound in this reaction is in the order: monoketone < aldehyde < diketone. Similarly, the presence of electron-withdrawing groups on the carbonyl function increase the reactivity. A possible mechanism is shown in Scheme 49 where $R^2$ is more electron-withdrawing than $R^1$.

\[ \text{Scheme 49} \]

Other phosphoranes have also been synthesised by the exchange reactions of the monocyclic alkoxypyrophoranes with alcohols, diols and amino alcohols. In these transformations the unsaturated ring is preserved as shown in Scheme 50.

The reactions of the dioxaphospholan (109) with a number of heterocumulenes have been investigated. Generally, trimethyl
phosphate is eliminated and non-phosphorus containing heterocycles are obtained. For example, the reaction of (109) with aryl and acyl isocyanates has been used to prepare 2-oxazoline-4-ones (Scheme 51). 184a,b

The phosphorane also undergoes the normal condensation reaction with phenyl isocyanate to produce new phosphoranes (108; \( R = R^1 = R^2 = Me \); \( R^3 = R^4 = NPh \)) which react further with more isocyanate to give
The reactions of the phosphorane with carbon disulphide and carbon suboxide have also been studied. A complex reaction occurs with the former to give sulphur heterocycles whereas the latter undergoes the normal carbonyl condensation.

The phosphorane reacts with acyl chlorides or anhydrides to give either the C-acylated product, the phosphate esters of 2-hydroxy-1,3-diketones, or the O-acylated product, the acylated enediol phosphates. 2-Ketophosphates are formed by the reaction of the phosphoranes with hydrogen chloride. Castelijns et al. have reported that, in the presence of less than one equivalent of fluorosulphonic acid in dichloromethane, and the enolphosphonium salt are in a temperature dependent equilibrium. The enolphosphonium salt isomerises to the keto-form above 0°C. The reaction with bromine yields either 1-bromo-2-ketophosphates or 2,2-dibromoketones as shown in Scheme 52.
The benzil/trimethyl phosphite adduct reacts with sulphenyl chlorides to give good yields of α-chloro-β-keto sulphides (Scheme 53) which are useful intermediates in the preparation of compounds such as α-keto aldehydes and α-hydroxy acids. 187

![Scheme 53](image)

The majority of these oxyphosphoranes are thermally stable under nitrogen at temperatures below 120°. Above this temperature cleavage to the starting materials can occur. This is followed by nucleophilic attack by the phosphite on the carbonyl carbon to give (113) as intermediate, which can then undergo an Arbuzov-type rearrangement to form the phosphonate (Scheme 54). 188a

![Scheme 54](image)

Thermolysis of the adducts of triethyl phosphite and various substituted benzils with excess triethyl phosphite gives good yields of diarylacetylenes via the intermediacy of the diarylketene (Scheme 55). 188b
Hexaco-ordinate phosphoranes can be prepared from the oxyphosphoranes.\textsuperscript{189a} For example, the adduct of hexafluorobiacetyl and 2-phenoxy-1,3,2-benzodioxaphospholan gave crystalline hexaco-ordinate phosphorus compounds with phenol in the presence of triethylamine (Scheme 56).

Stephenson and Falk\textsuperscript{190} have reported that the catalytic hydrogenation of the adducts of trimethyl phosphite and a number of diketones gives monoketones almost quantitatively (Scheme 57).
This provides a useful synthetic route to complex ketones from aldehydes via the diketones. In another illustration of the synthetic utility of (109), it has been reported that the reaction with arylidene malonitriles produces cyclopropanes. 191

Generally, the simple phosphoranes hydrolyse rapidly to give ring-opened and ring-closed products. 192 For example, the adduct (109) reacts with water to give both the product of ring retention, (115) and the 2-ketophosphate (Scheme 58). The mechanism possibly involves the hydroxyphosphorane (114). A more complex reaction occurs at higher temperatures and the products can also include the trialkyl phosphate and the enediol (Scheme 59). 192a
(b) **From α-Keto Imines and Phosphorus (III) Reagents**

Phosphites react with the α-keto imine from phenanthrene quinone, in a similar manner to their reaction with diketones to form quinquevalent phosphoranes (Scheme 60).\(^{193}\)

(c) **From α,β-Unsaturated Carbonyl Compounds**

Phosphites, phosphonites and their amino analogues react with the title compounds to form 1,2-oxaphospholenes\(^ {150,194-200}\) (Scheme 61). The mechanism of the addition is probably similar to that of the formation of the diketone adducts (Scheme 48). Thus, kinetic studies\(^ {196}\)
of the reaction of methyl vinyl ketone and the substituted cyclic phosphonites (116) provide evidence that phosphorus is acting as a nucleophile whereas e.s.r. studies indicate that radical intermediates are involved.

![Scheme 61](image)

There have been reports of $^1$H n.m.r. studies of a number of these phosphoranes. Generally, the results indicate t.b.p. structures with the ring spanning the $a,e$ position. Pseudorotation is inhibited at low temperatures as would be predicted by ring strain and apicophilicity considerations. In some cases pseudorotation is completely restricted even at room temperature. Thus, the n.m.r. spectra of the adduct of methyl diphenylphosphinite and 3-benzylidene-2,4-pentanedione (117) suggest the phosphorane exists, in solution, as the t.b.p. structure shown (117) and that no pseudorotation is occurring in the temperature range -60 to +110°C.

The adducts can exist in two forms, illustrated by (117) and (118). Similar considerations apply as for the phosphorane vs betaine.
formation in the dicarbonyl adducts. Thus, the adducts from the phosphines exist only in the dipolar form whereas bond rupture in (117) occurs only above 125°C to give (118). The corresponding phosphorane from trimethyl phosphite undergoes bond rupture at a higher temperature (155°C), as expected.

The phosphoranes hydrolyse easily to give the corresponding phosphonates (Scheme 62). Evans et al. have reported that the adduct from trimethyl phosphite and methyl vinyl ketone reacts exothermally with chlorotrimethylsilane to give the phosphonate (119) shown in Scheme 63. It has also been reported that the phosphoranes are useful O-alkylating agents which require only mild conditions.
(d) From Nitrogen Compounds

There are a number of cases of unsaturated nitrogen compounds undergoing 1,4-cycloaddition to phosphorus(III) reagents to form pentaco-ordinate phosphoranes. For example, triphenyl phosphite reacts with the azo compound (120) to form a phosphorane as shown in Scheme 64. 202

\[
\text{Scheme 64}
\]

Similarly, Burger and Penniger 203 have prepared the 1,4,2-diazaphosph(V)oles (122) in excellent yields by the reaction of (121) with triethyl and trimethyl phosphite and dimethyl phosphonite.

Burger and co-workers 204 have also obtained the 1,3,5-oxazaphospholidines (124), in high yields by the reaction of 1,1,1,3,3,3-hexa-fluoro-2-(acylimino)-propenes (123, \( R^1 = Pr^i, Bu^t, \) or \( Ph \)) with trimethyl, triethyl and triphenyl phosphites. The phosphoranes have proved to be useful synthetic intermediates since on thermolysis 205a or photolysis, 205b they eliminate trialkyl phosphates to give nitrile ylides (125). These ylides can be trapped to obtain products as shown in Scheme 65. 206 Other trapping agents that have been used include nitrosobenzene, benzonitrile, and acetylenes. 206
Dienes condense with cyclic phosphites to produce bicyclic phosphoranes as shown below:

\[
\begin{align*}
\text{Y} = &\ F, \text{OMe}, \text{NMe}_2, \text{Me}, \text{Ph} \\
\end{align*}
\]
**(f) From Nitro-alkenes**

The reaction of nitro-alkenes with phosphites and phosphonites affords the phosphoranes (127) which can be considered as arising from the Michael addition of the tervalent phosphorus reagent to the olefin. 207

\[
\begin{align*}
\text{R}_2^2\text{C}=\text{CHR}^1 & \quad + \quad \text{R}^3[\text{RO}]_2\text{P} \quad \rightarrow \quad \text{R}^3[\text{RO}]_2\text{P} \quad \text{CHR}^2
\end{align*}
\]

(126) (127)

The phosphorane derived from dimethyl phosphonite and the nitro-olefin (126; \(R^1 = \text{Pr}^1, R^2 = \text{H}\)) decomposed above 90°C to give the phosphinate (128) and dimethyl phenylphosphonate (129). 207a The presence of aromatic groups in the nitroalkene increases the stability of the phosphorane. 207c
B. 2 Phosphoranes from the Reaction of Tervalent Phosphorus Compounds and Monocarbonyl Compounds

Treatment of phosphites and other phosphorus (III) reagents with two equivalents of an activated monocarbonyl compound results in the coupling of the carbonyl compounds and the formation of a phosphorane containing the 1,3,2-dioxaphospholan ring (Scheme 66). The reaction occurs with hexafluoroacetone, fluorenone, phthalaldehydes, α-keto-esters, benzoyl cyanide, and o- and p-nitrobenzaldehydes, among others. The substituents on carbon, in these cases, delocalise the charge in the intermediate 1:1 adduct (131). However, carbonyl compounds such as benzaldehyde, choral and unsubstituted aliphatic monoaldehydes yield the 1,4,2-dioxaphospholans (133). The latter is the product of attack by the phosphite on the carbon of the carbonyl function via the intermediate (132), in which the negative charge

\[
\begin{align*}
R_3P + R^1 \text{C} \text{R}^2 & \rightarrow \quad \text{Scheme 66} \\
\text{(130)}
\end{align*}
\]

\[
\begin{align*}
\text{(131)} & \quad \text{(132)}
\end{align*}
\]

\[
\begin{align*}
\text{(133)} & \quad \text{(134)}
\end{align*}
\]
is localised on oxygen. In some cases, the initial product of the reaction is (133) which isomerises to (130).26

The 1,4,2-dioxaphospholane derived from chloral and phosphites (133; R1 = CCl3) decompose above −10°C to give the vinyl phosphates (134).208d The 1,3,2-dioxaphospholane derivatives of aromatic aldehydes and phosphites and hexamethylyphosphorus triamide form epoxides when heated by elimination of the phosphoryl compound.210 The hydrolysis of (130) is complex and the mechanism and products depend on the substituents and reaction conditions.150 The hydrolysis of the 1,4,2-dioxaphospholanes usually proceeds by fission of the ring P-O bond as shown in Scheme 67.198

\[
\begin{align*}
\text{(133)} & \quad \xrightarrow{\text{H}_2\text{O}} \quad \text{(134)} \\
\text{Scheme 67}
\end{align*}
\]

B.3 Phosphoranes from the Reaction of Tervalent Phosphorus Compounds with Alcohols, Diols and Related Compounds.

Phosphites, phosphorus amides, phosphorus trichloride, and other phosphorus reagents with good leaving groups, react with compounds containing two suitably separated acidic hydrogens to give P-H phosphoranes as shown in Scheme 68 (Z, Y = O, NR).211 A similar

\[
\begin{align*}
\text{(135)}
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 68}
\end{align*}
\]
reaction has been reported for phosphorus trichloride and \( \alpha \)-amino-acids. In a related reaction, 2-chloro-1,3,2-dioxaphospholans interact with \( \alpha \)-amino-acids and their conjugate bases to give phosphoranes e.g. as shown in Scheme 69.\textsuperscript{212}

\[
\begin{align*}
\text{Na}^+ & \quad \text{O} \\
\text{Cl} & \quad \text{R}^1\text{H} \text{N} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{P} \quad \text{O} \\
\text{R}^2\text{R}^3 & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{O} & \quad \text{P} \quad \text{O} \\
\text{R}^1\text{N} & \quad \text{R}^2\text{R}^3 \\
\end{align*}
\]

Scheme 69

Similarly, it has been demonstrated that compounds containing an acidic H e.g. alcohols, thiols, phenols, thiophenols, and carboxylic acids will add to \( \text{P}^{\text{III}} \) reagents to give P-H phosphoranes as shown in Scheme 70.\textsuperscript{213,214}

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

Scheme 70

In certain cases, especially for the amino-substituted phosphoranes (135; \( Z = \text{NR} \)), equilibria exist between the spirocyclic \( \text{P}^{\text{V}} \) structure (135) and the ring-opened \( \text{P}^{\text{III}} \) form (136).\textsuperscript{96,211}
These P-H phosphoranes are potential reducing agents. Heating or mild oxidation e. g. using iodine/sulphur can lead to the loss of hydrogen and the formation of new spirophosphoranes. For example, the phosphorane (137), which is produced by the reaction of catechol with 2-methyl 1,3,2-benzodioxaphospholan, gives (138) on heating above 0°C. A similar intermolecular reaction of the phosphoranes e. g. (135; Z, Y = O) with alcohols, in the presence of enamines as oxidising agents, produces alkoxySpirophosphoranes. Munoz and co-workers have reported that the oxidisation of the P-H phosphorane (139) by DMSO in DMF provides a synthetic route to the hydroxyporphoranes (140).

Laurenco and Burgada have reacted a number of P-H phosphoranes such as (135, Y = O) with aldehydes, ketones, imines, aminals, phenyl isocyanate and acid chlorides. In some cases, insertion into the
P-H bond occurs to give new spirophosphorenes which contain a P-C bond e.g. as shown in Scheme 71. In other cases, the reaction occurs with the \( \text{P}^{\text{III}} \) form (136) e.g. acid chlorides acylate the phosphite form (136).

\[ \text{Scheme 71} \]

B. 4 \textit{Phosphoranes from the Reaction of Tervalent Phosphorus Compounds with } \( \alpha \)-\textit{Keto- and } \( \alpha, \beta \)-\textit{Unsaturated Acids and Related Compounds.} Treatment of \( \alpha \)-keto-acids with cyclic phosphonates and phosphites gives cyclic acyloxyphosphoranes, presumably via a mechanism as shown in Scheme 72. 217 The acyclic phosphites gave the Arbuzov

\[ \text{Scheme 72} \]
An analogous reaction of acryclic acid and acrylamide leads to the isolation of the crystalline phosphoranes. Similar reactions have been reported for other α,β-unsaturated acids.

**B. 5 Phosphoranes from the Reaction of Phosphorus(III) Compounds with Peroxides and Related Compounds.**

Denney and co-workers have prepared alkoxyphosphoranes by the reaction of diethyl and dimethyl peroxides with a wide range of P{sup III} reagents including phosphites, phosphonites, phosphinites and phosphines (Scheme 73).

\[
\text{H}_2\text{O}-\text{OR}^1 + \text{R}_3\text{P} \rightarrow \text{R}_3\text{P(OR)}_2
\]

Scheme 73

As described for the Ramirez adducts (Scheme 50), those acyclic and monocyclic oxyphosphoranes which contain two or more alkoxy groups often undergo exchange with 1,2- and 1,3-diols to give other oxyphosphoranes containing one or two rings. This exchange
reaction has been used in the synthesis of non-phosphorus heterocycles. For example, treatment of triphenyldiethoxyphosphorane with 1,4-butanediol and 1,5-pentanediol gives tetrahydrofuran and tetrahydropyran, respectively, in good yields. The suggested mechanism involves monoexchange to give (144) which subsequently decomposes as shown in Scheme 74. It has also been reported that pentaethoxyphosphorane undergoes an exchange reaction with n-propyl alcohol to give new phosphoranes containing n-propyloxy groups.

\[
\text{Ph}_3\text{P}(\text{OEt})_2 + \overset{\text{HO}}{\left(\text{CH}_2\right)_n} \rightarrow \begin{array}{c}
\text{Ph}_3\text{P} \\
\overset{\text{O}}{\left(\text{CH}_2\right)_n}
\end{array} + \overset{\text{HO}}{\text{Ph}_3\text{PO}}
\]

**Scheme 74**

There are reports of 1,2-dioxan and 1,2-dioxetans adding to tervalent phosphorus to produce seven-membered and 5-membered ring phosphoranes respectively. For example, the reaction of triphenylphosphine with the trans-1,2-dioxetan gives the phosphorane (145) which decomposes at 50°C to form the cis-stilbene epoxide (Scheme 75).

\[
\begin{array}{c}
\text{PhH} \\
\text{PhH}
\end{array} + \overset{\text{O}}{\text{PPh}_3} \rightarrow \begin{array}{c}
\text{PhH} \\
\text{PhH}
\end{array} + \text{Ph}_3\text{PO}
\]

**Scheme 75**
Interestingly, the related three membered ring phosphoranes (146), which are formed by the low-temperature reaction of 3,3,4-trimethyl-1,2-dioxetan with 1-phenylphosphirane, fragment on warming to room temperature to give ethylene and the $P^{\text{III}}$ compounds as shown in Scheme 76. The dithiet (147) also adds to tervalent phosphorus compounds to give five membered ring phosphoranes (Scheme 77).

![Scheme 76](image)

![Scheme 77](image)

B. 6 Phosphoranes from the Reaction of Halophosphoranes with Alcohols, Amines and Thiols.

Fluoro and chloro pentavalent phosphorus compounds react with amines, alcohols, thiols, and their organometaloid or silicon derivatives to give rise to phosphoranes in which one or more halogen atoms are replaced by -OR, NR$_2$ and SR groups respectively. A few selected examples of this general reaction are given in Scheme 78. The sequence of reactions used to prepare (149) also illustrates a commonly used preparation of halophosphoranes e.g. (148) by the
treatment of tervalent phosphorus compounds with halogens and halogenating agents. Similar dihalophosphoranes are useful synthetic intermediates not only in the preparation of phosphoranes but also in general organic chemistry e.g. dichlorotriphenylphosphorane has been used for the specific conversion of allylic alcohols into allylic chlorides.
B. 7 Phosphoranes from the Reactions of Phosphorus Ylides, Phosphonium Salts and Related Compounds.

As noted earlier, pentaco-ordinate phosphoranes are assumed to be the intermediates in numerous reactions at tetrahedral phosphorus. Indeed phosphoranes have been isolated from reactions of phosphorus ylides, phosphonium salts and phosphoryl compounds and some of these will be discussed below.

(a) From Phosphorus Ylides and 1,3-Dipoles.

The general reaction as shown in Scheme 79 has obvious potential for the synthesis of quinquevalent phosphoranes (150, X = CR\(^1\)\(^2\), NR\(^1\), O, and S). However, so far only in the case of the methylenephosphoranes (150, X = CR\(^1\)\(^2\)) has the reaction proved to be a useful method of preparing isolable quinquevalent phosphoranes. In a typical example, Huisgen and Wulf\(^{227}\) have prepared 1,2,5-oxaazaphosph(v)olidenes by the reaction of nitrones with reactive ylides as shown in Scheme 80. Thermolysis of the adducts from diphenylnitrone gives the phosphine oxide (151) apparently by loss of benzyne.
The reaction of nitrile oxides with methylenephosphoranes has been the subject of many investigations and appears to involve the initial formation of a 4,5-dihydro-1,2,5-oxazaphosph(v)ole (154). The latter has proved isolable in a number of cases.\(^{228}\) The stability of the phosphoranes and their subsequent decomposition products depend on the mesomeric and inductive properties of the substituents \(R^1\), \(R^2\) and \(R^3\) (Scheme 81).\(^{228a}\) The adducts from the reactive ylides (152, \(R^1\), \(R^2\) = H, alkyl) are isolable. For example, Bestmann and Kunstmann\(^{228a}\)
have prepared the stable cycloadduct (154, \( R^1, R^2 = -(CH_2)_2, R^3 = \text{Ph} \)) in good yields by the reaction of benzonitrile oxide and cyclopropylene-triphenylphosphorane. Thermolysis of the \( P^V \) species gives the azirine (156, \( R^1, R^2 = -(CH_2)_2 \)) in 84% yield, presumably via the betaine (155). The adducts from isopropylidenetriphenylphosphorane eliminate triphenylphosphine to give \( \alpha,\beta \)-unsaturated oximes (157). Similarly, Gaudiano and co-workers \(^{228c}\) have reported that treatment of the aryl-nitrile oxides (153, \( R = \text{Ph}, (\text{CH}_3)_3\text{C}_6\text{H}_2 \)) with the reactive ylides (152, \( R^1 = \text{H}, R^2 = \text{CH}_3 \)) in dimethyl sulphoxide gives crystalline \( P^V \) compounds (154) which react with HBr to form 2-oximinophosphonium salts (158). In this case thermolysis of the phosphoranes affords azirines and/or ketenimines. \(^{228c}\)

(b) From Phosphorus Ylides and Epoxides

Oxaphospholans (159) and/or the isomeric betaines,
\[
\begin{align*}
R^3P^+CR^1R^2CR^3HCR^4HO^-,
\end{align*}
\]
have long been postulated as intermediates in the reaction of epoxides with methylenephosphoranes. \(^{229}\) The nature of the product of the reaction depends on the ylide and ring substituents.

\[
\begin{align*}
R^3P=CR^1R^2 + R^3H \rightarrow R^3P^+CR^1R^2CR^3HCR^4HO^-,
\end{align*}
\]

\[
\begin{align*}
[(\text{CH}_3)_3P^+-(\text{CH}_2)_3\text{OH}]\text{OH}^{-}
\end{align*}
\]

\[
\begin{align*}
[(\text{CH}_3)_3P^+-(\text{CH}_2)_3\text{OCH}_3]^{-}
\end{align*}
\]

Scheme 82
and, in some cases, particularly when basic ylides are involved, oxaphospholans have been isolated.\textsuperscript{228a,230} For example, Schmidbaur and Holl\textsuperscript{230a} have obtained distillable phosphoranes (159, $R_1^1, R_2^2, R_3^3, R_4^4, R_5^5 = \text{H}$) from the reaction of trimethyl and triethyl methylenephosphoranes with ethylene oxides. The authors assigned t. b. p. structures (with axial oxygen) to the compounds on the basis of the results of variable temperature $^1H$, $^{13}C$, and $^{31}P$ n.m.r. experiments. Some of the reactions of the phosphoranes are summarised in Scheme 82.

As shown, the phosphoranes undergo P-O bond fission by acids to give phosphonium salts. Hands and Mercer\textsuperscript{231} prepared the first examples of (159) by the treatment of 3-hydroxypropyltriphenylphosphonium halides with base. Schmidbaur and Holl\textsuperscript{230b} have also formed 1,2-oxaphospholans by the addition of oxiran to the P=C bond of the ylide (160). Huisgen and Wulf\textsuperscript{230c} have reported that reaction of styrene oxide

\[
\begin{align*}
\text{Me}_3\text{P} &= \text{N} \text{PMe}_2\langle \equiv \text{CH}_2 \rangle \\
(160) &
\text{PhHC(OH)}\text{CH}_2\text{CMe} \langle \equiv \text{CH}_2 \rangle \\
(161) &
\text{Ph}_3\text{P} \equiv \text{CHCH}_2\text{CMe}_2\langle \equiv \text{CH}_2 \rangle \\
(162) &
\text{PhHC(OH)}\text{CH}_2\text{CMe} \langle \equiv \text{CH}_2 \rangle \\
(161) &
\text{Li}^+
\end{align*}
\]

with isopropylene phosphorane gave the $P^V$ compound, (159, $R = R_5^5 = \text{Ph}, R_1^1 = R_2^2 = \text{CH}_3, R_4^4 = R_3^3 = \text{H}$) which decomposed to give the unsaturated alcohol (161), presumably via P-O bond fission followed by an $E^2$ elimination. Salmond et al.\textsuperscript{230e} have obtained the ylide (162) by treatment of the phosphorane (159, $R = \text{Ph}, R_1^1 = R_2^2 = R_3^3 = \text{H}, R_4^4 = R_5^5 = \text{Me}$) with butyl-lithium. The ylide forms trans-olefins with aldehydes.
There have been reports of the preparation of $P^V$ compounds by intramolecular reactions of epoxides with phosphorus ylides bearing suitable side chains.\textsuperscript{230} Thus Turcant and Le Corre\textsuperscript{232a} prepared the stable phosphoranes (163) by treatment of methyleneephosphoranes with

\[
\begin{align*}
\text{Ph}_3\text{P}^-\text{CHR}^1 + \text{Ph}_3\text{P}^-\text{CHR}^1 & \rightarrow \text{Ph}_3\text{P}^-\text{CHR}^1 \rightarrow \text{Ph}_3\text{P}^-\text{CHR}^1 \\
\text{ClCH}_2\text{C} & \rightarrow \text{ClCH}_2\text{C} \\
(163) & \\
R^1 = \text{H} & \text{base}
\end{align*}
\]

epichlorohydrin. A mechanism involving an intermediate ylide (164) was supported by its alternative formation from the action of base on the $\omega$-epoxy phosphonium salt (165). The same authors\textsuperscript{232b} also reported that a series of $\omega$-epoxymethyleneetriphenylphosphoranes gave both the oxaphospholans (166) and (167) on heating. Some of the

\[
\begin{align*}
\text{Ph}_3\text{P}^-\text{CHR}^1 + \text{C}_6\text{H}_5\text{CH}_3 & \rightarrow \text{Ph}_3\text{P}^-\text{CHR}^1 + \text{Ph}_3\text{P}^-\text{CHR}^1 \\
\text{(166)} & \\
\text{n} = 4 & \text{HCHO}
\end{align*}
\]
phosphoranes (166, n=1 and 166, n=3) were isolated and others e.g. (167, n=4) were identified by their ylide reactions.

Similarly, Kyba and Alexander\(^{232c}\) have prepared the oxazaphosph(v)oles by the Staudinger reaction of the azido epoxide (168, \(R^1 = R^2 = \text{Ph}, R^1 = \text{Me}, R^2 = \text{Bn}^t\)) with triphenylphosphine, methyl diphenylphosphonite, dimethyl phenylphosphinite, and trimethyl phosphite as shown in Scheme 83. Preliminary X-ray investigations of the phosphorane obtained from triphenylphosphine indicated a t.b.p. structure as in (169, \(R = R^1 = R^2 = \text{Ph}\)) with an equatorial oxygen.

The reversal of the normal apicophilicity of oxygen and nitrogen has been attributed to the lone pair effect since the \(sp^2\) nitrogen atom does not have a lone pair of electrons which can lie in the equatorial plane.

\(^1\)H N.m.r. studies have shown some of the phosphoranes to be fluxional. The authors also found that the chemistry of the compounds was complex. Thus, attempted hydrolysis of (169, \(R = R^1 = R^2 = \text{Ph}\)) in dichloromethane/water gave high yields of triphenylphosphine oxide and approximately 20% benzophenophene along with smaller amounts of at least three other, as yet unidentified, products.

(c) From Phosphorus Ylides and Carbonyl Compounds

There are several reports based on observations using low temperature \(^{31}\) P n.m.r. spectroscopy of oxaphosphetans as intermediates
in the Wittig reaction. An isolable oxaphosphetan (170) has been obtained from the reaction of hexafluoroacetone with hexaphenyldiprodiphosphorane.

\[
\begin{align*}
\text{Ph}_3\text{P}^-\text{C}^-\text{PPh}_3 & \quad \text{Ph}_3\text{P} \quad \text{PPh}_3 \\
+ & \quad \text{O} \quad (\text{CF}_3)_2\text{C} \equiv \text{O}
\end{align*}
\]

(170)

Similarly, as discussed earlier (Scheme 24), Schmidpeter and von Criegern obtained the [2+2] cycloadducts (171) by the reaction of cyclic iminophosphoranes with ketones. In a related reaction, Schmidpeter and co-workers also prepared phosphoranes by addition of isocyanates to cyclic iminophosphoranes as shown in Scheme 84.

N. m. r. spectroscopy showed that the phosphorus in the adducts was

\[
\begin{align*}
\text{Y} & \quad \text{Y} \\
\text{Ph}_2\text{N} & \quad \text{Ph}_2\text{N} \\
\text{Z} & \quad \text{Z}
\end{align*}
\]

(172) \( Y = \text{CO}_2\text{Et} \)

(173)

(174) \( Z = \text{CN} \) or \( \text{CO}_2\text{Me} \)

(175)
coupled to the methyl protons of the added isocyanate in the case when \( R = \text{Me} \). From this evidence, the authors concluded that the reaction proceeded by the addition of the ylidic \( \text{P}=\text{N} \) bond to the \( \text{C}=\text{N} \) and not the \( \text{C}=\text{O} \) group of the isocyanate to give pentaco-ordinate phosphoranes with structures (173) and (175). Depending on the nature of the five-membered ring and on the substituents at phosphorus, the adducts obtained from the foregoing reactions are stable or dissociate in solution and/or decompose in Wittig-type reactions. For example, the adduct of the phenyl derivative (172, \( X = \text{Ph} \)) and methyl isocyanate is stable whereas the corresponding adduct from the amino derivative (173, \( X = \text{NMe}_2 \), \( R = \text{Me} \)) is in equilibrium with (172) in solution. By contrast the adduct (175, \( R = \text{Me} \), \( Z = \text{CO}_2\text{Me} \), \( X = \text{Ph} \)) dissociates completely and cannot be isolated. The phosphoranes derived from (174, \( Z = \text{CO}_2\text{Me} \)) and especially (174, \( Z = \text{CN} \)) are generally less stable than those from (172) to dissociation and also to a Wittig-type decomposition to form the phosphine oxide. Phenyl isocyanate also adds to (172) to give stable adducts (173, \( X = \text{Me} \) or \( X = \text{Ph} \)). The \( ^{31}\text{P} \) resonance of the adduct (173, \( X = \text{Me} \), \( R = \text{Ph} \)) shifted to lower field with increasing solvent polarity indicating some contribution of the Zwitterionic form to the equilibrium. However, even in this case, the contribution from the Zwitterionic form seems limited and for those compounds with more electrophilic phosphorus e.g. (173, \( X = R = \text{Ph} \)) or more nucleophilic nitrogen e.g. (173, \( X = R = \text{Me} \)) it is absent. In contrast, the Zwitterionic forms appear to be more important for the corresponding isothiocyanate adducts.
(d) From Phosphonium Salts, Phosphorus Ylides and Hydroxy Compounds.

There are a number of preparations of phosphoranes which can be considered to involve either addition of an O-H group to the P=X bond of a phosphorus ylide (X = \( \text{CR}_1 \text{R}_2 \), \( \text{NR}_1 \)) or nucleophilic attack by OH on a phosphonium or aminophosphonium salt. For example, Schmidbaur and Holl, have obtained the phosphoranes (176, \( n=2 \)) and (176, \( n=1 \)) by the reaction of Scheme 85.

\[
\begin{align*}
\text{Scheme 85} \\
\text{Me} & \quad \text{Me} \\
\text{Me} & \quad \text{Me} \\
\text{OMe} & \quad \text{OMe} \\
(176)
\end{align*}
\]

Several groups have reported that phosphonium salts containing an \(-\text{hydroxy}\) group can cyclise to form \( P^V \) compounds when treated with base. Thus, Hands and Mercer have obtained the 2,2,2-triphenyl-1,2-oxaphosph(v)olan (177) by the reaction of 3-hydroxypropyltriphenylphosphonium iodide with sodium hydride. Oxaphospholans of this type have also been prepared by the action of epoxides on phosphorus ylides (see Scheme 82). Some of the reactions of (177) are summarised in Scheme 86.

\[
\begin{align*}
\text{Scheme 86} \\
\text{Ph}_3\text{P}(\text{CH}_2)_3\text{OH} & \quad \text{I}^- \\
\text{PhP}(\text{CH}_2)_3\text{OH} & \quad \text{O} \\
[\text{Ph}_3\text{P}(\text{CH}_2)_3\text{OH}] & \quad \text{OH} \\
\text{Ph}_3\text{P}(\text{CH}_2)_3\text{OH} \quad \text{PhNO} & \quad \text{PhNOH} \\
\text{Ph}_3\text{P}(\text{CH}_2)_3\text{OH} & \quad \text{Ph}_3\text{P}(\text{CH}_2)_3\text{OH} \\
(179a) & \quad (179b) \\
(179c)
\end{align*}
\]
Howe has reported that treatment of (E)-2-(N-hydroxyanilino)vinyltriphenylphosphonium bromide (178) with base gives a yellow solid which has both betaine and $P^V$ characteristics according to $^1H$ and $^{31}P$ n.m.r. studies. Thus, the compound existed solely as the $P^V$ compound in $\text{CCl}_4$, $\text{C}_6\text{D}_6$, and toluene but in $\text{CDCl}_3$ it formed an equilibrium mixture of the $P^V$ isomer (179a) and the betaines (179b) and (179c) with (179a) and (179b) in an equilibrium that was rapid on the n.m.r. time scale. In methanol, the product existed predominantly as the trans-betaine (179c). In general alcohol solvents and lithium bromide favoured (179c) over (179a) and (179b). Howe attributed the solvent effects to a combination of polar solvent stabilisation of the polar forms (179b) and (179c) [with (179c) more stabilised than (179b)] and also OH-bonding effects which favour (179c) over (179b).

Phosphonium salts containing an oxime group such as $R_3\text{P}^+\text{CH}_2\text{Car}(\text{NOH})^-$ undergo a similar intramolecular nucleophilic attack of oxygen on phosphorus to give phosphoranes. For example, Gaudiano and co-workers have reported that 4,5-dihydro-1,2,5-oxaphosph(v)oles (154) can be prepared by base treatment of the 2-oximinophosphonium salts (158). The salts were prepared in good yields by quaternisation of triphenyl- and tri-$n$-butyl-phosphine with the appropriate 1-aryl-2-chloroethan-1-one oxime and by oximation of the corresponding 2-ketophosphonium salts. The cyclisation is best performed by percolating an alcoholic solution of the salt through an ion exchange resin whereby (154) is obtained pure and in high yields. Cold aqueous sodium or potassium hydroxide can also be used but cold pyridine is not sufficiently basic. As noted earlier phosphoranes of
this type, which can also be prepared by addition of nitrile oxides to
phosphines, regenerate the salts on treatment with acid (see Scheme
81). Another example of the cyclisation reaction is provided by the
work of Shevchuk and co-workers, who prepared the phosphoranes
(180) by the reaction of the methylene phosphoranes (181, \(R^1 = \text{Me},
R^2 = \text{CH}_3\text{CO}\)) and (181, \(R^1 = \text{H}, R^2 = \text{EtO}_2\text{C}\)) with the chloro oximes
(182, \(R^3 = \text{CH}_3\text{CO}\)) and (182, \(R^3 = \text{PhCH}_2\)) respectively. It is worth
noting that treatment of the ylide (181, \(R^1 = \text{H}, R^2 = \text{CH}_3\text{CO}\)) with a
number of chloro ketoximes containing acyl or aroyl side chains (182,
\(R^3 = \text{RCO} \text{ or } \text{ArCO}\)) gave the isoxazoles (183).

\[ R^1R^2\text{C}==\text{PPh} + \text{Cl} \stackrel{\text{HON}}{\longrightarrow} \]

\[ \text{L}^3\text{P}==\text{PR}^2R^1 \]

\[ R^1 = \text{H}, R^2 = \text{COR}^4, R^3 = \text{COR}^5 \]

A number of the foregoing pentaco-ordinate phosphoranes,
e.g. (177) and (179) have ylidic characteristics and undergo Wittig
reactions especially at higher temperatures. Thus (177) condensed
with benzaldehyde at 90° for 2 h, \(p\)-chlorobenzaldehyde at 120° for 30
min, furfuraldehyde at room temperature exothermically and rapidly,
and acetophenone at 130° for 2 h to give \(\gamma\), \(\delta\)-unsaturated alcohols in
yields of 67, 77, 52 and 35% respectively (Scheme 88). By contrast,
no reaction was observed with acetone even after 3 h at 170°C. This lack of reactivity is presumably due to the greater steric hindrance of the ketones compared with the aldehydes. Similarly, treatment of the phosphonium salt of (179) with aromatic aldehydes in the presence of sodium methoxide methanol gave the α-styryl-N-phenylnitrones (184).

In the case of the iminophosphoranes, Stegmann and co-workers were the first to observe the intramolecular addition of the O-H group to the P=N bond to give pentaco-ordinate phosphoranes of type shown in Scheme 89. On the basis of n.m.r. studies, it was reported that

\[ \text{Scheme 89} \]

\[ \text{N-(2-hydroxyaryl)iminophosphoranes underwent what the authors called a 'valence tautomerism' between the iminophosphorane (185) and the } P^V \text{ form (186) the position of the equilibrium depending markedly on the solvent used, temperature and the phosphorus and ring substituents (X and R). It was reported that of the systems investigated, only the} \]
compounds (187) and (188a, b and c) existed solely in the $P^V$ form. In these cases, the $P^V$ form appears to be favoured either by the presence of electron-withdrawing groups on phosphorus which enhance its electrophilicity and/or by the presence of strongly electron-withdrawing groups in the ring. Polar, basic solvents favour the pentaco-ordinate isomer presumably by increasing the ionisation of the hydroxyl group. For example, the compound (188, $R_1 = R_2 = (CH_3)_3C$, $R = Ph$) existed as a mixture of the $P^{IV}$ and $P^V$ forms in CDCl$_3$ but only as the phosphorane in n-propylamine. However, increasing the temperature in the range -$50^\circ$C to $25^\circ$C resulted in an increase in the amount of iminophosphorane at the expense of the $P^V$ form.

The above reaction of iminophosphoranes with X-H compounds (X=O, N) appears to be quite general. Thus, Cadogan and co-workers 97
have reported that the Stegman system (186), prepared by the Staudinger reaction of 2-azidophenols and phosphites, or phosphonites, existed only in the $P^{V}$ form.

Wolf and co-workers\textsuperscript{96} have used a related reaction to prepare the phosphoranes (189, $Z = O$ or NMe, $R^1 = H$ or Me, $R^2 = Me$ or Ph) by the intramolecular addition of the $N$-H group to the $P=N$ bond of the iminophosphoranes (190). Thus, the Staudinger reaction of phenyl azide with the $P^{III}$ $P^{V}$ tautomeric equilibrium mixture (191) afforded pentacoordinate phosphoranes (Scheme 90). Preliminary attempts to detect the intermediate iminophosphorane (190) and also the triazine were reported to be unsuccessful although there was some $^{31}P$ evidence of the presence of $P^{IV}$ species in the crude reaction mixture.

The preparation of monocyclic and spirocyclic phosphoranes can also be achieved as shown in Scheme 91 by the reaction of aminophosphonium salts and iminophosphoranes with compounds containing two suitable acidic protons. In these reactions the amino function
is displaced from the phosphorus and serves to activate $R_3P$ and to act as a base. For example, Trippett and co-workers have devised a method of converting $P^{\text{III}}$ compounds into pentaco-ordinate phosphoranes using an intermediate aminophosphonium salt. Thus, treatment of a variety of tervalent phosphorus compounds with 1,2- and 1,3-diols at $-78^\circ\text{C}$; or with 1,2-amines and thiols at $-40^\circ\text{C}$ in the presence of $N$-chloroisopropylamine, gave the phosphorane (Scheme 92, $X, Y=O, N, S$). The reaction is believed to occur via the aminophosphonium salt (192) and was developed as an improvement on an earlier method using the intermediate (193) formed by reaction of $P^{\text{III}}$ reagents with diethyl azidoformate. In a related reaction, Cadogan and co-workers

\[
\begin{align*}
R_3^+PNP_2^+ & \overset{\text{Cl}^-}{\longrightarrow} \quad R_3^+PN(CO_2\text{Et})-\overset{\text{N}(CO_2\text{Et})}{\longrightarrow} \\
(192) & \quad (193) \\
(194) & \quad (195)
\end{align*}
\]
have prepared the spirocyclic tetraoxyphosphoranes of the type (194) by addition of diols to a mixture of phenyl azide and 1,3,2-dioxaphospholane via the intermediate iminophosphorane (195).

(e) Phosphonium Salts and Metal Alkyls

Turnblom and Katz \textsuperscript{242a} prepared the first stable penta-alkylphosphorane (196; \( R^1 = R^2 = \text{Ph} \)) by treatment of diphenylphosphonium-homocubane bromide with phenyl lithium (Scheme 93). The formation of the \( P^V \) compound rather than the expected ylide was attributed to the relief of strain in going from the 'highly strained' \( P^IV \) compound to the strain-free pentaco-ordinate phosphorane. These workers have extended the reaction to the preparation of other alkyl phosphoranes by the use of other cyclic phosphonium salts e.g. (197, \( R^1 = \text{Ph}, R^2 = \text{CH}_3; R^1 = R^2 = \text{CH}_3 \)) and by addition of methyl rather than phenyl-lithium. \textsuperscript{242b}

The phosphoranes undergo interesting fragmentation reactions upon heating, for example, (196, \( R^1 = R^2 = R^3 = \text{Ph} \)) at 120\(^\circ\)C for 10 minutes gave an 85\% yield of the 4:1 mixture of \textit{syn}-tricyclo[4.2.0.0\textsuperscript{2}]octa-3,7-diene (198) and (199) together with triphenylphosphine. \textsuperscript{242b}
On the basis of their experimental results, Turnbolm and Katz have noted that alkylphosphoranes in general should be preparable if two of the substituents are constrained in a ring that is sufficiently small. In keeping with this observation, Schmidbaur and co-workers have recently prepared the spirophosphorane (200) by the reaction of Scheme 94. The $^1$H and $^{13}$C n.m.r. spectra of (200) remained unchanged at $-105^\circ$C.

Scheme 94

The reaction of tetraarylphosphonium salts with aryl- and trityl-lithium is a well established method of preparing pentaco-ordinate phosphoranes (Scheme 95). Tetraphenyl- and triphenylmethyl phosphonium salts form ylides when treated with alkyl lithium. However, Hellwinkel has prepared stable spirocyclic tetra-
arylalkyl- and pentaarylphosphoranes containing the bis-2,2'-biphenylene nucleus by treatment of the corresponding phosphonium salts with lithium aluminium hydride or sodium borohydride and with alkyl- and aryl-lithiums as shown in Scheme 96.

Scheme 96

Cyclic and spirocyclic pentaarylphosphoranes have also been prepared by the reaction of N-tosyliminophosphoranes or N-methylated iminophosphoranes with aryllithium compounds (Scheme 97).  

Scheme 97

Treatment of phosphite tosylimines with aryllithium has also been reported to give pentaarylphosphoranes (Scheme 98).  

Scheme 98
(f) **From Phosphine Oxides**

While phosphine oxides are in many cases readily available, their use in synthesis of P\(^V\) compounds is less common than that of the phosphorus ylides due to the lessened reactivity of the former. None-the-less, there are cases of such preparations and some will be summarized below.

Turnbolm and Katz have developed a synthesis of phosphoranes starting from strained phosphine oxides. For example, the sequence of reactions shown in Scheme 99 was used to prepare the phosphorane (201) from the strained phosphine oxide.\(^{242a,b}\)

![Scheme 99](image)

Cavell and Leary\(^{243}\) also prepared the phosphorane (202) by treatment of tris(trifluoromethyl)phosphine oxide with hexamethyl disiloxane. Ramirez and co-workers\(^{244}\) have reported that the phosphate (203) isomerises to the silyloxyphosphorane (204) on treatment with tertiary amines. It is also reported that treatment of the phosphoryl compounds (205) and (207) with halogenating agents gives the phosphoranes (206) and (208), respectively.\(^{150}\) Schmidpeter and Luber\(^{245}\) have shown
\([\text{CF}_3)_3\text{PO} + (\text{Me}_3\text{Si})_2\text{O} \rightarrow (\text{CF}_3)_3\text{P(OSiMe}_3)^2\text{O}\)  

(202)

\[
\begin{array}{c}
\text{O} \\
\text{P} \\
\text{O} \\
\text{O} \\
\text{SiMe}_3
\end{array}
\]

(203)

\[
\begin{array}{c}
\text{O} \\
\text{P} \\
\text{O} \\
\text{O} \\
\text{SiMe}_3
\end{array}
\]

(204)

\(\text{RP(X)}_2\text{Y}_2 \xrightarrow{\text{SE}_4 \text{ or SbF}_3} \text{RPF}_4\)  

(205) \(X = O \text{ or } S; \ Y = F, \text{ Cl, or OH}\)

\(\text{R}^1\text{R}^2\text{P(X)}_2\text{Y} \xrightarrow{} \text{R}^1\text{R}^2\text{PCl}_3\)  

(207)

\(\text{Cl}_2, \text{PCl}_5 \text{ or CCl}_4\)

\(\text{R}^1\text{CONHNH}_2 + \text{R}^2\text{P(X)}_2\text{Cl}_2 \xrightarrow{X = O \text{ or } S} \)  

(209)

\(\text{R}^1\text{CONHNH}_2 + \text{Me}_2\text{P(O)}_2\text{Cl} \rightarrow \)  

(210)

\(\text{R}^3\text{PO} + (\text{CF}_3\text{SO}_3)_2\text{O} \rightarrow [\text{R}^3\text{P-O}^{+}\text{SO}_2\text{CF}_3][\text{CF}_3\text{SO}_3]^\text{−}\)  

\(2\text{HNPr}_2\text{i} \rightarrow \)  

\(2[\text{NH}_2\text{Pr}_2\text{i}][\text{CF}_3\text{SO}_3]^\text{−} + \text{R}^3\text{P} \)  

Scheme 100
that the products obtained from acyl hydrazides and phosphonic dichlorides are the spirophosphoranes (209), whereas the reaction with dimethylphosphinyl chloride gives the diazadiphosphetidine (210). Trippett and Antczak 246 attempted to develop a general route to $P^V$ compounds containing the 1,3,2-dioxaphospholan ring starting from the phosphine oxide as shown in Scheme 100. Thus, treatment of the salts obtained from phosphine oxides and trifluoromethane sulphonyl anhydride with 1,2-diols or catechols in the presence of di-isopropylamine gave the cyclic phosphorane (211) but the method could not be extended to phosphonic or phosphinic esters. Trippett and Antczak 246 have also prepared spirophosphoranes of the type (212) from phosphetan sulphides by alkylation with trimethyloxonium hexafluorophosphate followed by treatment with pyrocatechol but not with perfluoropinacol, in the presence of base (Scheme 101). Hellwinkel and Krapp 247 have reported the preparation of a number of well-characterised phosphoranes by reactions involving intramolecular additions to the $P=O$ bond as shown in Scheme 102.
Scheme 102
Denney and co-workers\textsuperscript{248} have obtained penta-alkoxyphosphoranes (213, \( R^2 = \text{Et, Me, Pr}^1, \text{PhCH}_2, \text{Me}_3\text{CCH}_2, \text{cyclo-C}_5\text{H}_9, \) or \text{cyclo-C}_6\text{H}_{11}\) from the reaction of tertiary phosphites with alkyl benzene sulphonates.

\[
2\text{PhSOR}^1 + (R^2\text{O})_3\text{P} \rightarrow (R^2\text{O})_3\text{P(OR}^1)^2 + (\text{PhS})_2
\]

Bestmann and co-workers\textsuperscript{249} have prepared the phosphorane (214) by heating the ylide (215) in toluene. The bicyclic phosphorane (216) was prepared from (214) as shown in Scheme 103.\textsuperscript{249}

\[
\begin{array}{c}
\text{Ph}_3\text{P=CCC(OEt)}_2 \\
\text{(215)}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph}_2\text{P} \rightarrow \text{Ph}_2\text{P}^+ \\
\text{MeCOCl} \rightarrow \text{Cl}^- \\
\text{NaN(SiMe}_3)_2 \\
\text{(214)}
\end{array}
\]

\[
\begin{array}{c}
\text{Ph}_2\text{P} \\
\text{(216)}
\end{array}
\]

Scheme 103

The reaction of 2-azido-phenols with phosphorochloridites, in the presence of base has been reported to give the diazadiphosphetidines (217).\textsuperscript{250}
1,2-Oxaphosphetans have been obtained from the reaction of some phosphines with hexafluoracetone \textsuperscript{251a,b} and also with phenyltrifluoromethyl ketone. \textsuperscript{150} The dioxaphospholans (218), formed as the primary adduct of hexafluoracetone and phosphines, rearranged on heating to give the 1,2-oxaphosphetans (219). \textsuperscript{234,251c} Decomposition of the oxaphosphetans gave the Wittig products (Scheme 104). Millar and Stewart \textsuperscript{252} have obtained the spirobicyclic acyloxyphosphorane (220) by heating 2-hydroxycinnamic acid with methyl diphenylphosphinite. The phosphorane hydrolysed rapidly to give (221) and underwent thermal rearrangement to the coumarin (222). Schmidpeter \textsuperscript{253} has outlined two general routes to bicyclic phosphoranes such as (224) and (228).
One route is exemplified by Scheme 105 and involves the addition of the phosphite (223) to activated olefins. \(^{253a}\)

The second route involves the use of o-heterodienyl-phenols such as (225) and (226) which are either reacted with chlorophosphines in the presence of base \(^{253b}\) (Scheme 106) or are added to the triaza-phosphole (227) to form phosphoranes such as (228). \(^{253c}\)
Scheme 106

(225)  
\[ \text{Z = C or N} \]
\[ \text{Y = C, N or O} \]

(226)

(227)

(228)
EXPERIMENTAL
1. **Abbreviations and Symbols**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>m. p.</td>
<td>melting point</td>
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<tr>
<td>b. p.</td>
<td>boiling point</td>
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<tr>
<td>i. r.</td>
<td>infrared</td>
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<tr>
<td>ν</td>
<td>wavenumber</td>
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<td>n. m. r.</td>
<td>nuclear magnetic resonance</td>
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<tr>
<td>s</td>
<td>singlet</td>
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<td>d</td>
<td>doublet</td>
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<td>t</td>
<td>triplet</td>
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<td>q</td>
<td>quartet</td>
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<tr>
<td>c</td>
<td>complex</td>
</tr>
<tr>
<td>J</td>
<td>coupling constant</td>
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<tr>
<td>u. v.</td>
<td>ultraviolet</td>
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<tr>
<td>λ</td>
<td>wavelength</td>
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<tr>
<td>m/e</td>
<td>mass to charge ratio</td>
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<tr>
<td>g. l. c.</td>
<td>gas liquid chromatography</td>
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<tr>
<td>t. l. c.</td>
<td>thin layer chromatography</td>
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<tr>
<td>h. p. l. c.</td>
<td>high performance liquid chromatography</td>
</tr>
<tr>
<td>l. p. l. c.</td>
<td>low pressure liquid chromatography</td>
</tr>
<tr>
<td>min, h, d.</td>
<td>minute, hour, day</td>
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<tr>
<td>i. d.</td>
<td>in diameter</td>
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2. Instrumentation and General Techniques

A Instrumentation

Infrared Spectroscopy. i.r. spectra were recorded on a Perkin-Elmer 157G Grating Spectrophotometer with polystyrene ν_{max} 1603 cm^{-1} as a reference for calibration purposes. Liquid samples were examined as thin films and solids as nujol mulls supported on NaCl discs. Solution spectra were obtained using matched cells (path length 0.1 mm) with sodium chloride cells.

Mass Spectroscopy. Mass spectra and exact mass measurements were recorded by Mr. D. Thomas on an A.E.I. MS 902 mass spectrometer.

Gas Liquid Chromatography. G.l.c. was performed using a Pye Series 104 chromatograph with a flame ionisation detector and 1.5 m x 4 mm columns. The carrier gas was nitrogen and the stationary phase was SE 30 or SE52 supported on Chromasorb W. G.l.c./mass spectroscopy was carried out by Dr. P. Bell and Mr. G. Jenkins using a Pye Series 104 Chromatograph coupled to a Micromass 12 mass spectrometer.

Thin Layer Chromatography. Chromatograms were obtained using 0.3 mm layers of alumina (Merck, Aluminium Oxide), deactivated to Brockman activity 3, or silica (Merck, silica gel G) with Woelm Fluorescent Green indicator (0.5%) on glass plates. The components of the developed chromatogram were detected using u.v. light or iodine vapour.

High Performance Liquid Chromatography. H.p.l.c. studies were carried out using 15 cm x 0.5 cm polished stainless steel columns slurry packed with 5 micron Spherisorb silica or alumina. The flow
rate was usually 2.0 ml/min. The pump was either an A.R.L. constant-pressure syringe-pump or a Jobling/Milton-Roy constant flow reciprocating pump. The detectors were u.v. types - either a Cecil CE 212 or a Jobling/LDC fixed at 254 n.m. Solvents were 25% water-saturated for use on alumina and 50% water saturated for silica.

**Low Pressure Liquid Chromatography.** Preparative chromatography using pressurised solvents was carried out using alumina (Merck Aluminium Oxide 90) or silica (Merck silica gel 60) in glass columns either 1000 x 15 mm or 1000 x 25 mm supplied by Jobling. The pump was a Metering pump and the flow rate was approximately 5 ml/min for the narrow (15 mm) columns and approximately 20 ml/min for the wide (25 mm) columns. A u.v. spectrometer, the 1 uv Monitor Model II set at 280 n.m. was used as detector.

**Column Chromatography.** Silica gel used was chromatography grade (80-200 mesh) obtained from Fisons Scientific Apparatus. Alumina used was from Laporte Industries Ltd grade H 100-200 mesh deactivated to Brockman activity 3. Dry column chromatography was carried out using 'C' gauge nylon tubing supplied by Walter Coles and Co. Ltd., London.

**Melting Points.** Melting points of new compounds were obtained using either a Reichert or a Kofler hot-stage microscope. Routine melting points were obtained using capillary tubes and Gallenkamp apparatus.

**Elemental Analysis.** Microanalyses for carbon, hydrogen and nitrogen were carried out by Mr. J. Grunbaum using a Perkin-Elmer 204 elemental analyser.
Molecular Weight Determinations. Molecular weights were determined on a Perkin Elmer Vapour Pressure Osmometer (Model 115) calibrated with benzin.

Ultraviolet Spectroscopy. A Unicam S.P. 800 spectrometer was used with a pair of matched silica cells.

Nuclear Magnetic Resonance Spectroscopy

(i) $^1$H N.m.r. spectra were recorded on a Varian HA 100 spectrometer at 100 MHz by Mr. J. Millar unless otherwise stated. This instrument was also used for decoupling studies. Routine spectra were obtained at 60 MHz using a Varian EM 360. Samples were examined in solution in deuterochloroform with tetramethylsilane as internal reference unless otherwise stated.

(ii) $^{13}$C N.m.r. spectra were recorded by Mr. J. Millar on a Varian CFT 20 spectrometer. Samples were examined in solution in deuterochloroform unless otherwise stated.

(iii) $^{31}$P N.m.r. spectra were obtained on a Jeol FX 60 Q instrument at 24.15 MHz, where relevant relative intensities are given in brackets. A few spectra were recorded by Dr. A. Boyd on a Varian XL 100 spectrometer. All spectra were proton noise decoupled. Samples were examined in solution in deuterochloroform unless otherwise stated. Chemical shifts were measured in p.p.m. relative to external phosphoric acid (85%). Upfield resonances are negative.
B. **General Procedures**

Care was taken to exclude moisture from water-sensitive compounds. These materials were handled in a dry box flushed with dry nitrogen and stored in sealed containers either in a dry box or in a desiccator over phosphorus pentoxide. All apparatus used was dried overnight at 130°C or above and cooled under dry nitrogen or in a desiccator over phosphorus pentoxide. Reactions were carried out under an atmosphere of dry nitrogen.

Light petroleum refers to that fraction with b. p. 40-60°C. Dry benzene and light petroleum were prepared by redistillation and storing over sodium wire. Cumene, t-butylbenzene, cyclohexane, diethyl ether, and n-hexane were dried by storing over sodium wire. All those solvents were 'super dried' by redistillation of the sodium dried solvent from calcium hydride or lithium aluminium hydride and stored over molecular sieve. Ethyl acetate was purified as described by Vogel. Triethylamine and diethylamine were stored over potassium hydroxide pellets. Ethanol and methanol were purified by distillation from activated magnesium as described by Vogel and stored over molecular sieve. Diols were dried over anhydrous magnesium sulphate (24 h) and redistilled on to molecular sieve. Chloroform and dichloromethane were purified as described by Vogel and redistilled from phosphorus pentoxide on to molecular sieve. Deuterated solvents were dried by addition of activated molecular sieve.

Nitrogen was dried by passing through concentrated sulphuric acid followed by potassium hydroxide.

Unless otherwise stated all starting materials were commercially available and redistilled or recrystallised before use.
3. **Preparation of Starting Materials**

(a) **Preparation of Azides:** 1-Phenyl-2-azidoethan-1-one was prepared by the method described by Boyer and Straw. 255 2-Bromo-1-phenylethan-1-one was treated with sodium azide at 0-5°C for 24 h. Filtration and recrystallisation from ether gave the product as colourless crystals (84%). Recrystallisation from light/petroleum ether gave the pure product, m. p. 17-18°C [(from ether/light petroleum) lit., 17°C]. The following azides were prepared in this manner. 1-(4-Bromophenyl)-2-azidoethan-1-one m. p. 86-87°C lit., 255 86-87°C; 1-(4-phenylphenyl)-2-azidoethan-1-one, m.p. 87-88°C (lit., 255 88-88.5°C); 1,2-diphenyl-2-azidoethan-1-one, m.p. 85-86°C lit., 255 85°C. The yields were 58-84%. 1-(4-Methoxyphenyl)-2-azidoethan-1-one was prepared by reaction of the bromide with sodium azide in acetone/ethanol/water as described by Zbiral and Stroh. 116 The azide was obtained as white crystals (69%), m. p. 73-74°C from ether, (lit., 116 72-73°C). Ethyl-2-azido-2-phenylacetate was prepared by the method of Boyer and Straw. 255 Reaction of ethyl phenylacetate with N-bromosuccinimide afforded ethyl-2-bromo-2-phenyl acetate (66%), b. p. 140-142°C/12 mmHg (lit., 255 130°C/8 mmHg). Treatment of the bromide with sodium azide at 3°C for 48 h in methanol/water afforded the azide as an oil, (84%), b. p. 100-104°C/2 mmHg (lit., 255 74/0.5 mmHg).

2-Azidocyclohexanone was prepared by the treatment of 2-chlorocyclohexanone with sodium azide in dimethylsulphoxide as described by Edwards et al. 256 The azide was obtained as a pale yellow oil (52%) and had the correct ¹H and i.r. spectroscopic data.

1-Phenyl-2-azidoethan-1-one oxime was prepared as described by
Forster and Muller. Treatment of 1-phenyl-2-azidoethan-1-one with hydroxylamine in water/ethanol afforded the oxime as an oil (60-85%), $\nu_{max}$ (neat) 3240 (br, OH), 2100 cm$^{-1}$ (br, N$^3$), $\delta$ 4.19, 4.43 (total 2H, each a s, syn and anti isomers CH$_2$), 7.20-7.70 (5H, m, ArH) and 9.70 (br, 1H, s, OH, disappears on shaking with D$_2$O). The new azide 1-(4-Bromophenyl)-2-azidoethan-1-one oxime was prepared in the same manner. The azide was obtained as colourless crystals (74-83%), m.p. 86-89°C (from ether/light petroleum) (Found: C, 37.4, H, 2.7, N, 21.7; C$_8$H$_7$Br$_1$N$_4$O requires C, 37.7; H, 2.8; N, 22.0%), $\nu_{max}$ 3200 (br, sh, OH) and 2100 cm$^{-1}$ (N$^3$), $\delta$ 4.18 and 4.43 (total 2H, each a s, syn and anti isomers, CH$_2$, peaks in ratio 1:5), 7.36-7.80 (4H, c, ArH) and 9.24 (br, 1H, s, OH, disappears on shaking with D$_2$O). Following the same procedure treatment of 1-phenyl-2-azidoethan-1-one with methoxyoxime hydrochloride gave 1-phenyl-2-azidoethan-1-one O-methyl-oxime as a colourless oil in quantitative yield, $\nu_{max}$ 2100 cm$^{-1}$ (N$^3$), $\delta$ 4.00 and 4.05 (total 3H, each a s, syn and anti-isomers, OMe), 4.35 and 4.45 (total 2H each a s, syn and anti isomers, CH$_2$) and 7.25-7.80 (5H, m, ArH).

(b) Preparation of Tervalent Phosphorus Reagents: Triethyl and trimethyl phosphite and tri-n-butylphosphine were allowed to stand over sodium wire for 24 h and then redistilled from fresh sodium in an atmosphere of dry nitrogen. The compounds were stored over molecular sieve. 2-Phenyl-1,3,2-dioxaphospholane was prepared by the reaction of phenylphosphorous chloride (45.0 g, 0.25 mol) with 1,2-ethanediol (15.5 g, 0.25 mol) in benzene in the presence of triethylamine as described by Mukaiyama et al.
The product was obtained as a colourless oil (26.4 g, 62%), b. p. 52°C / 0.05 mmHg, lit. 258 79-80°C / 0.8 mmHg, 3.75-4.10 (4H, m, 2 x CH₂) and 7.15-7.60 (5H, m, ArH) and ³¹P S +16.2. The product was stored at -10°C as it polymerises rapidly at room temperature and more slowly at lower temperature. ³¹P N. m. r. spectra of the compound were scanned prior to use. 2-Phenyl-1, 3, 2-dioxaphosphorinan, b. p. 90-92°C / 0.2 mmHg (lit., 259 86-89°C / 2 mmHg) was prepared by a modification of this method. Phenylphosphonous chloride (45.0 g, 0.25 mol) in benzene (250 ml) was added to a mixture of dry 1, 3-propanediol (19.0 g, 0.25 mol) and triethylamine (50.5 g, 0.50 mol) in benzene (250 ml). The mixture was then heated at approximately 45°C for 45 min and kept at 3°C for 12 h to complete precipitation of triethylamine hydrochloride. The product was obtained as a colourless oil (30.1 g, 66%), 1.40 (1H, d of m, J 14 Hz, one of C-5 protons), 2.15-2.70 (1H, m, one of C5 protons) 3.70-4.35 (4H, m, C-4 and C-6 protons) and 7.20-7.65 (5H, m, ArH) and ³¹P S 153.0.

Methyl diphenylphosphinite was prepared in the standard manner described by Quin and Anderson. 260 Treatment of diphenylphosphinous chloride with methanol in ether afforded the phosphinite as a colourless oil (75%), b. p. 97-98°C / 0.1 mmHg (lit., 260 151-152°C / 10 mmHg), 60 MHz, 3.60 (3H, d ³JHP 14 Hz, CH₃) and 7.10-7.80 (10H, m, ArH) and ³¹P S 117.0. Following the same procedure treatment of phenylphosphous chloride with methanol in the presence of triethylamine gave dimethyl phenylphosphonite as a colourless oil (68%), b. p. 104-105°C / 15 mmHg (lit., 261 101-102°C / 15 mmHg), 60 MHz, 3.50 (6H, d, ³JHP 10 Hz, 2 x CH₃) and 7.20-7.85 (5H, m, ArH) and ³¹P S +160.6. Diphenyl
phenylphosphonite was prepared from phenol and phenylphosphonous chloride in the presence of dimethylaniline as described by Arbuzov and co-workers. The product was obtained as a colourless oil (82%), b. p. 154-156°C/0.3 mmHg (lit. 230°C/14 mmHg).

2-Chloro-1, 3, 2-dioxaphospholan was prepared by Hudson's modification of the method of Arbuzov and co-workers. 2-Chloro-1, 3, 2-dioxaphospholan (77.4 ml, 1.37 mol) was added to a stirred solution of phosphorus trichloride (110 ml, 1.26 mol) in dry dichloromethane (250 ml), under a nitrogen atmosphere, at such a rate that the mixture refluxed gently. When evolution of hydrogen chloride ceased, the solvent was removed and the residual oil distilled, under a dry nitrogen atmosphere to give the product as a colourless oil (108.0 g, 68%), b. p. 44-46°C/12 mmHg (lit. 45-46°C/1 mmHg), \( \sum \) (60 MHz 3.70-4.70 (m, 2 x CH2) and 31P \( \sum \) 167.600).

2-N,N-Diethylamino-1, 3, 2-dioxaphospholan (b. p. 34°C/0.2 mmHg (lit. 50°C/2 mmHg) was prepared by Hudson's method. 2-Chloro-1, 3, 2-dioxaphospholan (73.0 g, 0.58 mol) in dry benzene (200 ml), under a nitrogen atmosphere, was treated with diethylamine (84.7 g, 1.16 mol), dropwise over a period of 1 h at room temperature. The mixture was then stirred for 2 h, filtered and the solvent removed in vacuo. The residue was distilled to give the product as a colourless oil (61.5 g, 65%), b. p. 34°C/0.2 mmHg (lit. 50°C/2 mmHg), \( \sum \) 1.05 (6H, t, \( J_{HH} \) 7.5 Hz, 2 x CH2CH3) and 3.07 (4H, q of d, \( J_{HP} \) 9.0 Hz, \( J_{HH} \) 7.5 Hz, 2 x CH2CH3) and 4.10-4.60 (4H, m, 2 x OCH2) and 31P 143.0.

1, 2, 5-Triphenylphosphole was prepared by Scott's modification of the method of Campbell et al. Reaction of 1,4-diphenyl-1, 3-butadiene
(48.1 g, 0.23 mol) and phenylphosphonous chloride (53.4 g, 0.30 mol) at 215°C gave the product as a yellow solid (24.0 g, 33%), m.p. 187-189°C (from chloroform) (lit. 187-189°C) and $^{31}$P $\delta$ 2.8. 1,4-Di-phenyl-1,3-butadiene m.p. 151-152°C (lit. 152.5-153.5°C), was prepared by the condensation of phenyl acetic acid and cinnamaldehyde in the presence of litharge as described by Corson. 265

1-Phenylphospholan was prepared by a modification of the method of Gruttner and Wiernik. 266 Dry 1,4-dibromobutane (216.0 g, 1.0 mol) in dry ether (150 ml) was added to magnesium turnings (51.0 g, 2.1 mol) in ether (300 ml) under an atmosphere of dry nitrogen at such a rate that the mixture refluxed gently. When addition was completed, the mixture was boiled under reflux for 1 h, cooled and filtered quickly through glass wool into an addition funnel. Phenylphosphonous chloride (89.0 g, 0.5 mol) was made up to the same volume as the Grignard reagent using ether as solvent. The solutions of the Grignard reagent and phosphorus(III) reagent were added simultaneously and at the same rate to acetone- and ice-cooled dry ether (2 l.) with vigorous stirring under an atmosphere of nitrogen over a period of 5 h. The mixture was then stirred at 0°C for 1 h and allowed to stand at room temperature for 12 h. The mixture was cooled using an acetone-ice bath and then diethylamine (500 ml) was carefully added with stirring. The resultant white suspension was passed through a short wide alumina or celite column to remove the salts. The solvent was removed in vacuo and the residual yellow oil distilled to give the phospholan as a colourless oil (45.0-29.0 g, 55-35%), b.p. 78-80°C/0.2 mmHg (lit. 97°C/3 mmHg), $\delta$ 1.52-2.40 (8H, m, 4 x CH$_2$) and 7.10-7.65 (5H, m, ArH) and $^{31}$P $\delta$ -15.8. Treatment of the
Grignard reagent with diphenylphenylphosphonite (147.0 g, 0.5 mol) in an identical manner as for phenylphosphonous chloride gives 1-phenylphospholan in similar yields. In the same manner, reaction of the appropriate Grignard reagent and phenylphosphonous chloride afforded 1-phenylphosphorinan (64%), b.p. 86-88°C/0.1 mmHg (lit., 267 119°C/3 mmHg) $^\circ\text{H} 1.00-2.35$ (10H, c, $5\text{CH}_2$) and 7.20-7.75 (5H, m, ArH) and $^{31}\text{P} 8.33.5$, and diethylphenylphosphine (72%), b.p. 62-64°C/2 mmHg (lit., 108-109°C/20 mmHg), $^\circ\text{H} 1.00$ (6H, t of d, $3\text{J}_{\text{HP}} 15\text{Hz}$, $3\text{J}_{\text{HH}} 7\text{Hz}$, $2\times\text{CH}_2\text{CH}_3$) 1.70 (4H, d of q, $\text{J}_{\text{HH}} 7\text{Hz}$, $2\times\text{CH}_2\text{CH}_3$) and 7.3-7.2 (5H, m, ArH) and $^{31}\text{P} 8-15.6$. Samples of ethyl diphenylphosphinite were supplied by Dr. H. McNab, 1-phenyl-3-methyl-3-phospholene by Mr. K. Wall and 1-phenyl-3-methyl-2-phospholene and 1, 2, 5-tritolylphosphole by Mr. T. Naisby. 2-Phenyl-1, 3, 2-benzodioxaphosphole and 2-phenyl-1, 3, 2-t-butylbenzodioxaphosphole were prepared from the appropriate catechol and phenylphosphonous chloride by Dr. B. Nay.

(c) Preparation of Miscellaneous Starting Materials: 1-Phenyl-2-bromoethan-1-one was prepared by the reaction of acetophenone with bromine in the presence of anhydrous aluminium chloride as described by Cowper and Davidson.269 The solid was obtained as colourless crystals (84%), m.p. 50-51°C (from methanol), lit., 269 49-51°C, $\nu_{\text{max}}$ 1695 (C=O).

1, 2-Diphenyl-2-bromoethan-1-one was prepared by the method of Patai and co-workers.270 Treatment of deoxybenzoin with bromine in acetic acid gave the bromide (65%), m.p. 52-53°C (lit., 270 53°C).

1, 2-Diphenyl-2-chloroethan-1-one was prepared by the reaction of benzoin
with thionyl chloride as described by Feiser and Okumura. The chloride was obtained as a colourless solid (72%, m. p. 66-67°C (lit., 66-67°C).

Bromoacetone was prepared by the bromination of acetone in the manner described by Levine. The product was a colourless oil (38%), b. p. 52-54°C/26 mmHg (lit., 40-42°C/13 mmHg) and δ 2.35 (3H, s, CH₃) and 3.90 (2H, s, CH₂).

4-t-Butylbromobenzene was prepared by the method of Tchitchibabine et al. by the reaction of bromine with t-butylbenzene using powdered iron as catalyst. The product had b. p. 114-116°C/22 mmHg (lit., 102-107°C/14 mmHg) ν_max 730 and 720 cm⁻¹ and M⁺, 214 and 212.

4-t-Butylbenzaldehyde was prepared by the addition of the diGrignard of 4-t-butylobromobenzene to triethylorthoformate in the manner described by Tchitchibabine et al. The product had b. p. 128-130°C/24 mmHg (lit., 238-240°C), ν_max 1690 cm⁻¹ (br, C=O), δ 1.20 (9H, s, (CH₃)₃C), 7.20-7.80 (4H, AB₄, ArH) and 9.80 (1H, s, HCO) and M⁺, 182.

1,2-Di-p-t-butyphenyl-2-diazoethan-1-one was prepared from the benzaldehyde following the standard procedure described by Vogel. Treatment of 4-t-butylbenzaldehyde with sodium cyanide gave 4,4'-di-t-butylbenzoin as colourless crystals (64%) m. p. 129-130°C (Found: C, 81.8; H, 8.3; M⁺, 324: C₂₂H₂₈O₂ requires C, 81.5; H, 8.7% and M⁺, 324), ν_max 3400 (OH), and 1675 (C=O), δ 1.25 and 1.40 (18H, 2x, 2x(CH₃)₃C), 460 (1H, d, 6Hz, CH), 6.00 (1H, d, J_HH 6Hz, OH) and 7.40-8.15 (8H, c incorporating an s at 7.4 and an ABq, 2x ArH). Treatment of the benzoin with cupric acetate and ammonium nitrate in acetic acid gave 4,4'-di-t-butylbenzil as colourless crystals (80%), m. p. 140-142 (Found:
C, 81.9; H, 8.3; M⁺, 322, C_{22}H_{26}O_2 requires C, 81.95; H, 8.1%; M⁺, 322) and \( \nu_{\text{max}} \) 1675 and 1600 cm⁻¹ (C=O). 4,4-Di-t-butylbenzil monohydrazone was obtained by treatment of the benzil with hydrazine hydrate. The monohydrazone was obtained as colourless crystals (60%), m.p. 174-176° (Found: C, 78.3; H, 8.6; N, 8.5; M⁺, 336: C_{22}H_{26}N_2O requires C, 78.5; H, 8.4; N, 8.4%; M⁺, 336), \( \nu_{\text{max}} \) 3280 (NH) and 1.32 (9H, s, (CH₃)₃C), 5.20 (br, 1H, s, NH) and 6.20-7.00 (4H, c, ArH). The monohydrazone was oxidised by mercuric oxide to give the diazo ketone as an orange solid (93%), m.p. 88-89°C (from ether) (Found: C, 78.7; H, 7.8; N, 8.0: C_{22}H_{26}N_2O requires C, 79.0; H, 7.8; N, 8.4%; \( \nu_{\text{max}} \) 2080 (CN₂) and 1605 cm⁻¹ (C=O). Following the same procedure, 1,2-diphenyl-2-diazoethan-1-one, m.p. 78-79°C (lit., 79°C), was prepared from benzil. The monohydrazone had m.p. 149-151°C (lit., 149-151°C). N-Bromoacetamide was prepared by the method of Oliveto and Gerold. Treatment of acetamide with bromine gave the product as colourless needles, m.p. 101-105° (lit., 102-105°).

Ethyl \( \alpha \)-bromoacetate was prepared by a modification of Smith's method. Treatment of ethylacetoacetate with bromine gave the halide as a colourless oil (54-82%) (100-103°C/12 mmHg, lit., 101-104°/12 mmHg).

**General Method.** Due to the instability of the phosphoranes towards hydrolysis, precautions were taken to exclude moisture from the compounds. All apparatus were carefully dried. The compounds were handled in the dry box. The preparations were carried out using benzene or ether. Benzene was dried in the usual manner with lithium aluminium hydride or calcium hydride and stored over molecular sieve. Ether was distilled from lithium aluminium hydride immediately before use.

A solution of the azide (1 mmol) in benzene or ether (5-10 ml) was added dropwise and with stirring under an atmosphere of dry nitrogen to a solution of the tervalent phosphorus reagent (1.2 - 1.5 mmol) in benzene or ether (5-10 ml) at room temperature. The mixture was stirred for 1 to 48 h during which time the phosphorane precipitated out of the solution. The precipitate was filtered off in a dry box and washed with either a little benzene then ether or ether only. The product was dried under reduced pressure over phosphorus pentoxide.

(a) Reaction of 1, 2-Diphenyl-2-azidoethan-1-one.

(i) With 2-phenyl-1, 3, 2-dioxaphospholan. A preliminary reaction showed complete conversion to the phosphorane. A mixture of the azide (0.3 g, 1.27 mmol) and phosphorus reagent (0.24 g, 1.4 mmol) in dry ether (12 ml) were stirred for 48 h. The resulting white solid was filtered, washed with ether, dried and identified as 2,4', 5'-triphenylspiro-[1, 3, 2-dioxaphospholan-2, 2'- Δ^4'-[1, 3, 2]-oxazaphospholine] (0.43 g, 89%), m. p.
88-95°C (decomp) (Found: C, 69.8; H, 5.3; N, 3.5; C_{22}H_{20}N_{1}O_{3}P_{1}
requires C, 70.0; H, 5.3; N, 3.7%), ν_{max} 3220 (N-H) and 1630 cm^{-1}
(C=C) δ 3.40-4.70 (4H, m, C^{4} and C^{5} protons), 5.01 (1H, d, 2J(HP)
14 Hz, NH) and 6.80-8.10 (15H, m, ArH), 31P δ -29.7, m/e 377 (M^{+},
100), 333 (M-C_{2}H_{4}O, 25, m^{*} 294.1 (377-333)) and 184 (25).

(ii) With 2-phenyl-1, 3, 2-dioxaphosphorinan. A preliminary
reaction showed complete conversion to the phosphorane 48 h after mixing.
The azide (0.5 g, 2.1 mmol) and the phosphorus reagent (0.42 g, 2.3
mmol) in dry ether (20 ml) were stirred together. After 48 h the solution
was evaporated to smaller volume under reduced pressure at room tem-
peraure. The white solid was filtered off, washed with ether, dried
and identified as 2,4', 5'-triphenylspiro-[1, 3, 2-dioxaphosphorinan-2, 2'-
\Delta^{4}-[1, 3, 2-oxazaphospholine] (0.79 g, 96%), m.p. 94-105°C (decomp)
(Found: M^{+}, 391.133850. C_{23}H_{22}NO_{3}P requires M^{+}, 391.133723,
N, 3.58%), ν_{max} 3225 cm^{-1} (N-H), δ 1.40-2.28 (2H, m, C^{5} protons,
2.6-5.08 (5H, m, NH and C^{4} and C^{6} protons) and 7.1-8.3 (15H, m, ArH),
31P δ -45.6, m/e 391 (M^{+}, 13), 333 (M-C_{3}H_{6}O, 8, m^{*} 283.6 (391-333),
198 (100), 159 (33), 142 (92), 141 (83), 140 (63) and 117 (71). Due to
the great instability of the product towards hydrolysis a satisfactory
analysis could not be obtained.

(iii) With methyl diphenylphosphinite. Reaction of the azide and
phosphinite gave a foam which could not be analysed but was identified as
2-methoxy-2, 4, 5-tetraphenyl-\Delta^{4}-1, 3, 2-oxazaphospholine on the basis
of 31P and ^1H n.m.r. Reaction of the phosphinite (105.7 mg, 0.49 mmol)
and the azide (124.1 mg, 0.52 mmol) in either benzene or ether was
vigorous with nitrogen being evolved. 31P N.m.r. of the reaction
mixture using a $^6$dimethylsulphoxide capillary lock showed complete conversion to the phosphorane at -42 p. p. m. - no other phosphorus compounds were detectable. The phosphorane was stable in solution. Evaporation of the solvent gave a yellow foam with $^{31}$P -41.4 p. p. m. with minor peaks at 33.4 (methyl diphenylphosphinate), 23.9 and -49.5 p. p. m. whose intensity were less than 10% of the phosphorane signal, and δ (60 MHz) 3.05 (3H, d, $^3$J(HP) 11Hz, OCH$_3$), 4.20 (1H, d, $^2$J(HP) 16 Hz, NH) and 6.7-8.2 (20H, m, ArH).

(b) **Reaction of 1-Phenyl-2-azidoethan-1-one**

(i) **With 2-phenyl-1, 3, 2-dioxaphospholan.** Addition of the azide (1.61 g, 1 mmol) in benzene (10 ml) to a solution of the phosphorus reagent (1.85 g, 1.1 mmol) in benzene (5 ml) gave, after stirring for 1 h, a white precipitate. The reaction was instantaneous, heat was evolved and nitrogen was given off. 2,5'-Diphenylspiro-[1, 3, 2-dioxaphospholan-2, 2'-Δ$^4$-[1, 3, 2]-oxazaphospholine] was obtained as a white powder (1.85 g, 61%) which tarnished rapidly, m.p. 84°C (decomp) (Found: C, 63.8; H, 5.3; N, 4.6; C$_{16}$H$_{16}$NO$_2$P requires C, 63.8; H, 5.35; N, 4.65%), $\nu_{\text{max}}$ 3380 (N-H) and 1630 cm$^{-1}$ (C=C), δ 3.30-4.60 (4H, m, C$^4$ and C$^5$ protons), 4.87 (br, 1H, d, $^2$J(HP) 18Hz, NH), 6.32 (1H, d of d, $^3$J(HP) 32Hz, $^3$J(HH) 3Hz, C$^{4'}$ proton) and 6.80-8.90 (10H, m, ArH), $^{31}$P 5 -25.4, m/e 301 (M$^+$, 100), 257 (M-C$_2$H$_4$O, 75, m* 219.4 (301-257) and 141 (65), 140 (45).

(ii) **With 2-phenyl-1, 3, 2-dioxaphosphorinan.** The reaction between the azide (0.5 g, 3.1 mmol) and the phosphorus reagent (0.7 g, 3.85 mmol) in benzene (15 ml) was rapid, nitrogen was evolved, the mixture
warmed and a white precipitate was formed. 2,5-Diphenylspiro-
[1,3,2-dioxaphosphorinan-2,2'-Δ4-[1,3,2]-oxazaphospholine] was
obtained as a white solid (0.8 g, 82%) which tarnished rapidly, m.p.
87°C (decomp) (Found: C, 64.7; H, 5.8; N, 4.3; \( C_{17}H_{18}NO_{3}P \)
requires C, 64.8; H, 5.75; N, 4.4%), \( \nu_{\text{max}} 3400 \text{ cm}^{-1} \) (N-H),
3.40-5.00 (5H, c, NH and C⁴ and C⁶ protons), 6.34 (1H, d of d, 3J(HP) 33Hz, 3J(HH) 3Hz, C⁴ proton) and
6.80-8.00 (1OH, s, ArH), \( ^{31}P 6-25.3, m/e 381 \) and 379 (M⁺, 100), 257
(M-C₃H₆, 53, m*, 209.6 (315-257)), 198 (60), 182 (27), 159 (20),
142 (45), 141 (73), 140 (27), 117 (33) and 105 (60).

(c) Reaction of 1-(4-bromophenyl)-2-azidoethan-1-one.

(i) With 2-phenyl-1,3,2-dioxaphospholan. A solution of the azide
(1.2 g, 5 mmol) in benzene (10 ml) was added to a solution of the
phosphorus reagent (1.0 g, 6 mmol) in benzene (5 ml). Rapid reaction
occurred with evolution of heat and nitrogen and immediate precipitation
of a white solid identified as 2-phenyl-5'-[(p-bromophenyl)spiro-[1,3,2-
dioxaphosphorinan-2,2'-Δ4-[1,3,2]-oxazaphospholine] (1.35 g, 71%),
m.p.85-120°C (decomp) (Found: C, 50.7; H, 3.9; N, 3.6; \( C_{16}H_{15}BrN_{3}O_{3}P \)
requires C, 50.55; H, 4.0; N, 3.7%), \( \nu_{\text{max}} 1640 \text{ cm}^{-1} \) (C=C), \( ^{31}P 6-25.3, m/e 381 \) and 379 (M⁺, 100), 337 and
335 (M-C₃H₄O₂, 60, m* 298.1 (381-337) and 296.1 (379-335), 185 and
183 (17), 168 (31), 141 (26) and 140 (49).

(ii) With 2-phenyl-1,3,2-dioxaphosphoran. A solution of the
azide (0.48 g, 2.0 mmol) was added to a solution of the phosphorus
reagent (0.40 g, 2.2 mmol) in benzene (10 ml). Nitrogen was evolved
and a precipitate was formed. 2-Phenyl-5'-(p-bromophenyl)spiro-[1,3,2-
dioxaphosphorinan-2, 2'-Δ^4'[1, 3, 2]-oxazaphospholene was obtained as a white solid (0.67 g, 85%) which turned brown rapidly m.p. 105-118°C (decomp) (Found: C, 51.6; H, 4.2; N, 3.3; C_{17}H_{17}BrNO_3P requires C, 51.8; H, 4.35; N, 3.55%), ν_{max} 3440 (N-H), 31P δ -40.8 and 1640 cm\(^{-1}\) (C=C), m/e 395 and 393 (M^+ 79), 337 and 335 (M-C_3H_6O, 63, m* 287.5 (395-337) and 285.6 (393-335)), 198 (32), 182 (61), 140 (32) and 141 (100).

(d) Reaction of 1-(4-Methoxyphenyl)-2-azidoethan-1-one.

(i) With 2-phenyl-1, 3, 2-dioxaphospholan. The azide (1.0 g, 5.2 mmol) and the phosphorus reagent (1.0 g, 6 mmol) in benzene (15 ml) gave, after 24 h, a white solid which was identified as 2-phenyl-5'-(p-methoxyphenyl)spiro-[1, 3, 2-dioxaphospholan-2, 2'-Δ^4'[1, 3, 2]-oxazaphospholene] (1.2 g, 73%), m.p. 99°C (decomp) (Found: C, 61.8; H, 5.3; N, 4.2; C_{17}H_{18}NO_4P requires C, 61.6; H, 5.5; N, 4.2%), ν_{max} 3400 (N-H) and 1645 cm\(^{-1}\) (C=C), δ 3.5-4.8 (8H, c, incorporating a singlet at 3.69 due to MeO and multiplet from 3.5-4.8 due to C^4 and C^5 protons and NH), 6.14 (1H, d of d, J(HP) 34Hz, J(HH) 3Hz, C^4 proton) and 6.66-8.00 (9H, c, aromatic), 31P δ -25.6, m/e 331 (M^+ 100), 292 (18, m* 257.6 (331-292)), 287 (52, M-C_2H_4O, m* 248.9 (331-287)), 184 (48) and 141 (95).

(ii) With 2-phenyl-1, 3, 2-dioxaphosphorinan. The azide (2.0 g, 10.5 mmol) and the phosphorus reagent (2.2 g, 12 mmol) in benzene (15 ml) gave, after 5 h, 2-phenyl-5'-(p-methoxyphenyl)spiro-[1, 3, 2-dioxaphosphorinan-2, 2'-Δ^4'[1, 3, 2]-oxazaphospholene] as a white solid (2.6 g, 74%), which turned brown rapidly, m.p. 102°C (decomp) (Found:
C, 62.3; H, 5.8; N, 4.0; \( \text{C}_{18}\text{H}_{20}\text{NO}_{4}\text{P} \) requires C, 62.6;
H, 5.8; N, 4.1\% \) \( \nu_{\text{max}} \) 3400 cm\(^{-1}\) (N-H), \( ^{31}\text{P} \delta \) -41.2, m/e 345
(M\(^+\), 100), 287 (M-C\(_3\)H\(_6\)O, 35, m\(^*\) 238.7 (345-287)), 141 (30) and
135 (31).

(e) Reaction of 1-(4-Phenylphenyl)-2-azidoethan-1-one.

(i) With 2-phenyl-1,3,2-dioxaphospholan. The azide (1.3 g, 5.5 mmol) and the phosphorus reagent (1.0 g, 6 mmol) in benzene, gave, after 12 h, 2-phenyl-5'-(p-phenylphenyl)spiro-[1,3,2-dioxaphospholan-2,2'-\( \Delta^4 \)-[1,3,2]-oxazaphospholine] as a pale pink solid (1.77 g, 85\%), m.p. 105\°C (decomp) (Found: C, 69.8; H, 5.3;
N, 4.0; \( \text{C}_{22}\text{H}_{20}\text{NO}_{3}\text{P} \) requires C, 70.0; H, 5.3; N, 3.7\%), \( \nu_{\text{max}} \) 3395 (N-H) and 1643 cm\(^{-1}\) (C=C), \( ^{31}\text{P} \delta \) -25.5, m/e 377 (M\(^+\), 100),
333 (M-C\(_2\)H\(_4\)O, 50, m\(^*\) 294.1 (377-333), 194 (17), 181 (17), 141 (20)
and 140 (24).

(ii) With 2-phenyl-1,3,2-dioxaphosphorinan. Reaction of the azide (1.5 g, 6.3 mmol) and the phosphonite (1.2 g, 6.6 mmol) in benzene (15 ml) gave the 2-phenyl-5'-(p-phenylphenyl)spiro-[1,3,2-
dioxaphosphorinan-2,2'-\( \Delta^4 \)-[1,3,2]-oxazaphospholine as a pink solid
(2.3 g, 93\%), m.p. 90\°C (decomp) (Found: C, 70.3; H, 5.5; N, 3.4;
\( \text{C}_{23}\text{H}_{22}\text{NO}_{3}\text{P} \) requires C, 70.6; H, 5.7; N, 3.6\%), \( \nu_{\text{max}} \) 3380 (NH)
and 1640 cm\(^{-1}\) (C=C), \( ^{31}\text{P} \delta \) -40.9, m/e 391 (M\(^+\), 100), 333 (M-C\(_3\)H\(_6\)O,
50, m\(^*\) 283.6 (391-333)), 210 (25), 198 (41), 181 (25), 182 (50), 151 (25),
152 (33), 142 (41) and 141 (75).
(f) Reaction of 1-Phenyl-2-azidoethan-1-one Oxime

(i) With 2-phenyl-1,3,2-dioxaphospholan. A solution of the azide (1.14 g, 6.5 mmol) in benzene (5 ml) was added to a solution of the phosphorus reagent (1.2 g, 7.2 mmol) in benzene (10 ml). After 10 min a white solid precipitated out. The mixture was stirred for a further 1 h. The precipitate was filtered, washed with a little benzene then ether and dried to give white crystals identified as 2,5-diphenylspiro-[1,3,6,2-oxadiaza-(1,2,3,4-tetrahydrophosphorin)-2,2'-Δ^5-[1,3,2]-dioxaphospholan] (1.29g, 62%), m.p. 133-135°C (decomp) (Found: C, 60.6; H, 5.4; N, 8.8; C_{16}H_{17}N_{2}O_{3}P requires C, 60.8; H, 5.4; N, 8.9%). ^ν_{max} 3400 cm\(^{-1}\) (N-H), 6 3.30-4.20 (7H, c, 3 x CH\(_2\) and NH), and 7.20-7.95 (1OH, m, ArH), 5 ((CD\(_3\))\(_2\)SO) 3.0-4.4 (6H, c, 3 x CH\(_2\)), 5.14 (1H, br d, 3\(^1\)J(HP) 18Hz, collapses to br s on ^31\(P\) irradiation, NH), and 7.2-7.86 (1OH, m, ArH), 31\(^P\) 37, 0, m/e 316 (M\(^+\), 35), 299 (M-OH, 6), 255 (299-C\(_2\)H\(_4\)O, 12, m* 217.5 (299-255)), 196 (18), 185 (27), 184 (24), 140 (50), 139 (18), 120 (29) and 103 (100).

(ii) With 2-phenyl-1,3,2-dioxaphosphorinan. The azide (0.78 g, 4.4 mmol) and the phosphorus reagent (0.9 g, 5 mmol) were reacted, in benzene (12 ml), to give 2,5-diphenylspiro-[1,3,6,2-oxadiaza-(1,2,3,4-tetrahydrophosphorin)-2,2'-Δ^5-[1,3,2]-dioxaphosphorinan] as white crystals (0.98g, 69%), m.p. 123-126°C (decomp) (Found: C, 61.7; H, 5.8; N, 8.6; C_{17}H_{19}N_{2}O_{3}P requires C, 61.8; H, 5.8; N, 8.5%), ^ν_{max} 3400 cm\(^{-1}\) (N-H), 6 1.50-2.00 (2H, m, C\(^5\') protons), 2.8-4.40 (7H, c, NH and C\(^4\), C\(^4\') and C\(^6\') protons) and 7.14-8.00 (1OH, m, ArH), 31\(^P\) 5-52.0, m/e 330 (M\(^+\), 6), 199 (28), 198 (22); 141 (46), 102 (64) and 103 (100).
(iii) **With 1-phenylphospholan.** A solution of the phosphine (0.72 g, 4.4 mmol) in benzene (10 ml) was added to a solution of the azide (0.71 g, 4 mmol) in benzene (10 ml). Nitrogen was evolved, the reaction mixture became warm and a white precipitate was formed 5 min after addition. **1′, 5-Diphenylspiro-[1, 3, 6, 2-oxadiaza-(1, 2, 3, 4-tetrahydrophosphorin)-2, 1″-Δ⁵-1′-phospholan] was obtained as a white solid (0.91 g, 73%), m.p. 107-112°C (decomp) (Found: C, 69.4; H, 6.8; N, 9.0; C_{18}H_{21}N_{2}OP requires C, 69.2; H, 6.8; N, 9.0%), \( \nu_{\text{max}} \) 3230 cm\(^{-1} \) (N-H), \( \delta \) 1.20-2.00 (8H, m, \( C^{2'}, C^{3'}, C^{4'} \) and \( C^{5'} \) protons), 4.07 (2H, d, \( 3J(HP) 16Hz, C^{4} \) protons) and 7.20-7.90 (10H, m, ArH), \( ^{31}\text{P} \) 5-33.0, m/e 312 (M\(^+\), 18), 295 (M-OH, 24, m\(^*\) 278.9 (312-295)) 192 (28), 180 (94), 164 (34), 152 (74), 124 (46), 105 (50), 104 (42) and 103 (100).

(iv) **With 2-phenyl 1, 3, 2-benzodioxaphosphole.** The azide (0.5 g, 2.8 mmol) in ether (15 ml) was added to a solution of the phosphorus reagent (0.61 g, 2.8 mmol) in ether (15 ml). **2′, 5-Diphenylspiro-[1, 3, 6, 2]-oxadiaza-(1, 2, 3, 4-tetrahydrophosphorin)-2, 2″-Δ⁵-[1, 3, 2]-benzodioxaphosphole was obtained as a white solid (0.15 g, 15%), m.p. 188°C (decomp.) (Found: C, 66.05; H, 4.7; N, 7.7: M\(^+\) 364; C_{20}H_{17}N_{2}O_{3}P_{1} requires C, 65.9; H, 4.7; N, 7.7%; M\(^+\) 364), \( \nu_{\text{max}} \) 3385 (N-H), and \( \delta \) (d\(^6\)-DMSO) 4.1 (2H, br d, J\(_{HP}\) 16Hz, CH\(_2\)), 5.9 (1H, d, J\(_{HP}\) 16Hz, NH), 6.5-7.2 (14H, m, ArH) and \( ^{31}\text{P} \)(d\(^6\)-DMSO -27.9.

(v) **With 2-phenyl-1, 3, 2-p-t-butylbenzodioxaphosphole.** The azide (0.5 g, 2.8 mmol) in ether (15 ml) was added to a solution of the phosphorus(III) reagent (0.9 g, 3.3 mmol) in ether/benzene (50/50, 15 ml). **2′, 5-Diphenylspiro-[1, 3, 6, 2]-oxadiaza-(1, 2, 3, 4-tetrahydrophosphorin)-2, 2″-Δ⁵-[1, 3, 2]-p-t-butylbenzodioxaphosphole was obtained as a white solid (0.11 g, 13%) m.p. 174°C; M\(^+\) 420;
max $3420 \text{ cm}^{-1}$ (NH), $\delta$ (d$^6$-DMSO), 1.7 (9H, d, (CH$_3$)$_3$, 2 isomers), 4.4 (2H, br d, $J_{HF}$ 16Hz, CH$_2$), 6.2 (br d, $J_{HF}$ 16Hz, NH) and 6.4-8.2 (13H, m, Ar) and $^{31}$P $\delta$ -33. The product could not be obtained pure due to its inability to crystalise.

(g) **Reaction of 1-(4-Bromophenyl)-2-azidoethan-1-one Oxime.**

(i) *With 2-phenyl-1, 3, 2-dioxaphospholan.* The azide (1.0 g, 3.9 mmol) and the phosphorus reagent (0.80 g, 4.8 mmol) were reacted in benzene (15 ml) to give 2-phenyl-5-(p-bromophenyl)spiro-[1, 3, 6, 2-oxadiaza-(1, 2, 3, 4-tetrahydrophosphorin)]-2, 2'-$\Delta^5$-[1, 3, 2]-dioxaphospholan as white crystals (1.02 g, 66%), m. p. 153-160°C (decomp) (Found: C, 48.7; H, 4.0; N, 7.0; C$_{16}$H$_{16}$BrN$_2$O$_3$P requires C, 48.6; H, 4.1; N, 7.1%), $\nu_{max}$ $3420 \text{ cm}^{-1}$ (N-H), $\delta$ 3.40-4.20 (7H, c, aliphatic and NH) and 7.20-8.00 (9H, c, ArH), $^{31}$P $\delta$ -36.9, m/e 396 and 394 (M$^+$, 59), 379 and 377 (M-OH, 9), 335 and 333 (335 and 333 - C$_2$H$_4$O, 21, m$^*$ 296.1 (379-335) and 294.1 (377-333)), 196 (74), 185 (100), 183 and 181 (62), 166 (44), 141 (71), 140 (79) and 102 (85).

(ii) *With 2-phenyl-1, 3, 2-dioxaphosphorinan.* Reaction of the azide (0.5 g, 2.0 mmol) and the phosphorus reagent (0.4 g, 2.2 mmol) in benzene (10 ml) gave 2-phenyl-5-(p-bromophenyl)spiro-[1, 3, 6, 2-oxadiaza-(1, 2, 3, 4-tetrahydrophosphorin)]-2, 2'$\Delta^5$-[1, 3, 2]-dioxaphosphorinan as white crystals (0.69 g, 86%), m. p. 104-106°C (decomp) (Found: C, 50.2; H, 4.55; N, 6.5; C$_{17}$H$_{18}$BrN$_2$O$_3$P requires C, 49.9; H, 4.4; N, 6.85%), $\nu_{max}$ $3400 \text{ cm}^{-1}$ (NH), $\delta$ 1.60-2.00 (2H, m, C$^{5'}$ protons), 3.60-4.40 (7H, c, C$^{4'}$ and C$^{6'}$ protons and NH) and 7.20-8.00 (9H, c, ArH), $^{31}$P $\delta$ -51.9, m/e 183 and 181 (97) and 102 (100),
(iii) With 1-phenylphospholan. The azide (0.70 g, 2.75 mmol) and the phosphine (0.50 g, 3.05 mmol) were reacted (12 ml) in benzene to give \( \text{1'-phenyl-5-(p-bromophenyl)spiro-[1, 3, 6, 2-oxadiaza-(1, 2, 3, 4-tetrahydrophosphorin)]-2, 1'-\Delta^5-1'-phospholan} \) as a white solid (0.79 g, 74\%), m. p. 90\(^\circ\)C (decomp) (Found: C, 55.25; H, 5.1; N, 6.9;
\[ C_{18}H_{20}BrN_2OP \] requires C, 55.3; H, 5.2; N, 7.2\%), \( \nu_{\text{max}}^{\text{N-H}} 3275 \text{ cm}^{-1} \), 6.1.20-2.20 (8H, c, C\(^2\), C\(^3\), C\(^4\), and C\(^5\) protons), 4.00 (2H, d, \( ^3J(HP) 16\text{Hz} \), C\(^4\) protons) and 7.10-7.90 (9H, c, ArH), \( ^{31}P 3275 \text{ cm}^{-1} \), m/e 183 (95), 181 (96), 180 (100), 152 (76) and 102 (80).

(iv) With 2-phenyl-1,3,2-benzodioxaphosphole: The azide (1.07 g, 4.2 mmol) in ether (15 ml) was added to a solution of the phosphorus(III) reagent (1.2 g, 4.4 mmol) in ether (15 ml). \( \text{2'-Phenyl-5-(p-bromophenyl)spiro-[1, 3, 6, 2-oxadiaza-(1, 2, 3, 4-tetrahydrophosphorin)]-2, 2'-\Delta^5-[1, 3, 2]-benzodioxaphosphole} \) was obtained as a white solid (0.5 g, 27\%), m. p. 185\(^\circ\)C (Found: C, 54.4; H, 3.7; N, 6.1; \( M^+ 444.442; C_{20}H_{18}BrN_2OP \) requires C, 54.2; H, 3.6; N, 6.3\%) and \( M^+ 444.442, \nu_{\text{max}}^{\text{DMSO}} 3400 \text{ cm}^{-1} \), (d\(^6\) DMSO) 4.1 (2H, br d, J\(_{HP} 16\text{Hz} \), CH\(_2\)) \( J_{HP} \), 5.2, (1H, d, J\(_{HP} 16\text{Hz} \), NH) and 6.5-8.9 (13H, m, ArH) and \( ^{31}P 3400 \text{ cm}^{-1} \).

(v) With 2-phenyl-1,3,2-\( \text{p}^+ \)-butylbenzodioxaphosphole. The azide (1.07 g, 4.2 mmol) in ether (15 ml) was added to a solution of the phosphorus(III) reagent (1.2 g, 4.4 mmol) in ether (15 ml). \( \text{2'-Phenyl-5-(p-bromophenyl)}-\]
\[ \text{spiro-[1, 3, 6, 2-oxadiaza-(1, 2, 3, 4-tetrahydrophosphorin)]-2, 2'-\Delta^5-[1, 3, 2]-p^+ \text{butyl benzodioxaphosphole} \) (0.82 g, 39\%), m. p. 175-177\(^\circ\)C (Found: C, 57.9; H, 5.0; N, 5.5; \( M^+ 500.498; C_{24}H_{24}BrN_2O_3P \) requires C, 57.7; H, 4.85; N, 5.6\% and \( M^+ 500.498, \nu_{\text{max}}^{\text{DMSO}} 3410 \text{ cm}^{-1} \) (NH), (d\(^6\)-DMSO), 1.7 (9H, d, (CH\(_3\))\(_3\) 2 isomers), 4.4 (2H, br d, J\(_{HP} 16\text{Hz} \), CH\(_2\)), 6.2 (br d, J\(_{HP} 16\text{Hz} \), NH) and 6.8-8.2 (12H, m, Ar) and \( ^{31}P 33.6 \).
(i) **Reaction of Ethyl 2-Azido-2-phenylacetate.**

The azide (2.05 g, 10 mmol) was treated with the phosphorus reagent (1.68 g, 10 mmol) in benzene (20 ml). Nitrogen was evolved. After 3d at room temperature a cake of white solid was present. The solid was washed out using ether and worked up as before. At room temperature the solid was practically insoluble in chloroform, benzene and ether - a satisfactory $^1$H n.m.r. could not be obtained. The solid (1.35 g) had m.p. 129-131°C, (Found: C, 63.4; H, 5.9; N, 3.9; $C_{\text{H}_{20}}N_{\text{O}_{4}}P$, requires C, 62.6; H, 5.8; N, 4.1%), $\nu_{\text{max}}$ 1750 cm$^{-1}$, $^{31}$P 543.8 (8) and 44.5 (9).

(ii) **Reaction of 1-Phenyl-2-azidoethan-1-one O-Methyloxime.**

The azide (0.5 g, 2.6 mmol) and the phosphorus reagent (0.5 g, 3.0 mmol) were stirred in benzene (10 ml) at room temperature for 16 h. Super dry light petroleum was added dropwise until crystals came out of solution. The mixture was kept overnight at -10°C then filtered to give the 5,7-diphenyl-6,12-bis(2-phenyl-2-methoxyiminoethyl)-1,4,8,11-tetraoxa-6,12-diaza-5,7-diphospha-(5,7-$P^V$)dispiro[4.1.4.1]dodecane as white crystals (685 mg, 80%), m.p. 140-142°C (Found: C, 61.8; H, 5.8; N, 8.3; $C_{\text{H}_{38}}N_{\text{O}_{6}}P_{2}$ requires C, 61.8; H, 5.8; N, 8.5%), $\delta$ 2.8-4.02 (total 7H, c incorporating a singlet at 3.92 (OMe and broad complex bands from 2.8 to 3.46 and from 3.46 to 4.02 due to the ring CH$_2$'s), 4.38 (2H, t, $^3$J(HP), 28Hz, collapses to a singlet on $^{31}$P irradiation, CH$_2$) and 6.84-7.70 (10H, m, ArH), $^{31}$P $\delta$ 48.7 (12), 55.0 (11) and 55.6 (90), m/e 660 (M$^+$, 0.3), 331 (1), 330 (2), 299 (330-OMe, 38, *m* 270.9 (330-299)), 195 (51), 196 (299-PhCN, 100) and 152 (196-C$_2$H$_4$O).
6. Preparation of Iminophosphoranes: Reaction of α-Azido Carbonyl Compounds and α-Azido Oximes with Tervalent Phosphorus Reagents.

General method. The procedure was the same as that followed for the preparation of pentacoordinate phosphoranes outlined in section (5).

(a) Reaction of 1, 2-Diphenyl-2-azidoethan-1-one.

(i) With 1-phenylphosphorinan. To a solution of 1-phenylphosphorinan (0.98 g, 5.5 mmol) in ether (5 ml) was added a solution of the azide (1.2 g, 5 mmol) in ether (10 ml). After 4 h excess 'super dry' light petroleum (b.p. 40-60°C) was added and the mixture was stirred for an additional 3 h. The precipitate was filtered off, washed with light petroleum and dried to give N-(1, 2-diphenyl-2-oxoethyl)imino-1-phenylphosphorinan as white crystals (1.55 g, 80%), m.p. 133-135°C (from benzene/light petroleum) (Found: C, 77.3; H, 6.3; N, 4.6; C_{25}H_{26}N_{OP} requires C, 77.5; H, 6.8; N, 3.6%). ν_{max} 1640 (C=O), 1170, 690 and 695 cm^{-1}, 0.90-2.40 (10H, c, 5 x CH_{2}', s), 4.29 (1H, d, J(HP) 21Hz, CH) and 6.78-8.10 (15H, c, ArH), 31P 518.3, m/e 387 (M^+, 6), 384 (8), 297 (10), 282 (27), 210 (10), 194 (21), 178 (23), 166 (8), 150 (8), 140 (8), 124 (16), 123 (8), 106 (27), 105 (46) and 104 (100).

(b) Reaction of 1-Phenyl-2-azidoethan-1-one Oxime

(i) With triphenylphosphine. The azide (0.83 g, 4.7 mmol) and the phosphine (1.31 g, 5 mmol) in benzene (15 ml) gave white crystals after 1.5 h identified as N-(2-phenyl-2-hydroxyiminoethyl)iminotriphenylphosphine (1.43, 74%), m.p. 146-148°C (Found: C, 76.1; H, 5.7; N,
6.6; C_{26}H_{23}N_2OP requires C, 76.1; H, 5.65; N, 6.8%); δ 4.47
(2H, d, ^3J(HP) 14Hz, CH_2) and 7.08-7.80 (21H, c, ArH and OH, 20H on
shaking with D_2O), ^31P δ 17.6, m/e 410 (M^+, <0.1), 278 (30), 277 (58),
201 (15), 183 (15), and 103 (100).

(ii) With 1-phenylphosphorinan. A mixture of the azide (0.50 g,
2.8 mmol) and the phosphine (0.60 g, 3.4 mmol) in benzene (10 ml) gave
a white precipitate after 5 min. The precipitate was washed with a little
benzene, followed by ether, and dried. N-(2-Phenyl-2-hydroxyiminoethyl)imino-1-phenylphosphorinan was obtained as white crystals (0.71 g, 78%),
m.p. >155°C (decomp) (Found: C, 70.1; H, 7.1; N, 8.3; C_{19}H_{23}N_2OP
requires C, 69.9; H, 7.1; N, 8.6%), ν_{max} 2500 cm\(^{-1}\) (br, O-H,
hydrogen bonded), ^31P δ 19.3, m/e 326 (M^+, <0.1), 194 (65), 195 (25),
165 (41), 140 (37), 125 (90), 124 (25), 104 (20) and 103 (100).

(iii) With diethylphenylphosphine. The azide (1.76 g, 10.0 mmol)
in benzene (12 ml) was added to a solution of the phosphine (1.8 g, 10.8
mmol) in benzene (12 ml). Nitrogen was evolved and the solution turned
yellow. After 12 h the precipitate was filtered off, washed with a little
benzene, followed by ether, and dried. N-(2-Phenyl-2-hydroxyiminoethyl)iminodiethylphenylphosphine was obtained as a white solid which
decomposed on standing, (0.95 g, 30%), m.p. >90°C (decomp) (Found:
C, 68.6; H, 7.2; N, 8.9; C_{18}H_{23}N_2OP requires C, 68.8; H, 7.4;
N, 8.9%), ν_{max} 2500 cm\(^{-1}\) (br, OH, H bonded), δ 1.09 (6H, of
^3J(HP) 16Hz, ^3J(HH) 9Hz, CH_2CH_3), 1.70-2.30 (4H, c, CH_2CH_3), 4.42
(2H, d, ^3J(HP) 17Hz, NCH_2), 7.00-7.90 (10H, c, ArH), ^31P 531.5,
m/e 182 (20), 154 (82), 153 (100), 125 (31), 103 (25) and 77 (19).
(c) Reaction of 1-(4-Bromophenyl)-2-azidoethan-1-one Oxime.

(i) With triphenylphosphine. A mixture of the azide (0.30 g, 1.18 mmol) and the phosphine (0.35 g, 1.34 mmol) in benzene (15 ml) was stirred for 1 h. Light petroleum was added and the resultant precipitate was filtered off, washed with a little benzene followed by ether and dried. N-(2-p-Bromophenyl-2-hydroxyiminoethyl)imino-triphenylphosphine was obtained as white crystals (0.54 g, 94%), m.p. >137°C (decomp) (Found: C, 64.0; H, 4.6; N, 5.7; C₁₂₂H₂₂BrN₂O₃P requires C, 63.8; H, 4.5; N, 5.7%), δ 4.45 (2H, d, 3J(HP) 14Hz, CH₂) and 7.20-7.80 (20H, c, ArH and NH, 19H on shaking with D₂O), ³¹P δ 18.3, m/e 181 and 183 (97) and 102 (37).

(ii) With 1-phenylphosphorinan. The azide (0.6 g, 2.4 mmol) and the phosphine (0.5 g, 2.8 mmol) in benzene (10 ml) gave N-(2-p-bromophenyl-2-hydroxyiminoethyl)imino-1-phenylphosphorinan as a white solid (0.92 g, 94%), m.p. 127-130°C (decomp), (Found: C, 56.5; H, 5.5; N, 6.8; C₁₉₂₂BrN₂O₃P requires C, 56.3; H, 5.5; N, 6.9%), νmax 2500 (br, OH, hydrogen bonded), δ (60 MHz) 1.1-2.4 (10H, c, ring CH₂'s), 4.2 (2H, d, 3J(HP) 18Hz, CH₂) and 7.1-8.2 (9H, c, ArH) and ³¹P δ 19.1.

(d) Reaction of 1-Phenyl-2-azidoethan-1-one O-Methyloxime.

(i) With 2-phenyl-1,3,2-dioxaphosphorinan. The azide (0.4 g, 2.1 mmol) was reacted with the cyclic phosphonite (0.4 g, 2.2 mmol) in benzene (15 ml). Addition of petroleum ether after 1 h caused precipitation of a gum. The liquid was decanted, the residue washed several times with light petroleum and identified as N-(2-phenyl-2-methoxyiminoethyl)-imino-2-phenyl-1,3,2-dioxaphosphorinan δ 1.6-2.4 (2H, br, ring CH₂),
4.2-5.2 total 9H, c, incorporating a singlet at 4.36 (3H, OMe) and a doublet at 4.81 (2H, \(^3J(HP) 28\)Hz, collapses to singlet on \(^{31}P\) irradiation CH\(_2\)) and a broad multiplet from 4.2-5.2 (4H, 2xOCH\(_2\)) \(^{31}P \delta 11.4\).

6. **Reactions of \(\alpha\)-Azido Carbonyl Compounds with Tervalent Phosphorus Reagents proceeding with Decomposition of the Resulting Phosphorane.**

(a) **Reaction of 1-Phenyl-2-azidoethan-1-one.**

(i) **With triphenylphosphine.** A solution of the azide (84.8 mg, 0.53 mmol) in 'super dry' benzene (0.5 ml) was added to a solution of triphenylphosphine (142.6 mg, 0.54 mmol) in benzene (0.5 ml). Nitrogen was evolved and the colour of the mixture turned yellow, followed by dark brown, and finally dark red. The reaction was monitored by \(^{31}P\) n.m.r. After 4 h all the triphenylphosphine was consumed and most of the initially formed phosphoranes had been converted to triphenylphosphine oxide. On standing at room temperature for 12 h a few crystals came out of solution. The mixture was evaporated to dryness in vacuo. Preparative t.l.c. of the residue using light petroleum and 30% dichloromethane on alumina gave two major fractions: (1) a white solid \((R_f=0.5)\) identified as 2,5-diphenylpyrazine (40.1 mg, 65%), m.p. and mixed m.p. 192-196°C (lit, 192-196°C), δ 7.30-7.70 (3H, m, ArH), 7.87-8.22 (2H, m, ArH) and 9.05 (1H, s, HCN); (2) a yellow tarry solid \((R_f=0)\) (140.1 mg, 95%) identified as crude triphenylphosphine oxide, m.p. and mixed m.p. 155-156°C (from ether/light petroleum), as \(\nu_{\text{max}} 1195 \text{ cm}^{-1} (P=O)\) and \(^{31}P \delta 29.2\) (authentic 29.2).
(ii) **With 1-phenylphospholan.** The azide (109.2 mg, 0.68 mmol) and 1-phenylphospholan (111.7 mg, 0.68 mmol) were reacted as in (i) above. Preparative t.l.c. gave 2,5-diphenylpyrazine (62.7 mg, 80%), m.p. and mixed m.p. 189-195°C, δ 7.30-7.70 (3H, m, ArH), 7.87-8.22 (2H, m, ArH) and 9.05 (1H, s, \( \text{HC=N} \)) and 1-phenylphospholan oxide (110.2 mg, 90%), \( \nu_{\text{max}} \) (neat) 1180 cm\(^{-1} \) (P=O) and \(^{31}\)P δ 60, identical with authentic.

(iii) **With 1-phenylphosphorinan.** Following the procedure described in (i)-above the azide (103.9 mg, 65 mmol) and 1-phenylphosphorinan (114.9 mg, 0.65 mmol) gave 2,5-diphenylpyrazine (40.7 mg, 54%), m.p. and mixed m.p. 190-196°C, δ 7.30-7.70 (3H, m, ArH), 7.87-8.22 (2H, m, ArH) and 9.05 (1H, s, \( \text{HC=N} \)) and 1-phenylphosphorinan oxide (109.4 mg, 87%), m.p. and mixed m.p. 124-128°C and \(^{31}\)P δ 26.9 (authentic 26.9).

(b) **Reaction of 1,2-Diphenyl-2-azidoethan-1-one.**

(i) **With 1-phenylphospholan.** A solution of the azide (105.9 mg, 0.45 mmol) in 'super dry' benzene (1.0 ml) was added to a solution of 1-phenylphospholan (73.3 mg, 0.45 mmol) in benzene (0.5 ml). \(^{31}\)P n.m.r. of the mixture after 48 h showed complete conversion to the phospholan oxide. Evaporation of the solvent from the mixture gave a white solid which was washed with ether, dried and identified as 2,3,5,6-tetraphenylpyrazine (76.0 mg, 88%), m.p. 252-253°C (from ethanol) (lit, 246°C), \( \nu_{\text{max}} \) 760 and 690 cm\(^{-1} \), \(^{13}\)C δ 150.6 (quaternary C, C-Ph), 141.1 (C=N), 136.2 (quaternary C, Ar), 129.6 (tertiary C para to C=N), 128.9 and 126.7 (Ar) and \( M^+ \), 384.
7. Miscellaneous Reactions of Phosphoranes.

(a) Pyrolysis of Phosphoranes. Attempted flash vacuum pyrolysis of the pentacoordinate phosphoranes failed as they did not sublime.

(i) $2',5'$-Diphenylspiro-[1,3,2-dioxaphosphan-2, 2'$-\Delta^4$-[1, 3, 2]-oxazaphospholine (326.9 mg, 1.1 mmol) was refluxed for 12 h in cumene. $^{31}$P spectra of the solution showed complete conversion to the 2-phenyl-1, 3, 2-dioxaphospholan oxide (35.6 p.p.m.). The solvent was removed in vacuo. The tarry residue was chromatographed on alumina. Light petroleum and 30% dichloromethane eluted 2,5-diphenylpyrazine (103.7 mg, 81%), m.p. 189-196°C (from dichloromethane/light petroleum), lit; $^{118}$190-196°C, i.r., $^1$H n.m.r. identical with authentic.

(ii) $2',5'$-Diphenylspiro-[1,3,6,2-oxadiaza-1, 2, 3,4-tetrahydrophosphorin] -2, 2'$-\Delta^5$-[1, 3, 2]-dioxaphospholan (471.3 mg, 1.49 mmol) was pyrolysed at 150°C/0.1 mmHg using a bulb distillation unit. The colourless, sweet smelling distillate (84.7 mg, 55%) was identified as benzonitrile $\nu_{max}$ 2225, i.r. identical with authentic. A $^{31}$P spectra of a deuterated chloroform solution of the involatile residue showed 11 peaks - the major ones being at 56.1 (53), 39.3 (49), 38.9 (25) (possibly 2-phenyl-1, 3, 2-dioxaphospholan oxide), 32.6 and 33.0 p.p.m.

(iii) 2-phenyl-5-(p-bromophenyl)-spiro-[1,3,6,2-oxazadiaza-(1, 2, 3,4-tetrahydrophosphorin]-2, 2'$-\Delta^5$-[1, 3, 2]-benzodioxaphospholan. The phosphorane (0.5 g, 1.1 mmol) in t-butylbenzene under reflux for 2 h. The reaction mixture was evaporated to dryness and chromatographed on an alumina column. Chloroform eluted 4-bromobenzonitrile (0.04 g, 20%) m.p. 110°C identical with authentic.
(iv) \(2'-\text{phenyl}-5-(\text{p-bromophenyl})\text{-spiro-[1,3,6,2]-oxadiaza-(1,2,3,4-tetrahydrophosphorin)}-2,2'-\text{[1,3,2-p-t}b\text{utylbenzodioxaphosphole (a)}

The phosphorane (0.5 g, 1.0 mmol) was heated in t-butylbenzene under reflux for 1 h. Work up as in (iii) above afforded 4-t-butylbenzonitrile (0.07 g, 39%).

(b) The phosphorane was pyrolysed under flash vacuum conditions (inlet temperature 200°, oven temperature, 600°, pressure 0.001 mmHg) for 10 h. 4-Bromobenzonitrile was obtained (0.024 g, 75% of pyrolysed phosphorane), 0.0139 g of phosphorane was recovered unchanged.

(b) Hydrolysis of Phosphoranes

(i) The phosphoranes, obtained from the reaction of 1,2-diphenyl-2-azidoethan-1-one and 2-phenyl-1,3,2-dioxaphospholan and dioxophosphorinan, were easily hydrolysed by exposure of benzene solutions to air for 12 h. \(^{31}\text{P}\) showed complete conversion to the corresponding cyclic phosphonates. Chromatography on alumina gave low (20-30%) yields of 2,3,5,6-tetraphenylpyrazine m.p. 250-253°C (from ethanol), spectra identical with authentic.

(ii) A solution of 1',5-diphenylspiro-[1,3,6,2-oxadiaza-(1,2,3,4-tetrahydrophosphorin)]-2,1'-Δ^5-1'-phospholan (102.6 mg, 0.33 mmol) in benzene (15 ml) was left exposed to air for 12 h. Evaporation of the solvent and repeated triturations with ether gave 1-phenyl-2-aminoethan-1-one oxime as white crystals m.p. 138-141°C (from ethanol), lit; 140°C

\[\nu_{\text{max}} = 3300, 3360 (\text{N-H}) \text{ and } 2600 \text{ cm}^{-1} (\text{br, O-H, hydrogen bonded}), \text{ m/e} 150 (M^+, 30), 133 (M^+OH, 16), 119 (16), 104 (37) \text{ and } 103 (100).

Evaporation of the mother liquor gave 1-phenylphospholan oxide, i.r., \(^{31}\text{P}\) δ identical with authentic.
(c) Reaction of Phosphoranes with Alcohols

(i) 2,5'-Diphenylspiro-[1, 3, 2-dioxaphospholan-2, 2'-Δ^4-[1, 3, 2]-oxazaphospholine] (342.7 mg, 1.14 mmol) was heated in ethanol at 70°C for 3 h. The reaction was monitored by n.m.r. The solvent was removed in vacuo and the residue chromed on alumina. Light petroleum and 30% dichloromethane eluted 2,5-diphenylpyrazine as a white solid (113.7 mg, 85%), m.p. from dichloromethane/light petroleum, and mixed m.p. 240-246, i.r. and ^1H n.m.r. identical with authentic. Reaction in methanol under the same conditions gave a similar result.

(ii) 2,5-Diphenylspiro-[1, 3, 6, 2-oxadiaza-(1, 2, 3, 4-tetrahydro-phosphorin)-2, 2'-Δ^5-[1, 3, 2]-dioxaphospholan (495.3 mg, 1.6 mmol), suspended in ethanol (15 ml), was stirred overnight at r.t. Very little reaction had occurred possibly due to the insolubility of the starting phosphorane. The mixture was kept at 60-70°C for 0.75 h during which time all the phosphorane went into solution. Evaporation of the solvent and repeated ether triturations of the residue gave a white solid identified as 1-phenyl-2-aminoethan-one oxime (232.5 mg, 97%) m.p. 139-141°C (from ethanol) (lit, 140°C), ν max 3300, 3360 (N-H) and 2600 cm⁻¹ (br, O-H, hydrogen bonded). I.r. was identical with that of the product from hydrolysis of the corresponding 1-phenylphospholan phosphorane.

Commercial lead tetraacetate, stored under acetic acid to prevent hydrolysis, was used. Dry material was prepared by washing the paste with dry ether, on a filter funnel, and sucking dry for a few minutes in the dark. The material was weighed and used immediately. For large scale oxidations, excess lead tetraacetate was destroyed after the reaction by addition of a few drops of ethylene glycol before addition of water to prevent precipitation of brown lead dioxide.

(i) 2-Phenyl-1,3,2-dioxaphospholane oxide. Lead tetraacetate (4.87 g, 11 mmol) was added slowly and in small portions to a stirred solution of 2-phenyl-1,3,2-dioxaphospholane (1.68 g, 10 mmol) in dry dichloromethane (30 ml) at room temperature. The reaction was instantaneous. Heat was evolved and a thick white slurry was deposited. The reaction mixture was stirred for an additional 30 min. The slurry was filtered off, the filtrate was washed with water, dried over anhydrous magnesium sulphate and the solvent removed under reduced pressure giving an oil which on bulb to bulb distillation yielded the oxide as a colourless oil (1.62 g, 88%) b. p. 120°C/0.05 mmHg (oven temperature) (lit; 210°C/6-7 mmHg), ^\text{max} \nu (\text{neat}) 1445 \text{ (P-Ph) and 1270 cm}^{-1} \text{ (P=O)}, \delta 3.50-4.75 (4H, m, aliphatic H) and 7.15-7.85 (5H, m, ArH). ^{31}\text{P} \delta 36.8, \text{ m/e 184 (M}^+, 59), 141 (100), 124 (61) and 77 (63). On standing the pure oxide formed a white solid, m. p. 55-57°C (lit; 56-58°C).

(ii) 2-Phenyl-1,3,2-dioxaphosphorinan oxide. Following the procedure outlined in (i) above 2-phenyl-1,3,2-dioxaphosphorinan (1.82 g,
10 mmol) and lead tetraacetate (4.87 g, 11 mmol) gave the oxide as a
colourless oil (1.85 g, 95%), b. p. 180-182°/0.1 mmHg (oven temperature)
(lit; 175°C/0.05 mmHg), ν_max( neat) 1230 cm⁻¹ (br, P=O) δ (60 MHz),
1.80-2.40 (2H, m, OCH₂CH₂CH₂O), 3.90-5.00 (4H, m, OCH₂CH₂CH₂O)
and 7.10-8.15 (5H, m, ArH), 31P δ 14.8 and M⁺, 198.

(iii) 1-Phenylphospholan oxide. 1-Phenylphospholan (1.64 g, 10
mmol) was treated with lead tetraacetate (4.87 g, 11 mmol) as in (i)
above. Bulb distillation gave the oxide as a colourless oil (1.44 g, 80%),
b. p. 110°C/0.15 mmHg (lit, 176-180°/3 mmHg), ν_max( neat) 1440 (P-Ph)
and 1180 cm⁻¹ (P=O), δ 1.60-2.50 (8H, m, aliphatic H), 7.20-7.65 (3H,
m, meta and para, ArH) and 7.65-7.95 (2H, m, ortho ArH), 31P δ 60.1,
m/e 180 (M⁺, 100) and 152 (80). On standing the oil solidifies forming
waxy white crystals m. p. 55-57°C (lit; 56-57°C).

(iv) 1-Phenylphosphorinan oxide. Lead tetraacetate (2.64 g, 6.0
mmol) was reacted with 1-phenylphosphorinan (1.0 g, 5.6 mmol) as in
(i) above. The crude product was obtained as a white solid which on
bulb distillation gave the pure oxide (1.08 g, 99%), m. p. 127-128°C (lit;
125-128°C), ν_max(nujol) 1165 cm⁻¹ (P=O), δ 1.20-2.40 (10H, m,
aliphatic H), 7.28-7.60 (3H, m, meta and para, ArH) and 7.60-7.88
(2H, m, ortho ArH), 31P δ 26.9, m/e 194 (M⁺, 81), 166 (59), 140 (56),
and 125 (100).

(v) Dimethyl phenylphosphonate. Dimethyl phenylphosphonite (1.70
g, 10 mmol) and lead tetraacetate (4.87 g, 11 mmol) were reacted as in
(i) above to give the phosphonate as a colourless oil (1.67 g, 90%), b. p.
70°C/0.75 mmHg (oven temperature (lit; 115°C/0.9 mmHg), δ 3.70
(6H, d, 3J(HP) 12Hz, 2 x OCH₃), 7.28-7.64 (3H, m, meta and para
ArH) and 7.64-7.96 (2H, m, ortho ArH), 31P δ 21.5, m/e 186 (M⁺, 100), 185 (84), 156 (40), 155 (34) and 131 (56).

(vi) **Methyl diphenylphosphinate.** Methyl diphenylphosphinite (1.0 g, 4.63 mmol) was oxidised with lead tetraacetate (2.3 g, 5.2 mmol) as in (i) above. The oxide was obtained as a colourless oil (1.06 g, 99%), b.p. 120/0.05 mmHg (oven temperature) (lit; 178°C/2.4 mm), νmax (neat) 1440 (P-Ph) and 1220 cm⁻¹ (P=O), δ 3.70 (3H, d, 3J(HP) 11Hz, OCH₃), 7.25-7.50 (6H, m, meta and para ArH) and 7.50-8.00 (4H, m, meta aromatic H), 31P δ 33.4 (lit; 32.2), m/e 232 (M⁺, 86) and 231 (100).

(vii) **Ethyl diphenylphosphinate.** Ethyl diphenylphosphinite (1.15 g, 5.0 mmol) on treatment with lead tetraacetate (2.42 g, 5.5 mmol) as in (i) above gave the phosphinate as a colourless oil (1.19 g, 97%), b.p. 158/0.3 mmHg (oven temperature) (lit; 160°C/0.4 mmHg), νmax (neat) 1445 (P-Ph) and 1220 cm⁻¹ (P=O), δ 1.30 (3H, t, 3J(HH) 7Hz, OCH₂CH₃), 4.08 (2H, q of d, 3J(HP) 12Hz, 3J(HH) 7Hz, OCH₂CH₃), 7.20-7.40 (6H, m, meta and para ArH) and 7.40-7.95 (4H, m, ortho ArH), 31P δ 31.5, m/e 246 (M⁺, 58), 218 (31), 217 (100) and 202 (31). The compound solidified forming waxy white crystals m.p. 38-40°C (lit; 39-41).

(viii) **2-N,N-Diethylamino-1,3,2-dioxaphospholan oxide.** 2-N,N-Diethylamino-1,3,2-dioxaphospholan (7.7 g, 47.2 mmol) was reacted with lead tetraacetate (23.0 g, 51.9 mmol) as in (i) above to give the oxide as a colourless oil (6.19 g, 73%), b.p. 150°C/0.3 mmHg (oven temperature) (lit; 117-117.5°C/2 mmHg), νmax (neat) 1470 (br, P-Ph) and 1270 cm⁻¹ (P=O), δ 1.20 (6H, t, 3J(HH) 7Hz, NCH₂CH₃), 3.08 (4H,
q of d, \(^3J(HP)\) 12Hz, NCH\(_2\)CH\(_3\)) and 4.18-4.60 (4H, m, ring CH\(_2\)), \(^{31}P\) 526.6,

(ix) 1,2,5-Triphenylphosphole oxide. 1,2,5-Triphenylphosphole (1.56 g, 5.0 mmol) was reacted with lead tetraacetate (2.44 g, 5.5 mmol) to give a yellow solid which was dissolved in methylene chloride and chromatographed on alumina (grade III). Elution with methylene chloride gave the oxide as yellow crystals (1.4 g, 86%), m.p. 237-239°C (from methanol) (lit; 237-239°C), \(\nu_{\text{max}}\) (nujol) 1185 cm\(^{-1}\), \(\delta\) 6.80-8.10 (m, ArH), \(^{31}P\) 541.7.

(x) 1,2,5-Tritolylphosphole oxide. 1,2,5-Tritolylphosphole (1.77 g, 5 mmol) was treated with lead tetraacetate (2.44 g, 5.5 mmol) as in (ix) above. Elution with ethylacetate and methanol (1:1) gave the oxide as a yellow solid (1.74 g, 94%), m.p. 242-245°C. An analytical sample was prepared by recrystallisation from methanol (40% recovery) and drying the yellow needles obtained over phosphorus pentoxide under reduced pressure at 100°C for 48 h. The pure oxide had m.p. 248-249°C (Found: C, 81.0; H, 6.25. C\(_{25}H_{23}OP\) requires C, 81.1; H, 6.3%), \(\nu_{\text{max}}\) (nujol) 1185 (P=O) and 825 cm\(^{-1}\), \(\delta\) 1.25 (9H, s, \(=CH\)) and 6.70-7.80 (14H, m, \(=CH\) and ArH), \(^{31}P\) 542.2, m/e 370 (M\(^+\), 100).

(xi) 1-Phenyl-3-methyl-2-phospholene oxide. 1-Phenyl-3-methyl-2-phospholene (1.0 g, 5.7 mmol) and lead tetraacetate (2.8 g, 6.3 mmol) were reacted to obtain the oxide as a low melting solid (0.91g, 83%), b.p. 134/0.3 mmHg, (lit; 150°/15 mmHg), \(\nu_{\text{max}}\) (neat) 1445 (P-Ph) and 1200 and 1170 cm\(^{-1}\), 1.80-3.00 (4H, m, ring CH\(_2\)), 2.06 (3H, s, CH\(_3\)), 5.90 (1H, d, \(^2J(HP)\) 24Hz, \(=CH\)), 7.28-7.90 (5H, m, ArH), \(^{31}P\) 561.6, m/e 192 (M\(^+\), 100) and 153 (39).
(xii) **1-Phenyl-3-methyl-3-phospholene oxide.** 1-Phenyl-3-methyl-3-phospholene (1.76 g, 11 mmol), was oxidised with lead tetraacetate (4.87 g, 11 mol) to give the oxide as a colourless oil (1.69 g, 88%), b.p. 150°C/0.1 mmHg (oven temperature) (lit: 136°C/2.0 mmHg), $\nu_{\text{max}}$ (neat) 1440 cm$^{-1}$ (P-Ph) and 1220 cm$^{-1}$ (P=O), $\delta$ 1.88 (3H, m, CH$_3$), 2.40-3.00 (4H, m, ring CH$_2$), 5.62 (1H, complex d, $^3$J(HP) 32 Hz, olefinic H), 7.24-7.60 (3H, m, ortho and para ArH) and 7.60-7.94 (2H, m, meta aromatic H), $^{31}$P $\delta$ 57.4, m/e 192 (M$^+$, 100), 191 (38), 180 (38), 152 (33) and 125 (29).

(xiii) **Triphenylphosphine oxide.** Triphenylphosphine (1.31 g, 5 mmol) was oxidised with lead tetraacetate (2.44 g, 5.5 mmol) in methylene chloride (20 ml) as in (i) above. The crude product was chromatographed on alumina (grade 111) with ethyl acetate as eluant. The oxide was obtained as white crystals (1.29 g, 93%), m.p. and mixed m.p. 155-156°C $\nu_{\text{max}}$ (neat) 1195 cm$^{-1}$ (P=O), $\delta$ 7.20-7.85 (m, ArH), $^{31}$P $\delta$ 29.1, m/e 278 (M$^+$, 86) and 277 (100).

(xiv) **Tri-n-butylphosphine.** Tri-n-butylphosphine (2.02 g, 10 mmol) and lead tetraacetate (4.88 g, 11 mmol) were reacted as in (i) above to give the oxide as a low melting solid (2.03 g, 93%), b.p. 150°C/0.2 mmHg (oven temperature) (lit: 300°C/760 mmHg), $\nu_{\text{max}}$ (neat) 1160 cm$^{-1}$ (P=O), $\delta$ 0.70-1.15 (3H, m, CH$_3$) and 1.15-1.90 (6H, m, 3 x CH$_2$), $^{31}$P $\delta$ 49.4, m/e 218 (M$^+$).

(xv) **Diethylphenylphosphine oxide.** Diethylphenylphosphine (1.0 g, 6 mmol) and lead tetraacetate (2.92 g, 6.6 mmol) after reaction and work-up as in (i) above, gave the oxide as a white solid (0.91 g, 83%), m.p. 55-56°C $\nu_{\text{max}}$ (neat) 1165 cm$^{-1}$ (P=O), $\delta$ 1.05 (6H,
t of d, $^3$J(HP) 15Hz, $^3$J(HH) 5Hz, CH$_3$, 1.55-2.25 (4H, m, CH$_2$) and 7.20-7.90 (5H, m, ArH), $^{31}$P δ 44.3, m/e 182 (M$^+$, 22), 154 (81), 153 (100) and 125 (32).

9. Preparation of Phosphonium Salts and Ylides

(i) 1-(2-Ethoxy-2-oxoethylidene)-1,2,5-triphenylphosph(v)ole.

The method of Campbell et al. was used. A solution of 1,2,5-triphenylphosphole (4.0 g, 13 mmol) and ethyl bromoacetate (4.1 g, 24.6 mmol) in benzene (50 ml) was heated under reflux for 47 h. Evaporation of the solution to dryness gave the crude phosphonium salt which was dissolved in water (2.0 l.). Aqueous sodium hydroxide (3 ml, 4N) was added to the solution. The orange precipitate was collected, washed with water and dried under reduced pressure over phosphorus pentoxide. Recrystallisation from dry ethylacetate/light petroleum gave the ylde as orange crystals (3.1 g, 60%), m.p. 162-164°C (lit. 161-163°C).

(ii) 1-(2-Oxopropyl)-1,2,5-triphenylphospholium bromide.

Reaction of 1,2,5-triphenylphosphole and bromoacetone in benzene did not yield the phosphonium salt. Reaction at room temperature in benzene gave an immediate red solution which deposited red crystals. Attempted isolation of the red crystals gave a tar whose major component was 1,2,5-triphenylphosphole oxide. Reaction of the bromide and phosphole in refluxing benzene gave a tar whose major component was identified as 1,2,5-triphenylphosphole oxide. Use of dimethoxyethane as solvent resulted in the desired product.
Bromoacetone (2.6 g, 19 mmol) was added to 1, 2, 5-triphenylphosphole (4.9 g, 15.7 mmol) in dry dimethoxyethane (50 ml). The mixture was heated under reflux for 48 h with stirring under an atmosphere of dry nitrogen. On cooling the yellow crystals were filtered off washed with ether and dried. The crude phosphonium salt (6.0 g, 70%) had m.p. 215-219°C. Recrystallisation from ethanol/ether gave the pure bromide (74% recovery), m.p. 220-221°C (Found: C, 66.6; H, 4.9; C\textsubscript{25}H\textsubscript{22}BrOP requires C, 66.8; H, 4.9%), \(\nu\)\textsubscript{max} 1720 cm\textsuperscript{-1} (C=O), \(\delta((CD\textsubscript{3})\textsubscript{2}SO)\) 2.25 (3H, s, CH\textsubscript{3}), 5.85 (br, 2H, d, \(^2J(HP)\) 20Hz, CH\textsubscript{2}) and 7.0-8.7 (17H, c, ring =CH's + ArH) and \(\delta\) 19.0.

(iii) 1-(2-Oxopropylidene)-1, 2, 5-triphenylphosph(v)ole. The ylide was prepared by reaction of the phosphonium salt with either sodium hydride or sodium carbonate. (a) Sodium hydride (0.3 g, 12.5 mmol) was added to 1, 2, 5-triphenyl-(2-oxopropyl)phosphonium bromide (1.0 g, 2.2 mmol) in dry dimethoxyethane (30 ml). The reaction mixture was heated at 60°C for 5 min under dry nitrogen and then stirred at room temperature for 3 h. The orange precipitate was filtered, dissolved in ethylacetate, the solution was evaporated to smaller volume, ether added and the solution allowed to crystallise. The ylide was obtained as orange crystals (0.3 g, 37%), m.p. 198-200°C (decomp) (Found: C, 79.6; H, 5.5; M\textsuperscript{+}, 368.132742. C\textsubscript{25}H\textsubscript{21}OP requires C, 81.5; H, 5.75%; M\textsuperscript{+}, 368.132996), \(\nu\)\textsubscript{max} 1540 cm\textsuperscript{-1}, \(\delta\) 2.15 (3H, d, \(^4J(HP)\) 2Hz, CH\textsubscript{3}), 3.85 (1H, d, \(^2J(HP)\) 29Hz, PCH) and 7.10-8.20 (17H, c, ring =CH and ArH) and \(\delta\) 19%. A satisfactory analysis could not be obtained due to the instability of the ylide towards hydrolysis.

(b) The salt (8.5 g, 18.9 mmol) was slowly added to a stirred mixture of 10% aqueous sodium carbonate solution (24 ml) and chloroform (24 ml).
A red coloration appeared in the organic layer. The mixture was stirred for a further 10 min after addition. The chloroform layer was separated, washed with water (2 x 25 ml), dried over anhydrous magnesium sulphate and evaporated to smaller volume. Excess ether was added and the solution allowed to crystallise. The ylide was obtained as orange crystals (5.3 g, 76%), m. p. and mixed m. p. 197-200°C (decomp).

(iv) 1-Phenyl-1-(2-oxo-2-ethoxypropyl)phospholonium Bromide.

Ethyl bromoacetate (1.67 g, 10 mmol) was added to a solution of 1-phenylphospholan (1.64 g, 10 mmol) in dry benzene (15 ml). A white precipitate was formed. The mixture was heated under reflux overnight under an atmosphere of dry nitrogen. Excess ether was added and the white solid was filtered and dried to give the salt (3.0 g, 91%), m. p. 111-112.5°C (from dichloromethane/ether) (Found: C, 50.5; H, 6.1; C_{14}H_{20}BrO_{2}P \text{ requires C, 50.8; H, 6.1%}). ν_{\text{max}} 1710 \text{ cm}^{-1} (\text{C=O}), \ δ \ 1.15 (3H, t, \ 3J(\text{HH}) 7\text{Hz}, \ CO_2\text{CH}_2\text{CH}_3), \ 1.70-3.60 (8H, c, \text{ ring CH}_2's), \ 4.09 (2H, q, \ 3J(\text{HH}) 7\text{Hz}, \ CO_2\text{CH}_2\text{CH}_3), \ 5.00 (2H, d, \ 2J(\text{HP}) 14\text{Hz}, \ P\text{CH}_2) \text{ and } 7.20-8.40 (5H, c, \text{ ArH}), \ ^{31}\text{P} \ δ \ 46.0 \text{ and m/e 250 (M}^+ - \text{HBr}).
Miscellaneous Reactions

(i) **Preparation of 2,4,5-triphenyloxazole.** Following Schonberg's method, benzil (5.0 g) was heated in a sealed tube with concentrated aqueous ammonia (10 g) for 7 h. The white crystalline precipitate was washed with water and chromatographed on alumina. Benzene eluted the oxazole as a white solid (2.7 g, 76%), m. p. 113-114°C (from ethanol) (lit: 114-115°C), $\nu_{\text{max}}$ 695 and 770 cm$^{-1}$ and $\delta$ 6.70-8.20 (m, ArH).

(ii) **Preparation of 3,4,5-triphenylisoxazole.** This was prepared by a method suggested by J. Barnes based on studies of the cycloaddition reactions of 1,3-dipoles. Diphenylacetylene (1.78 g, 10 mmol) and diphenylfuroxan (1.19 g, 5 mmol) were heated under reflux in diphenyl-ether (25 ml) for 1 h. T.l.c. (alumina, light petroleum and 10% ether) showed all the acetylene had been consumed. The mixture was left standing at room temperature for 12 h. The white crystals were filtered off, washed with ether and dried to give the crude isoxazole (0.67 g, 23%), m. p. 205-206°C (lit: 212-213°C). Recrystallisation from dichloromethane/ether gave the pure isoxazole as white needles m. p. 216-217°C (lit: 212-213°C) (Calc. for $C_{21}H_{15}NO$: C, 84.8; H, 5.1; N, 4.7; M$^+$, 297. Found: C, 84.65; H, 5.1; N, 4.65%; M$^+$, 297). T.l.c. of the filtrate from the reaction mixture showed a quantitative conversion to the isoxazole.

(iii) **Preparation of 2,3-di-(4-t-butylphenyl)-1-azirine.** The azirine was prepared using Hassner's general preparation of azirines by pyrolysis of vinyl azides obtained from the action of iodine azide on olefins.
(a) p-t-Butylbenzyltriphenylphosphonium bromide. Redistilled p-t-butylbenzyl bromide (11.4 g, 50 mmol) was added, with stirring, to a solution of triphenylphosphine (13.1 g, 50 mmol) in dry benzene (50 ml). The mixture was heated under reflux for 0.5 h. The white precipitate was filtered off, washed with dry ether and dried. The bromide was obtained as white crystals (24.0 g, 98%) m. p. 214-215°C, \( \nu_{\text{max}} \) 1440 (P-Ph), \( \delta \) 1.20 (9H, s, (CH\(_3\))\(_3\)C), 5.22 (2H, d, \( ^2J(\text{HP}) \) 14Hz, CH\(_2\)) and 6.90-8.0 (19H, m, ArH), 31P \( \delta \) 22.9, m/e 408 (M\(^+\)-HBr, 29), 393 (408-CH\(_3\)) 16), 262 (100), 183 (58) and 147 (45).

(b) 4,4-t-Butylstilbene. Sodium ethoxide was prepared by adding sodium (0.23 g, 10 mmol) to rectified ethanol (25 ml). The sodium ethoxide solution was added dropwise and with stirring, to a solution of p-t-butylbenzaldehyde (1.62 g, 10 mmol) and p-t-butylbenzyltriphenylphosphonium bromide (4.89 g, 10 mmol) in ethanol (rectified, 25 ml) under an atmosphere of dry nitrogen. The mixture was heated under reflux for 4 h and then left stirring at room temperature for 12 h. The mixture was filtered, washed with a little water then ethanol and dried to give the stilbene as white plates (1.14 g, 39%), m. p. 180-181°C. An analytical sample was prepared by recrystallisation from n-hexane and had m. p. 181-182°C (Found: C, 90.15; H, 9.5; M\(^+\), 292. \( C_{22}H_{28} \) requires C, 90.35; H, 9.65%; M\(^+\), 292), \( \nu_{\text{max}} \) 1550 cm\(^{-1}\) (C=C) and \( \delta \) 1.31 (9H, s, (CH\(_3\))\(_3\)C), 7.20 (1H, s, =CH) and 7.20-7.60 (4H, m, ArH).

(c) 1-Azido-2-iodo-1,2-di-(4-t-butylphenyl)ethane. Iodine monochloride (5.1 g, 31.4 mmol) was dropped slowly to an ice-methanol cold stirred slurry of sodium azide (4.5 g, 69.2 mmol) in redistilled acetonitrile (25 ml). The orange slurry was stirred for an additional 30 min then
4, 4-t-butyl stilbene (8.11 g, 27.8 mmol) was added. The mixture was allowed to warm up to room temperature and stirred for an additional 20 h. The slurry was poured onto a solution of sodium thiosulphate (5.0 g) in water (100 ml). The white precipitate was washed with water and dried. The crude iodo-azide was obtained in quantitative yield. The compound was unstable decomposing in solution to form iodine. Recrystallisation from methanol gave the iodoazide as white crystals (42%) with m.p. 90-94°C and $\nu_{\text{max}}$ 2100 (N$_3$).

(d) 1-Azido-1, 2-di-(4-t.-butylphenyl)ethylene. Potassium t-butoxide (0.67 g, 6 mmol) was added to a solution of the iodoazide (2.31 g, 5 mmol) in dry ether (25 ml) with stirring at room temperature. T.l.c. (alumina, light petroleum and 10% ether) of the reaction mixture 15 h after mixing suggested the reaction was not completed. After 21 h more base (0.67 g, 6 mmol) was added. The mixture darkened and t.l.c. suggested the reaction was complete. The reaction mixture was worked up by washing with water (2 x 50 ml) and drying over anhydrous magnesium sulphate. Evaporation of the solvent gave a pale yellow solid (1.45 g, 87%) identified as the vinyl azide with a small amount of the azirine, the decomposition product, from t.l.c. (alumina, light petroleum) and i.r. spectra, $\nu_{\text{max}}$ 1745 (C=N of azirine), 1630 (C=C of vinyl azide) and 1610 cm$^{-1}$ (C=C of aromatics of azirine). The vinyl azide had a tendency to decompose slowly forming the azirine. The azide was purified by chromatography on alumina. Light petroleum eluted a fraction which yielded a pale yellow solid (1.15 g, 79% recovery). Dry column chromatography on alumina using light petroleum as developer gave the pure vinyl azide as a white solid (45% recovery), m.p. 72-75°C, $\nu_{\text{max}}$ 2120 (N$_3$) and 1630 cm$^{-1}$.
(C=N), δ 1.30 (18H, s, 2 x (CH₃)₃C), 5.95 (1H, s, C=CH) and 7.0-7.8 (8H, m, ArH).

(e) 2,3-Di-(4-t-butylphenyl)-1-azirine. The vinyl azide (175 mg) was heated under reflux in 'super dry' cyclohexane (15 ml) under an atmosphere of dry nitrogen for 2 h. The reaction was monitored by h.p.l.c. (alumina, hexane and 7% ether). The cyclohexane was evaporated off at room temperature under reduced pressure giving a white solid (154 mg, 96%), m.p. 136-140°C. Preparative t.l.c. (alumina, light petroleum and 10% ether) gave the pure azirine (53% recovery). Two successive recrystallisations from n-hexane gave the azirine as balls of white needles, m.p. 140-142°C, (Found: C, 86.6; H, 9.0; N, 4.5; M⁺, 305. C₂₂H₂₇N requires C, 86.5; H, 8.9; N, 4.6%; M⁺, 305), νmax 1745 (C=N) and 1610 (aromatic C=C), δ 1.26 and 1.32 (18H, 2 x s, 2 x (CH₃)₃C), 3.23 (1H, s, CH), 7.05 and 7.26 (each 2H, 2 x d, AB quartet, J 8Hz, ArH) and 7.52 and 7.82 (each 2H, 2 x d, AB quartet, J 8Hz, ArH).

(iv) Preparation of 2,2,5,5-tetra-(4-t-butylphenyl)dihydropyrazine.
The pyrazine was prepared by in situ condensation of the corresponding amino aldehyde which was obtained by a multi stage preparation.²⁹²

(a) 1,1-Di-(4-t-butylphenyl)ethanol. The Grignard of p-t-butyldromobenzene was made in the usual manner. p-t-Butyldromobenzene (148.0 g, 0.7 mol) in 'super dry' ether (200 ml) was added to magnesium (15.96 g, 0.67 mol) in 'super dry' ether (100 ml) at such a rate as to maintain gentle reflux. The reaction was initiated with a crystal of iodine. When addition was completed the mixture was heated under reflux for 1 h. The mixture was cooled in an ice-bath and pure, dry ethyl acetate (26.59 g, 29 ml, 0.3 mol) in dry ether (30 ml) was added with stirring. A vigorous
reaction occurred. On completion of addition the mixture was stirred at room temperature for 2 h. The mixture was cooled in an ice-bath and an aqueous ammonium chloride solution (117 ml, 50 g in 150 ml) added slowly with stirring and cooling. A pasty white solid separated out. The ether layer was decanted and the paste washed with ether (500 ml). The combined ether extracts were dried over anhydrous magnesium sulphate. Evaporation of the solvent gave a white solid (96.34 g). T.l.c. (alumina, light petroleum) of this solid suggested the components were the corresponding biphenyl and the carbinol. Chromatography on alumina was the best method of purification. Light petroleum eluted the biphenyl and ether eluted the carbinol (48.87 g, 53%) as white crystals. Similar results were obtained using dry column chromatography with light petroleum as developer. An analytical sample was prepared by preparative t.l.c. (alumina, light petroleum) and recrystallisation from n-hexane to give the carbinol as white crystals m.p. 133-135°C (Found: C, 85.0; H, 9.8; \( \text{C}_{22}\text{H}_{30}\text{O} \) requires C, 85.1; H, 9.7%), \( \nu_{\text{max}} \approx 3570 \text{cm}^{-1} \) (OH), \( \delta 1.30 \) (18H, s, \( 2 \times (\text{CH}_3)\text{C} \)), 1.93 (3H, s, CH\(_3\)), 2.19 (br, 1H, s, OH) and 7.32 (8H, s, ArH).

(b) 1,1-Di-(4-t-butylphenyl)ethylene. 1,1-Di-(4-t-butylphenyl)ethan-1-ol (31.87 g) was heated in a melt at approximately 300°C for 15 min. The residue was dissolved in n-hexane, the solution filtered and allowed to crystallise giving the olefin as white crystals (17.79 g), m.p. 97-99°C. A further crop of crystals (7.88 g, total yield 86%) was obtained. An analytical sample was prepared by recrystallisation from n-hexane to give the olefin as white translucent plates m.p. 98-100°C (Found: C,
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\[ \text{C}_{22} \text{H}_{28} \text{BrO} \] requires C, 67.9; H, 7.5; M\(^+\), 390 and 388; C\(_2\text{H}_2\text{BrO}\) requires C, 67.9; H, 7.5%; M\(^+\), 390 and 388; \( \nu_{\text{max}} \) 3560 and 3540 (OH), 2.05 and 2.00 (1H, s, OH, disappear on shaking with \( \text{D}_2\text{O} \)), 4.07 (2H, s, CH\(_2\)) and 7.30 (8H, s, ArH).

(c) 1,1-Di-(4-t-butylphenyl)-2-bromoethan-1-ol. A solution of N-bromoacetamide (7.59 g, 55 mmol) in water (25 ml) and t-butanol (12.5 ml) was added to a rapidly stirred suspension of 1,1-di-(4-t-butylphenyl)-ethylene (18.6 g, 64 mmol) in t-butanol (85 ml) and water (35 ml). The reaction mixture was heated under reflux for 2 h. The solution was allowed to stand at room temperature for 12 h. Cooling the mixture in an ice-acetone bath caused precipitation of a white solid which was washed with water and dried over phosphorus pentoxide under vacuum.

The bromoethanol (13.86 g), m.p. 85-88°C. A further crop of crystals (2.34 g, 78%) was obtained on addition of water to the mother liquor. An analytical sample was prepared by recrystallisation from n-hexane to give the bromoethanol as white crystals, m.p. 87-89°C (Found: C, 67.9; H, 7.4; M\(^+\), 390 and 388; C\(_{22}\text{H}_{29}\text{BrO}\) requires C, 67.9; H, 7.5%; M\(^+\), 390 and 388; \( \nu_{\text{max}} \) 3560 and 3540 (OH), 2.05 and 2.00 (1H, s, OH, disappear on shaking with \( \text{D}_2\text{O} \)), 4.07 (2H, s, CH\(_2\)) and 7.30 (8H, s, ArH).

(d) 1,1-Di-(4-t-butylphenyl)ethylene oxide. A solution of potassium hydroxide (3.44 g, 61.3 mmol) in water (30 ml) was added to a solution of 1,1-di-(4-t-butylphenyl)-2-bromoethan-1-ol (21.67 g, 55.7 mmol) in methanol (80 ml) at room temperature with stirring. The mixture was cooled in an ice-salt bath, the precipitate was filtered and washed with ether. The ether extracts were evaporated to smaller volume and allowed to crystallise to give the ethylene oxide as a white solid (11.21 g,
65%), m. p. 99-101°C, (Found: C, 85.8; H, 9.1; M\(^+\) 308; C\(_{22}\)H\(_{28}\)O requires C, 85.7; H, 9.15%; M\(^+\) 308), \(\nu_{\text{max}}\) 1115, 1015, 920, 835 and 805 cm\(^{-1}\), \(\delta\) 1.27 (18H, s, 2 x (CH\(_3\))\(_3\)), 3.22 (2H, s, CH\(_2\)) and 7.28 (8H, s, ArH).

(e) 2,2-Di-(4-t-butylphenyl)ethan\(\alpha\). To a solution of 1,1-di-(4-t-butylphenyl)ethylene oxide (12.32 g, 40.0 mmol) in dry ether (250 ml) was added, with stirring under an atmosphere of dry nitrogen, trifluoroborate diethyl ether etherate (32 ml). The mixture was stirred for a further 2.5 h. The ether was washed well with water (2 x 50 ml), dried over anhydrous magnesium sulphate and evaporated to dryness to give a white solid. Recrystallisation from n-hexane gave the pure acetaldehyde (7.81 g, 63%), m. p. 107-109°C (Found: C, 85.8; H, 9.1; M\(^+\) 308; C\(_{22}\)H\(_{28}\)O requires C, 85.7; H, 9.15%; M\(^+\) 308), \(\nu_{\text{max}}\) 1725 cm\(^{-1}\) (C=O), \(\delta\) 1.28 (18H, s, 2 x (CH\(_3\))\(_3\)), 4.68 (1H, d, \(^3J(HH)\) 2Hz, CH), 7.04-7.50 (8H, m, ArH) and 9.89 (1H, d, \(^3J(HH)\) 2Hz, HC=O). Irradiation at 9.89 p. p. m. causes the signal at 4.68 p. p. m. to collapse to a singlet.

(f) 2,2-Di-(4-t-butylphenyl)-2-chloroethan\(\alpha\). Many attempts to chlorinate the acetaldehyde using thionyl chloride and sulphonylchloride were tried. Chlorination was usually slow leading to impure product. In the best example 2,2-di-(4-t-butylphenyl)ethan-1-one (1.73 g, 5.62 mmol) and sulphonyl chloride (15 ml) in ether (60 ml) were heated under reflux for 64 h under an atmosphere of dry nitrogen. The solvents were evaporated in vacuo giving a tar. Repeated triturations with ice-cold n-hexane gave the chloride (1.40 g, 72%), m. p. 135-142°C. An analytical sample was prepared by repeated recrystallisations from n-hexane giving the chloride as white plates, m. p. 153.5-154°C, (Found:
C, 77.3; H, 7.9; \( \text{M}^+ 344 \text{ and } 342 \); \( \text{C}_{22}\text{H}_{27}\text{ClO} \) requires C, 77.1;
H, 7.9; \( \text{M}^+ 344 \text{ and } 342 \), \( \nu_{\text{max}} \) 1735 cm\(^{-1}\) (C=O), \( \delta 1.25 \) (18H, s, 2 x \((\text{CH}_3)_3\text{C})\), 7.20-7.50 (8H, m, ArH) and 9.70 (1H, s, CH).

(g) 2, 2, 5, 5-Tetra-(4-t-butylphenyl)dihydropyrazine. Use of ethanol as solvent for the reaction gave various unidentified products. 2, 2-Di-(4-t-butylphenyl)-2-chloroethan-1-one (174 mg, 0.5 mmol) in dimethoxyethane (5 ml) was added dropwise to a stirred ice-cooled solution of ammonia (1.0 g) in dimethoxyethane (40 ml) under an atmosphere of dry nitrogen. The mixture was stirred at room temperature for 18 h. A white precipitate was formed. The mixture was refluxed for a total of 22 h. The mixture was cooled, the precipitate was filtered off, washed well with dimethoxyethane, dried and dissolved in dichloromethane. The solution was filtered and evaporated to dryness to give the pyrazine as a white solid (76.7 g, 50%), m. p. >300°C. The solid was insoluble in water and sparing soluble in organic solvents. An analytical sample was prepared by repeated washings with n-hexane. Recrystallisation from benzene, methylene chloride and n-hexane failed. The pure dihydropyrazine had m. p. >300°C, (Found: C, 86.4; H, 8.8; N, 4.4; \( \text{M}^+ 610 \); \( \text{C}_{44}\text{H}_{54}\text{N}_2 \) requires C, 86.5; H, 8.9; N, 4.6%; \( \text{M}^+ 610 \)), \( \nu_{\text{max}} \) 1655 cm\(^{-1}\) (C=N) and \( \delta \) (CDCl\(_3\)) 1.25 (18H, s, 2 x \((\text{CH}_3)_3\text{C})\), 7.0-7.5 (8H, m, ArH) and 8.55 (1H, s, HC=N).

(v) Preparation of 2, 5-Diphenylpyrazine. This was prepared by a modification of Zbiral's method. Triphenyl phosphine (1.31 g, 5 mmol) in 'super dry' benzene (20 ml) was added to a solution of 1-phenyl-2-azidooethan-1-one (0.80 g, 5 mmol) in 'super dry' benzene (20 ml). The solution was heated under reflux for 14 h. A calcium chloride guard
The solvent was evaporated from the mixture and the residue chromatographed on alumina. Light petroleum and 30\% dichloromethane eluted the pyrazine as a white solid (0.55 g, 95\%), m.p. 189-196\(^\circ\)C (lit. 190-196\(^\circ\)C), \(\delta\) 7.30-7.70 (3H, m, ArH), 7.87-8.22 (2H, m, ArH) and 9.05 (1H, s, HC=N) and \(M^+\) 232.

11. **Reaction of Diazo Ketones with Tervalent Phosphorus Reagents:**

**Preparation and Decomposition of Phosphinazines**

**Preparation of phosphinazines.**

**General method.** A solution of the phosphine (15 mmol), in super-dry ether (10 ml) was added, with stirring to a solution of the pure diazo ketone (10 mmol) in super-dry ether (25 ml) under an atmosphere of dry nitrogen. A red coloration appeared which gradually disappeared. After 24 h., the yellow precipitate was filtered off, washed with dry ether and dried in vacuo, over phosphorus pentoxide. Where necessary the phosphinazines were recrystallised from dry dichloromethane/ether.

(a) **1,2-Diphenyl-2-(1-phenylphosphalanazine)-ethan-1-one-2-ylidene.** Reaction of 1-phenylphosphalan and 1,2-diphenyl-2-diazo-ethan-1-one gave the phosphinazine as a yellow solid (50-80\%), m.p. 103-107\(^\circ\)C (decomp.) (Found: C, 74.3; H, 5.9; N, 7.4; \(C_{24}H_{23}NO_2P\) requires C, 74.6; H, 6.0; N, 7.3\%), \(\nu_{\text{max}}\) 1625 cm\(^{-1}\), \(\delta\) 1.60-2.60 (8H, C, ring CH\(_2\)'s) and 7.06-8.00 (15H, C, ArH) and \(^{31}\)P \(\delta\) 55.4.
(b) 1,2-Diphenyl-2-(triphenylphosphinazine)ethan-1-one-2-ylidene. Reaction of triphenylphosphine and 1,2-diphenyl-2-diazoethanone gave the phosphinazine as a yellow solid (70-80%), m.p. 114-116 °C (decomp.) (lit.7 115-117 °C) (Calc. for C_{32}H_{25}N_{2}O_{1}P_{1} C, 79.3; H, 5.2; N, 5.8; Found: C, 79.1; H, 5.5; N, 5.7%), ν_{max} 1655 cm^{-1} (C=O), δ (60MHz) 6.70-8.20 (m, ArH) and ^{31}P δ 21.2.

(c) 1,2-Di-p-t-butylphenyl-2-(1-phenylphospholanzine)ethan-1-one-2-ylidene. Reaction of 1-phenylphospholane and 1,2-di-(4-t-butylphenyl)-2-diazoethanone gave the phosphinazine as a yellow solid (30-50%), m.p. 84-85 °C (decomp.) (Found: C, 77.0; H, 8.0; N, 5.6; C_{32}H_{39}N_{2}O_{1}P_{1} requires C, 77.1; H, 7.9; N, 5.6%), ν_{max} 1610 and 1600 cm^{-1}, δ 1.32[18H, s, 2 x C(CH_{3})_{3}], 1.50-2.40 (8H, c, ring CH_{2}'s) and 7.12-7.96 (13H, c, ArH), ^{31}P δ 55.5.

(d) 1,2-Di-p-t-butylphenyl-2-(tri-n-butylphosphinazine)-ethan-1-one-2-ylidene. Reaction of tri-n-butylphosphine and 1,2-di-(4-t-butylphenyl)-2-diazoethanone gave the phosphinazine as a yellow solid (54%), m.p. 104-106 °C (decomp.) (Found: C, 75.9; H, 10.0; N, 5.2; C_{34}H_{53}N_{2}O_{1}P_{1} requires C, 76.1; H, 9.95; N, 5.2%), ν_{max} 1620 cm^{-1} (C=O), δ 0.07-1.00 (9H, m, 3 x CH_{3}(CH_{2})_{3}) 1.10-2.04 (36H, C incorporating two sharp singlets at 1.27 and 1.29 due to (CH_{3})_{3}C, 3 x CH_{3}(CH_{2})_{3} and 2 x (CH_{3})_{3}C) and ^{31}P δ 44.8.

(e) 1,2-Di-p-t-butylphenyl-2-(triphenylphosphinazine)-ethan-1-one-2-ylidene. Reaction of triphenylphosphine and 1,2-di-(4-t-butylphenyl)-2-diazoethanone gave the phosphinazine as a yellow solid (60%),
m. p. 142-145°C (decomp.) (Found: C, 80.3; H, 6.7; N, 4.5.  
C_{40}H_{41}N_2O_1P_1 requires C, 80.5; H, 6.9; N, 4.7%). ν_{max} 1630 cm\(^{-1}\) (C=O), δ 1.22 (9H, s, (CH\(_3\))\(_3\)C), 1.29 (9H, s, (CH\(_3\))\(_3\)C) and 6.86-7.00 (23H, c, ArH) and \(^{31}\)P δ 21.6.

**Decomposition of Phosphinazines**

**General method.** All apparatus was baked dry in an oven at 130°C.

The sand was cleaned by washing with ethanol, then with ether and dried by heating for 24 h at 130°C. The apparatus and sand were allowed to return to room temperature in a desiccator over phosphorus pentoxide.

The phosphinazine (0.5-3.0 g) was ground together with sand (5-7 g) and the mixture pyrolysed under reduced pressure using the Kugelrohr bulb-to-bulb technique. The volatiles were collected and identified using preparative t.l.c. and g.l.c./mass spectroscopy. The involatile residues were extracted with dichloromethane.

(a) 1,2-Di-p-t-butylphenyl-2-(1-phenylphospholanazine)-ethan-1-one-2-ylidene. (i) The phosphinazine was pyrolysed either adsorbed onto sand or in a melt at 125°C at pressures varying between 1.0 and 0.5 mm Hg. Analysis of the volatiles using g.l.c. (2½% SE 30 at 190°C) and preparative t.l.c. (alumina, n-hexane 20% ether) showed the presence of 1-phenylphospholan (34%), \(^{31}\)P δ-15.8, m/e 164 (M\(^+\)); 1-phenylphospholan oxide (61%), ν_{max} (neat) 1180 cm\(^{-1}\) (P=O), \(^{31}\)P δ +59.7, m/e 180 (M\(^+\)); and 4-cyano-t-butylbenzene (12%) ν_{max} (neat) 2230 cm\(^{-1}\) (C≡N) and m/e 159 (M\(^+\), 20), 144 (M\(^+\)-CH\(_3\), 100) and
Extraction of the volatiles with dichloromethane gave a residue which varied from a tar to a yellow powder (69-74%, based on weight of starting diazo ketone), m. p. 50-60°C, $\nu_{\text{max}}$ 1670 cm$^{-1}$, $\delta$ 1.28 (unequal d, 9H, $(\text{CH}_3)_3\text{C}'$s), 5.05 (s, <1H, Ar$_2\text{CHC}=\text{N}$) and 7.20-7.80 (m, 4H, ArH). H. p. l. c. and t. l. c. under various conditions indicated the presence of a single major component as well as several minor components. Various methods of purification of the residue were tried, the most successful being chromatography over alumina using a mixture of n-hexane and ether as eluant. Typically, the phosphinazine (10.9361 g) was pyrolysed in three batches to give a tarry brown residue (9.50 g) which on chromatography (n-hexane - 10% ether) afforded di-(4-t-butylphenyl)cyanomethane as colourless crystals (970 mg, 14%), m. p. 183-185°C (Found: C, 86.3; H, 8.8; N, 4.3; M$^+$, 305, C$_{22}$H$_{27}$N$_1$ requires C, 86.5; H, 8.9; N, 4.6, and M$^+$, 305), $\nu_{\text{max}}$ 2205 cm$^{-1}$ (C≡N), $\delta$ 1.27 (18H, s, $(\text{CH}_3)_3\text{C}$), 5.04 (1H, s, CH) and 7.12-7.44 (8H, m, ArH) and $^{13}$C $\delta$ 31.27 $(\text{CH}_3)$, 34.56 (CCH$_3$)$\equiv$C), 41.82 (Ar$_2\equiv$C), 120.03 (C≡N), 127.36 and 126.07 (Ar) and 151.19 and 133.04 (Ar). Sublimation at 120/1.0 mmHg gave the pure nitrile as colourless needles m. p. 185-188°C.

Further chromatography using n-hexane - 20% ether as eluant gave the major component as a colourless solid (2.57 g, 33%), m. p. 120-130°C, which on recrystallisation from n-hexane gave colourless crystals (1.68 g, 68%), m. p. 194-195°C (Found: C, 84.5; H, 8.3; N, 4.3%), $\nu_{\text{max}}$ 1670, 1605, 1365, 1270, 1245, 1185, 1110, 1020, 1015 (sh), 985, 905, 845 (sh), 830 and 730 cm$^{-1}$, $\delta$ 1.28 (unequal d,
18H. \((\text{CH}_3)_3\text{C}\) and 7.80-7.20 (9H), \(^{13}\text{C}\) \(\delta 165.69\) (9), 157.93 (13), 154.97 (15), 151.16 (25), 138.50 (13), 133.63 (15), 133.43 (18), 129.51 (45), 127.82 (52), 126.86 (103), 125.64 (120), 124.80 (6), 119.54 (6), 35.25 (15), 34.91 (15), 34.52 (32), 31.28 (180) and 31.08 (135), m/e \((180^\circ\text{C})\) 306 (11), 305 (34), 291 (25), 290 (305-15, \(M^*\) 275.74, (305 \(\rightarrow\) 290), 100), 279 (3), 249.5 (3), 172 (1), 161 (4), 157 (4), 137.5 (6), 123.5 (3), 109.5 (7), m/e \((210^\circ\text{C})\) 624 (<0.1), 609 (<0.1), 598 (<0.1), 463 (1.6), 438 (1), 305 \((\text{C}_{22}\text{H}_{27}\text{N}_1)\), 22), 304 \((\text{C}_{22}\text{H}_{26}\text{N}_1)\), 50, 291 (18), 290 \((\text{C}_{22}\text{H}_{27}\text{N}_1)\) \(-\text{CH}_3\), \(M^*\) 275.7, 305 \(\rightarrow\) 290, 274 (10), 161 \((\text{ArC} \equiv \text{O}^+, 10^\circ\) and 57 [(\(\text{CH}_3)_3\text{C}^+, 18] . Molecular weight determination gave a value of 612 m.w. from 12.5 m.g. /ml. and 614 m.u. from 7.8 m.g. /ml.

(ii) Using a different approach, chromatography of the crude residue on alumina using light petroleum-ether as eluant afforded a yellow tarry solid which was repeatedly recrystallised from light petroleum, then finally from n-hexane to give a colourless solid. Sublimation of this solid at \(120^\circ\text{C}/1.00\text{ mmHg}\) pressure gave the nitrile as colourless crystals (10\%). Recrystallisation of the un sublimed residue from n-hexane yielded colourless crystals, m.p. 194-197\(^\circ\text{C}\) (Found: C, 86.3; H, 8.6; N, 4.5\%), \(^{13}\text{C}\) \(\delta 165.67\), 157.97, 154.94, 151.16, 133.61, 133.41, 129.51, 127.83, 126.85, 125.66, 125.43, 34.92, 35.26, 31.28 and 31.10. The i.r. and \(^1\text{H}\) n.m.r. spectra of these crystals were identical to those of the residue obtained by chromatography in (i).

(iii) The phosphinazine was thermolysed in solvents at different temperatures and the amount of the di-(4-t-butylphenyl)cyano methane
determined by g. l. c. (2½% S. E. 30, 120°C). The amount of the major component was determined by h. p. l. c. (n-hexane - 5% ether). After one hour in boiling chlorobenzene (b. p. 130°C), the yield of nitrile was 11% and that of the major component, 36%; whilst in boiling t-butylbenzene (b. p. 169°C) the yields were 14% and 24%, respectively.

(iv) The phosphinazine was decomposed as in (i) above but in the presence of copper powder. Chromatography of the involatile residue over alumina using n-hexane - 10% ether as eluant afforded a pale green solid (62%) whose i. r. and ¹H n. m. r. spectra were identical to that of the products from the decomposition without copper. H. p. l. c. and g. l. c. analysis of the crude residue, as before, indicated a 31% of the major component and a 12% yield of di-(4-t-butylphenyl)cyano-methane.

(b) 1,2-Di-p-t-butylphenyl-2-(triphenylphosphinazine)-2-ethan-1-one-2-ylidene. The phosphinazine (3.985 g, 6.67 mmol) was adsorbed onto sand and pyrolysed at 135°C for 2.5 h to give a colourless oil contaminated by a colourless solid. Careful redistillation of the volatiles afforded p-t-butylcyanobenzene (100.5 mg, 10%), b. p. 50-60°C and triphenylphosphine (240.0 mg, 14%), m. p. (from light petroleum) and mixed m. p. 80°C, ³¹P δ -5.1 (authentic -5.1). Extraction of the residue with dichloromethane afforded a tar (3.36 g) whose i. r. and ¹H n. m. r. spectra identified it as a mixture of triphenylphosphine oxide and the same products from the pyrolysis of the 1-phenylphospholanazine. Chromatography of the tar over alumina with n-hexane-ether as eluant yielded di-p-t-butylphenylcyanomethane (12%) and the same major
component as from (a) (1.16 g, 57%). Further elution with ethyl acetate afforded triphenylphosphine oxide (1.34 g, 72%), \(^{31}\)P 29.1, m.p. 150-154°C. Recrystallisation from ether gave the pure oxide.

(c) \(1,2\)-Di-p-t-butylphenyl-2-(tri-n-butylphosphinazine)-2-ethan-1-one-2-ylidene. Pyrolysis of the phosphinazine on sand at 125°C for 4.5 h gave a clear sweet-smelling oil which was identified as a mixture of tri-n-butylphosphine and the corresponding phosphine oxide and \(p\)-cyano-t-butylbenzene from \(^{31}\)P n.m.r. and i.r. spectra. Extraction of the involatile residue followed by chromatography yielded the di-p-t-butylphenylcyanomethane (44.19 mg, 12%) and the same major component as in (a).

(d) \(1,2\)-Diphenyl-2-(1-phenylphosphanazine)-ethan-1-one-2-ylidene. Pyrolysis of the phosphinazine on sand at 125-145°C gave a distillate which sometimes had a reddish tinge which was attributed to trace amounts of diphenyl ketene (\(v_{\text{max}}\) 2230 cm\(^{-1}\)). Analysis of the oil by t.l.c. (alumina, light petroleum - 10% ether) and g.l.c. (2½% SE 30, 195°C) identified its components as 1-phenylphosphan (30-35%) and 1-phenylphosphan oxide (60-72%) (i.r. and n.m.r. spectra identical with authentic samples), and diphenylcyanomethane (22%), \(v_{\text{max}}\) 2245 cm\(^{-1}\) (C≡N), \(\delta\) 5.2 (s, \(1^H, \text{Ph}_2\text{CH}\)) and m/e 193 (M\(^+\), 100). Work-up of the involatile residue in the usual way afforded a yellow tarry solid (36-51%) m.p. 50-60°C, \(v_{\text{max}}\) 1635 and 1670, \(\delta\) 7.0-8.0 (Ph) and m/e (110°C): 416 (<0.1), 387 (<0.1), 384 (<0.1), 297 (33), 295 (2), 192 (4), 167 (19), 165 (19), 105 (100) and 77 (48). T.l.c. analysis of the solid on both alumina and silica using various solvent systems: light petroleum with varying amounts of ether and toluene showed the presence
of a multitude of products. Attempted isolation by chromatography and/or recrystallisation of the major component failed although trace amounts of 2,3,4,5-tetraphenylpyrazine (approx. 2%) and triphenyloxazole (approx. 1%) were obtained by chromatography over alumina. The pyrazine and oxazole were identified by comparison with authentic samples. Recrystallisation of the crude residue from ethanol gave colourless to yellow crystals having varying melting points and analyses and i.r. spectra identical to that of the crude residue. In one instance, recrystallisation gave pale yellow crystals (0.40 g from 1.45 g residue) m.p. 130-135°C, which on further recrystallisation afforded yellow crystals m.p. 146-147°C (Found: C, 82.2; H, 5.0 and N, 6.9%), m/e (140°C), 416 (<0.1), 3.84 (3), 301 (1), 295 (4), 193 (31), 192 (100), 165 (49), 105 (100) and 77 (43). In another instance, chromatography (alumina, light petroleum-ether) followed by recrystallisation gave yellow crystals (3%) m.p. 190-194°C (Found: C, 79.1; H, 5.0; N, 6.34%; C_{28}H_{20}N_{2}O_{2} requires C, 80.80; H, 4.8; N, 6.7%), m/e 416 (M^+, 6), 311 [M^+-105, 36, M^* 232.5 (416->311)], 178 (6), 105 (PhC≡O^+, 100) and 77 (50). Trace amounts of colourless needles m.p. 182-182.5°C (Found: C, 75.9; H, 4.5; N, 4.2%), ω max 1700 cm⁻¹ and m/e 329 (4), 301 [329-28, 3, M^* 275.4 (329-301)], 226 [329-Ph≡N, 28, M^* 155.3 (329-226)], 224 [329-PhC≡O, 12, M^+ 152.5 (329-224)], 198 (2), 105 (100) and 77 (61), were also obtained.
DISCUSSION
Reactions of 2-Azido Ketones with Tervalent Phosphorus Reagents.

As described in the Introduction, Scott has reported that thermolysis of the small ring iminophosphoranes (1), prepared by the Staudinger reaction of 1-azido-2-nitrobenzenes and cyclic tervalent phosphorus compounds, generally afford good yields of benzofurazans as shown in Scheme 1, whereas the corresponding acyclic ylides, prepared from open-chain phosphorus reagents, usually do not undergo this thermal rearrangement. Scott has also shown that the formation of the benzofurazans most probably involves nucleophilic attack of oxygen at the phosphonium centre to give a $P^V$ intermediate (2) which subsequently collapses to the products. There have been several other reports concerning the ability of small rings to influence the course of reactions of phosphorus compounds.
example, Westheimer\textsuperscript{30a} attributed the high rate of acid hydrolysis of the cyclic phosphate (3) and its methyl ester compared to acyclic analogues, mainly to the relief of angle strain on going to the t.b.p. intermediate (4). Generally, incorporation of phosphorus into a small ring leads to an increase in the rate of nucleophilic attack and a decrease in the rate electrophilic attack at tetrahedral phosphorus relative to the acyclic compounds (see Scheme 2).\textsuperscript{30b,c} These effects can be explained by considering the change involved in the angle at phosphorus during the course of the reaction. Small ring four-coordinate phosphorus compounds such as (1) or (3) are assumed to possess a certain degree of strain since, in the idealised state, the four or five membered ring should accommodate a tetrahedral angle of approximately 109°. In contrast,
no such strain is involved in the t. b. p. intermediate formed in the nucleophilic substitution since the ring can readily span the strain-free a.e (90°) position. However, Hudson and Brown \(^{301b,c}\) have suggested that part of the acceleration observed for nucleophilic attack at cyclic phosphorus may be due to an increase in entropy in the transition state associated with an increase in the pseudorotational motion of the ring on passing to the five co-ordinate state. This is in accord with several reports \(^{301b,c}\) that entropy factors play an important part in the rate differences of cyclic and acyclic compounds. For example, Asknes and Bergenson \(^{301d}\) have reported that the phospholanium salts (5) underwent alkaline hydrolysis to the phospholan oxide 1300 times faster than the corresponding reaction of the six membered and open chain analogues but that the activation energies were nearly equal in all cases. The high rate of the five membered compound was found to be due to a high frequency factor.

The original aim of this present study was to extend Scott's observations to other bisfunctional azides and to examine their reactions with a variety of cyclic tervalent phosphorus reagents in the hope that the iminophosphoranes obtained would be sufficiently strained as to
collapse to a strain-free $P^V$ phosphorane intermediate, which in turn would decompose to synthetically interesting products. For example, it was thought that use of 2-azido ketones (6) as a substrate might lead to a worthwhile synthesis of azirines (8) via an intramolecular reaction involving a $P^V$ intermediate (7) as shown in Scheme 3. This expected pathway is to be contrasted with that observed by Zbiral and Stroh for the corresponding reaction with the acyclic phosphorus (III) reagent, triphenylphosphine, in benzene under reflux. In this instance, pyrazines (9) were obtained, presumably via a double intermolecular Wittig-type reaction.

\[
\begin{align*}
(6) + \text{Ph}_3\text{P} & \rightarrow [\text{Ph}_3\text{P}^V \text{NCHR}_2^2\text{COR}_1^1] \\
\text{Ph}_3\text{P}^\text{O} + & \rightarrow (9)
\end{align*}
\]

In the event, azirines were not obtained during this present study but the investigation of the reaction of bisfunctional azides with
tervalent phosphorus reagents led to a general route to a new class of pentaco-ordinate phosphoranes and also provided some insight into the factors affecting pentaco-ordinate versus four co-ordinate phosphorane formation.

a) Formation of Pentaco-ordinate Phosphoranes

The idea that pentaco-ordinate phosphoranes could be isolated from the reaction of 2-azido ketones and certain organophosphorus (III) reagents arose from the attempted preparation of an iminophosphorane by the Staudinger reaction of 1-phenylphospholan and 1,2-diphenyl-2-azidoethan-1-one (10) in dry benzene at room temperature. The reaction was monitored by $^{31}$P n.m.r. spectroscopy. When nitrogen evolution had ceased spectra of the reaction mixture showed the absence of any phosphorus (III) reagent. The major absorption observed was at -28 p.p.m. which was attributed to a highly shielded pentaco-ordinate phosphorus species (12), together with a minor absorption at +55 p.p.m. which was assigned to 1-phenylphospholan oxide (15). The latter assignment was verified by peak enhancement and isolation. After two hours a small absorption appeared at +34 p.p.m. which was attributed to a four co-ordinate phosphorus species, possibly the iminophosphorane (14). For a while, the intensity of the signals at +34 and +55 p.p.m. increased at the expense of that at -28 p.p.m. After 48 h the only phosphorus-containing species present in the reaction mixture was the phospholan oxide. On work up, 2,3,5,6-tetraphenylpyrazine (17) was isolated in 88% yield. All attempts to isolate the intermediate phosphorane failed.

The order of appearance of the n.m.r. signals suggested that the
tervalent phosphorus compound reacted with the azido ketone to form the pentaco-ordinate phosphorane (12), presumably via the triazine (11). The $P^V$ species then isomerised to the iminophosphorane (14) via the betaine (13) which was formed by fission of the P-O bond. Finally, two molecules of the iminophosphoranes underwent an intermolecular Wittig reaction to form the dihydropyrazine (16) which was rapidly oxidised to the pyrazine.

The proposal that pyrazine formation involved the Wittig reaction of two molecules of iminophosphorane is supported by similar observation for the corresponding carbon ylide. Thus, Griffin and Witschard. 293
reported that treatment of 2-benzoylethyltriphenylphosphonium bromide with base gave 1,4-diphenylcyclohexa-1,4-diene via the intermolecular Wittig reaction of the resultant ylide as shown in Scheme 5. It is also known that the nitrogen analogues of cyclohexa-1,4-diienes, the 2,5-dihydropyrazines, readily undergo oxidation to form the pyrazines.

(i) Preparation of Spirophosphoranes from Cyclic Phosphonites

In view of the large number of known phosphoranes containing the 1,3,2-dioxaphospholane ring, it seemed reasonable to expect that the reaction of the azide (10) with 2-phenyl-1,3,2-dioxaphospholan (19, n=2) might lead to the formation of an isolable phosphorane. This expectation was encouraged by preliminary examination of the reaction by $^{31}P$ n.m.r. spectroscopy which showed the rapid and quantitative formation of a $P^V$ species at -30.6 p.p.m. On a preparative scale, treatment of an ethereal solution of the azide with the cyclic phosphonite, under anhydrous conditions at room temperature, gave the phosphorane (20, $R=Ar=Ph$, n=2) as a colourless precipitate in 89% yield. This reaction proved quite general. Indeed, reaction of the 2-azido ketones (18, $R=H$ or Ph) with 2-phenyl-1,3,2-dioxaphospholan (19, n=2) and -1,3,2-dioxaphosphorinan (19, n=3) in dry benzene or ether provided a mild route to many new isolable amino-oxyphosphoranes (20, $R=H$ or Ar; n=2 or 3). Table 1 lists the phosphoranes prepared in this manner,
### TABLE 1

<table>
<thead>
<tr>
<th>ArC—CHR + PhP(CH₂)ₙ</th>
<th>Ph</th>
<th>Ar</th>
<th>O</th>
<th>P(CE₂)₁ᵢ⁺</th>
<th>Phₚ</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorane (20)</td>
<td>δ (³¹P) Yield</td>
<td>m.p. (°C)</td>
<td>C</td>
<td>H</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>(a) Ar=R=Ph, n=2</td>
<td>-29.7</td>
<td>89</td>
<td>88 (decomp)</td>
<td>69.8</td>
<td>5.3</td>
<td>3.5</td>
</tr>
<tr>
<td>(b) *Ar=R=Ph, n=3</td>
<td>-45.6</td>
<td>96</td>
<td>94 (decomp)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) Ar=Ph, R=H, n=2</td>
<td>-25.4</td>
<td>61</td>
<td>84-86 (decomp)</td>
<td>63.8</td>
<td>5.3</td>
<td>4.6</td>
</tr>
<tr>
<td>(d) Ar=Ph, R=H, n=3</td>
<td>-41.1</td>
<td>82</td>
<td>87 (decomp)</td>
<td>64.7</td>
<td>5.8</td>
<td>4.3</td>
</tr>
<tr>
<td>(e) Ar=4-BrC₆H₄, R=H, n=2</td>
<td>-25.3</td>
<td>71</td>
<td>85 (decomp)</td>
<td>50.7</td>
<td>3.9</td>
<td>3.6</td>
</tr>
<tr>
<td>(f) Ar=4-BrC₆H₄, R=H, n=3</td>
<td>-40.8</td>
<td>85</td>
<td>105 (decomp)</td>
<td>51.6</td>
<td>4.2</td>
<td>3.3</td>
</tr>
<tr>
<td>(g) Ar=4-MeOC₆H₄, R=H, n=2</td>
<td>-25.6</td>
<td>73</td>
<td>99 (decomp)</td>
<td>61.8</td>
<td>5.3</td>
<td>4.2</td>
</tr>
<tr>
<td>(h) Ar=4-MeOC₆H₄, R=H, n=3</td>
<td>-41.2</td>
<td>74</td>
<td>102 (decomp)</td>
<td>62.3</td>
<td>5.8</td>
<td>4.0</td>
</tr>
<tr>
<td>(i) Ar=4-PhC₆H₄, R=H, n=2</td>
<td>-25.5</td>
<td>85</td>
<td>105 (decomp)</td>
<td>69.8</td>
<td>5.3</td>
<td>4.0</td>
</tr>
<tr>
<td>(j) Ar=4-PhC₆H₄, R=H, n=3</td>
<td>-40.9</td>
<td>93</td>
<td>90 (decomp)</td>
<td>70.3</td>
<td>5.5</td>
<td>3.4</td>
</tr>
</tbody>
</table>

* A satisfactory analysis could not be obtained because of the hydrolytic instability of the compound. Exact mass measurements shows M⁺, 391.133850, C₂₃H₂₂NO₃P requires M⁺, 391.133723.
together with their $^{31}$P n.m.r. chemical shifts, yields, melting points and elemental analyses.

The phosphoranes were colourless solids with a tendency to decompose on heating near their melting points. The compounds (20, $R=H$) derived from the phenacyl azides were insoluble in ether and sparingly soluble in benzene and chloroform. The other phosphoranes (20, $R=Ar=Ph$) were sparingly soluble in ether and quite soluble in benzene and chloroform.

Those phosphoranes (20, $R=Ar$) containing the double bond of the amino-oxy ring conjugated with two aryl groups were hygroscopic and hydrolysed rapidly on exposure to the atmosphere. However they were stable indefinitely in the absence of moisture, both in the solid state and in solution. By contrast, the phosphoranes (20, $R=H$), in which the double bond was conjugated with only one aryl group, were less readily hydrolysed but underwent some surface decomposition on standing. The compounds (20, $R=H$) appeared to be light sensitive. Solutions of (20, $R=H$) in dry benzene or chloroform turned brown or yellow on standing for a few hours. $^{31}$P N.m.r. spectra of these coloured solutions indicated that the $P^V$ species was decomposing to form several phosphorus-containing species, one of which was identified as the cyclic phosphonate (24, $n=2$ or 3). A possible explanation for this instability of (20, $R=H$) and the formation of (24) is outlined in Scheme 6. The $P^V$ species undergoes P-O bond fission to give the betaine (21) which can rearrange to the iminophosphoranes (22) and (23). Subsequent decomposition of the latter, e.g. by intermolecular Wittig reactions, leads to the formation of the phosphoryl compound (24). Attempts to isolate
In summary, it would appear that conjugation of the double bond of the amino-oxy ring with two aryl groups enhances the stability of the $P^V$ form relative to $P^IV$ forms. Thus (20, $R=Ar$) did not exhibit any tendency to ring open to form $P^IV$ species at room temperature. This ability of aryl groups to stabilise the $P^V$ form has also been observed for the Ramirez adducts (25, $R^1=R^2=Ph$). 159, 181

The phosphoranes (20, $R=H$ or $Ar$) were identified mainly on the
basis of the following spectroscopic data which ruled out alternate P\textsuperscript{IV} forms such as the betaines or iminophosphoranes.

The $^{31}$P n.m.r. spectra of all the compounds exhibited upfield absorptions relative to phosphoric acid. These negative shifts are characteristic of highly shielded P\textsuperscript{V} species.\textsuperscript{11,295} It was observed that decreasing the ring size of the starting tervalent phosphorus reagent from six ($19, n=3$) to five ($19, n=2$) caused the phosphorus nucleus of the resultant spirophosphorane (20) to be deshielded by 15.5-15.8 p.p.m. A similar effect also occurs in the P\textsuperscript{V} dioxaphospholenes which were prepared by reaction of diketones with phosphite esters and amides as outlined in Scheme 7. Thus, Ramirez\textsuperscript{25} has reported that the $^{31}$P chemical shifts of the spirocyclic P\textsuperscript{V} adducts of diketones and six membered cyclic P\textsuperscript{III} compounds shifts were ca 20-23 p.p.m. more negative than those of the P\textsuperscript{V} adduct from the corresponding five membered cyclic P\textsuperscript{III} reagents.

$^1$H N.m.r. spectra of the more reactive phosphoranes (20, R=H) were sometimes difficult to obtain because of their tendency to decompose in solution. However, even in those cases where satisfactory integrations could not be obtained the olefinic proton gave rise to a characteristic doublet of doublets with $J_{HP}$ and $J_{HH}$ of 32 and 3Hz, respectively.

The $^1$H n.m.r. spectra of one of the phosphoranes (20, R=H, Ar=Ph, n=2) is reproduced in Fig. 1. The doublet of doublets at
Fig. 1 \( ^1\)H N.m.r. spectrum of (20o). Insets: effects of double resonance irradiation on amino and olefinic signals; (i) \(^{31}\)P decoupled; (ii) \(^3\)P decoupled, irradiated at 8 4.87; (iii) \(^{31}\)P decoupled, irradiated at 8 6.82.
6.32 p.p.m. \( J_{HP} = 32 \text{Hz} \) and \( J_{HH} = 3 \text{Hz} \) and the broad doublet at 4.87 p.p.m. were assigned to the olefinic and amino protons, respectively. Double resonance experiments confirmed that the olefinic and amino protons were coupled to each other and to phosphorus. The broad multiplet at 3.30-4.60 p.p.m., which was assigned to the methylene protons of the dioxaphospholanan ring, indicated that these protons were non-equivalent. Similarly, the ring protons of the dioxaphorinan ring in the six membered spirocyclics (20, \( n=3 \)) are non-equivalent as illustrated by the \( ^1 \text{H n.m.r.} \) spectrum of (20, \( R=H, Ar=Ph, n=3 \)) (Fig. 2). The two multiplets at approximately 2 and 4 p.p.m. were assigned to the \( \text{CH}_2 \) and \( \text{OCH}_2 \) protons respectively. Fig. 3 illustrates the \( ^1 \text{H n.m.r.} \) of another of the phosphoranes (20, \( R=Ar=Ph, n=2 \)). The broad doublet at 5.01 p.p.m., \( J_{HP} = 14 \text{Hz} \), was assigned to the amino proton. As in the other phosphoranes the non-equivalence of the methylene protons was indicated by the broad multiplet between 3.4 and 4.7 p.p.m. assigned to these protons.

The \( ^{13} \text{C n.m.r.} \) spectrum of one of the phosphoranes (20, \( R=Ar=Ph, n=2 \)), reproduced in Fig. 4, had only one resonance in the aliphatic region at 66.5 p.p.m., showing that the carbons of dioxaphospholanan ring are equivalent.

The i.r. spectra of the amino-oxyphosphoranes showed N-H stretching frequencies near 3220 cm\(^{-1}\) for those derived from 1,2-diphenyl-2-azidoethan-1-one and near 3,400 cm\(^{-1}\) for those derived from the 2-azidoacetophenones. The C=C stretch absorptions were in the region 1625-1645 cm\(^{-1}\) with the less symmetrical double bonds (20, \( R=H \)) generally giving rise to more intense signals than the more
Fig. 2 $^1$H N.m.r. spectrum of (20d). Insets: effects of double resonance irradiation on amino and olefinic signals.

Fig. 3 $^1$H N.m.r. spectrum of (20a)
symmetrical ones \((20, R=\text{Ar}=\text{Ph})\). Fig. 5 illustrates the above mentioned features of the i.r. spectra of one of the phosphoranes \((20, R=\text{H}, \text{Ar}=\text{p-BrC}_6\text{H}_4, n=2)\).

Fig. 4 \(^{13}\text{C N.m.r. spectrum of (20a) (CDCl}_3\)}\)

Fig. 5 I.r. spectrum (nujol mull) of (20e).
Stereochemistry of the Spirophosphoranes

The exact conformation of these new pentaco-ordinate amino-oxyphosphoranes (20) is not yet known unequivocally because an X-ray structural analysis could not be obtained owing to their hydrolytic sensitivity in some cases and to their tendency to surface decompose in others. Nonetheless, as discussed in the Introduction, p. 53, recently published data, both theoretical and experimental, has provided information as to the preferred conformation of a number of pentaco-ordinate phosphoranes. On the basis of this information, it is possible to predict the relative energies of the different conformers of a particular phosphorane with varying degrees of success.\textsuperscript{19,156} Thus, in the case of (20, \( n = 2 \)) the lowest energy t.b.p. conformer is (27).

This structure obeys both the 'element effects' rule, which states that the more electronegative ligands preferentially occupy the apical position, and the 'ring strain' rule which implies that less strain is present when a four or five membered ring occupies the \( a, e \) positions. This conformation also concurs with the known preference of lone pairs for the equatorial plane of the t.b.p., and also with the greater lone
pair effect of \( sp^3 \) nitrogen compared to oxygen. 19, 156, 232c

Little structural information exists as to the preferred geometry of six-membered ring pentaco-ordinate phosphoranes. As expected, ring-strain considerations are not very important and the six-membered ring can span both the \( a,e \) and the \( e,e \) positions without much difficulty. For example, the structure of the phosphorinan derivative (29) is similar to that of its acyclic analogues and, in agreement with the polarity rule, contains a diequatorial ring. This contrasts with the situation for four- and five-membered ring phosphoranes where ring strain can play a decisive part in determining the preferred conformation. For example, the fluorophosphorane (30) possesses a structure which contains an \( a,e \) ring and an equatorial fluorine. 303 In this case ring strain clearly predominates over electronegativity considerations. Interestingly, the phospholan derivative (31) appears to contain an \( e,e \) ring at low temperatures but, unlike (29) undergoes rapid pseudorotation at room temperature. This pseudorotatory process involves isomers which violate the 'element effects' rule by having equatorial fluorines and apical carbons, but allows the ring to occupy the strain-free \( a,e \) position.

As described in the Introduction, p. 68, molecular models indicate that, in the case of six-membered ring phosphoranes containing \( \alpha \)-hetero-
atoms, the a, e boat form is favoured over other conformations owing to the lone pair effect. This observation is supported by an X-ray structural analysis of the phosphorane (31) which showed that the six-membered amino-oxy ring existed in an a, e boat conformation with nitrogen in an equatorial position.

From the foregoing discussion it seems likely that the most favourable t. b. p. conformation of (20, n=3) is (32) in which the six-membered ring exists in the a, e boat conformation.

The above t. b. p. representations (27) and (32) are in accord with the $^1$H n.m.r. data of the compounds (20, n=2 and 3, respectively). For example, the observed non-equivalence of the protons of the dioxa rings is consistent with structures (27) and (32) which do not pseudorotate. The rigid t. b. p.'s would be expected to display different apical and equatorial protons and also different protons cis and trans to the
phenyl group. Alternatively, the $^1$H n.m.r. data can be interpreted as indicating that the t.b.p. is undergoing pseudorotation which is limited to the ring ligands switching from apical to equatorial; thus the non-equivalence of the protons cis and trans to the phenyl group is preserved (path a, Scheme 8) for the dioxaphospholan case. The latter interpretation is supported by the $^{13}$C n.m.r. spectroscopic studies of (20a) which show that the carbons of the dioxa ring are equivalent. If (27, R=Ar=Ph) is the correct conformation of (20a), there must be rapid interchange of the apical and equatorial carbons of the dioxa ring by an exchange process which allows the ring protons to

Scheme 8

(20a)
remain non-equivalent, viz., path a, Scheme 8. Moreover, for the t. b. p.'s (27) and (32), ring strain considerations imply that a B. P. R. process which made the ring protons equivalent, is energetically unfavourable since it involves topomers containing diequatorial rings (path b, Scheme 8). \textsuperscript{154a}

Whilst it is generally accepted that the preferred geometrical configuration of the majority of acyclic, monocyclic and fused bicyclic phosphoranes is the t. b. p.,\textsuperscript{19, 151, 304} that of spirobicyclic systems such as (20, n=2 and 3) is less definite.\textsuperscript{154, 156, 304} Some of these are exclusively t. b. p., but others show considerable distortion towards s. p. geometry which is the preferred structure of the ground state isomer in some cases.

Only small energy differences exist between the two basic five coordinate geometries;\textsuperscript{149} in the case of acyclic P\textsuperscript{V} systems, theoretical predictions using molecular orbital\textsuperscript{304, 305} and electrostatic\textsuperscript{151, 304, 306} models show that the t. b. p. is more stable than the s. p. form but only by ca. 5-10 kcal mol\textsuperscript{-1}. Gillespie's\textsuperscript{151} valence shell electron pair repulsion model which assumes that electron pairs in the valence shell preferentially adopt an arrangement to minimise repulsion between themselves, predicts that the presence of electronegative ligands should lower the slight preference in stability of the t. b. p. relative to the s. p. because of lessened repulsion between the bond pairs. Support for this prediction has come from X-ray diffraction studies\textsuperscript{154, 156, 304} of a number of spirocyclic phosphoranes of general structure (33, X=O, N, or S, Y=H, alkyl, aryl or halogen) which show that increasing electronegativity of X results in increasing stabilisation of the s. p. relative to
Holmes has suggested that the reason a number of spiro-oxyphosphoranes e.g. (33, X=O, Y=CH₃ or F) have s.p. structures is due to a combination of electronic and ring strain factors. The s.p. geometry allows the highly electronegative oxygens to occupy the electron-rich basal positions whereas in a t.b.p. two would be forced to take up an electronically unfavourable equatorial placement. In addition, the s.p. form has the possibility of enhanced structural stability from electron delocalisation as a more extensive basal bonding system is present. Also, the s.p. structure allows the P-O bonds of each ring to assume more or less equal character, depending on the electronic requirements of the attached substituent. By contrast the residual ring strain in the t.b.p. form must be greater as the P-O linkages are forced to occupy the different apical and equatorial positions.

In view of this evidence one cannot ignore the possibility that the phosphoranes (20, n=2 or 3) may display s.p. geometry. Observations concerning the preferred arrangement of ligands in s.p. phosphoranes indicate that the lowest energy s.p. representation of (20, n=2) is as shown in (34). For example, ring strain is minimised in this
structure since both small rings adopt the basal-basal (approx. 88°) rather than apical-basal (approx. 104°) arrangement. In addition (34) is in accord with 'element effect' predictions since the basal positions of the s.p. are assumed to be equivalent to the apical positions of the t.b.p. The structure is consistent with the n.m.r. data of the phosphoranes which indicated that for the dioxa ring, the protons are non-equivalent whereas the carbon atoms are equivalent.

It is possible to evaluate the relative stability of the t.b.p. (27) and s.p. (34) isomers of (20, n=2) using the model developed by Holmes. This model incorporates terms dealing with the major factors determining \( P^V \) geometry, viz. element effects (apicophilicities, etc) and ring strain and steric considerations. Holmes has constructed tables of numerical values of these terms mainly on the basis of the activation energies governing the fluxional behaviour of known phosphoranes and also, from the results of spectroscopic and theoretical studies defining t.b.p. and s.p. energy differences. The procedure is first to sum up the element effects for each isomer using the values derived by Holmes. Next, the total steric and ring strain terms are derived in the same manner. Also the total value of miscellaneous effects is determined. Thus there is an energy term associated with the loss in \( \pi \) bonding when \( sp^3 \) nitrogen occupies other than the equatorial location of a t.b.p. There is also a term \( \Delta=7 \text{ kcal mol}^{-1} \) which must be added to obtain the energy of an s.p. relative to a t.b.p. phosphorane. This term reflects the inherent instability of the acyclic s.p. relative to the t.b.p. isomer. The sum of these terms (element effects, ring strain, steric and others) gives the total relative energy value associated with each isomer. It has been
TABLE 2

Relative Isomer Energies of Phosphoranes (kcal mol\(^{-1}\))

(a) element effects

<table>
<thead>
<tr>
<th>Effect</th>
<th>Energy (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 x apical O</td>
<td>2.6</td>
</tr>
<tr>
<td>1 x equatorial O</td>
<td>2.8</td>
</tr>
<tr>
<td>1 x equatorial N</td>
<td>2.2</td>
</tr>
<tr>
<td>1 x equatorial Ph</td>
<td>1.7</td>
</tr>
</tbody>
</table>

\[ \Sigma \text{Ph} = 9.3 \]

(b) Ring strain

<table>
<thead>
<tr>
<th>Ring</th>
<th>Energy (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) dioxa ring</td>
<td>2.0</td>
</tr>
<tr>
<td>(ii) oxaza ring</td>
<td>2.0</td>
</tr>
</tbody>
</table>

\[ \Sigma = 4.0 \]

(c) Steric terms

\[ \Sigma = 0.0 \]

\[ 13.3 \text{ kcal} \]

\[ \Delta = 18.4 \text{ kcal} \]

R=H

\[ \Sigma = 9.3 \]

\[ \text{Ring strain} = 4.0 \]

\[ \text{Steric terms} = 0.0 \]

\[ \Delta = 7.0 \]

R=Ph

\[ \Sigma = 9.3 \]

\[ \text{Ring strain} = 4.0 \]

\[ \text{Other terms} = 3.0 \]

\[ \Delta = 7.0 \]

* For R=Ph a steric term arises due to a, e interaction of the phenyl groups in the amino-oxy ring.
reported that the model gives relative isomer energies in excellent agreement with those obtained from ab initio calculations and reproduces $\Delta G$ for intramolecular ligand exchange of a range of phosphoranes to within 1.56 kcal mol$^{-1}$ the model has also been used to the ground state isomer representations of a number of spirophosphoranes. Although the result in this case is qualitative, it has been shown that the model gives predictions which are in good agreement with the observations of X-ray diffraction studies.

The relative energies of the two isomers (27) and (34) are summarized in Table 2. As shown the elements effects and ring strain terms favour the t.b.p. over the s.p. form. However, inclusion of the terms dealing with the loss in $\pi$ bonding in (34) and the term $\Delta$ result in the t.b.p. (27) being favoured by 5.1 kcal mol$^{-1}$. Although the structure of (20, n=2) is predicted to be closer to the t.b.p. rather than the s.p. form, in view of this small energy difference some distortion of the t.b.p. towards the s.p. cannot be ruled out for the amino-oxyphosphoranes (20, n=2). In this connection it is noteworthy that Cadogan and co-workers have shown by X-ray crystallography that the structure of a 1,3,2-benzothiazophosphole is much distorted towards the s.p. form as shown in Fig. 6.

![Fig. 6](image-url)
Interestingly the X-ray data of the amino-oxyphosphoranes (33, $X^1 = X^4 = O$, $X^2 = X^3 = NH$, $Y = H$) display t. b. p. geometry (35) but with a 23% displacement towards s. p. geometry. Holmes model predicts that in this case the t. b. p. is favoured over the s. p. form by 10.2 kcal mol$^{-1}$. This contrasts with the observed and predicted s. p. geometry of the tetra-oxySpirophosphoranes (33, $X = O$, $Y = CH_3$) and is in accord with electronegativity considerations. The replacement of oxygen by the more electropositive nitrogen is expected to result in greater t. b. p. stabilisation for (33, $X^1 = X^4 = O$, $X^2 = X^3 = NH$) relative to (33, $X = O$). Hence the predicted distorted t. b. p. configuration of (20, $n = 2$) is reasonable.

The model was also used to predict the ground state isomer of the product (20, $n = 3$) from the reaction of 2-azido ketones with 2-phenyl-1,3-oxaphosphorinan.

In this case also the t. b. p. isomer (32) is favoured over the s. p. (36) but by 6.1 kcal mol$^{-1}$. The lessened ring strain considerations in (20, $n = 3$) compared with (20, $n = 2$) suggest that the structure of the former would show less distortion towards the s. p.
(ii) **Formation of other Phosphoranes**

The preparation of amino-oxyphosphoranes by the reaction of 2-azido ketones with cyclic phosphonites, at room temperature in benzene, is capable of extension to a variety of other phosphorus (111) reagents albeit the products were not isolated in many cases. Thus, preliminary $^{31}$P n.m.r. studies of the reaction of 1,2-diphenyl-2-azidoethan-1-one (37, R=Ph) with methyl diphenylphosphinite (38) indicated the complete conversion to a pentaco-ordinate phosphorane (40, R=Ph) with a chemical shift of -43 p.p.m. In the same manner, the reaction with $\text{2N,N-diethylamino-1,3,2-dioxaphospholan}$ (39) led to the quantitative formation of a product resonating at -35 p.p.m. This resonance was assigned to the $P^V$ species (41).

As in the case of the reaction of the azide with 2-phenyl-1,3,2-dioxaphospholan and 1,3,2-dioxaphosphorinan, no resonances were observed which could be attributed to intermediates.

The phosphoranes (40, R=Ph) and (41) were stable indefinitely in solution in the absence of moisture and showed no tendency to isomerise.
to $^4P$ species. However, attempts to isolate (40, $R=Ph$) gave a foam which hydrolysed rapidly to a mixture of phosphorus-containing products. The foam was identified as the phosphorane (40) on the basis of its $^{31}P$ (CDCl$_3$) at -49.5 p.p.m. The $^1H$ n.m.r. spectrum also showed the expected three proton doublet at 3.05 p.p.m. ($J_{HP}=11$Hz) and one proton doublet at 4.20 p.p.m. ($J_{HP}=16$Hz) for the methoxy and amino protons, respectively. The major phosphorus-containing hydrolysis products of (40) exhibited $^{31}P$ n.m.r. resonances at 34 and 24 p.p.m. The former absorption was assigned to methyl diphenyl-phosphonate (42) by peak enhancement. The other phosphorus product was a white solid which was insoluble in benzene and chloroform. This compound was identified tentatively as the phosphorus amide (43) mainly on the basis of its spectroscopic data. Thus the mass spectrum had a molecular ion at m/e 411 and showed the expected fragmentation pattern for (43). The major fragment ions occurred at m/e 306, 210, 201, 105 and 104 and were assigned to $Ph_2P(O)\overset{\text{N}}{\overset{\text{O}}{\text{N}}}CHPh$, $H_2\overset{\text{N}}{\overset{\text{O}}{\text{N}}}C(Ph) - C(0)Ph$, $Ph_2PO$, $Ph\overset{\text{O}}{\overset{\text{O}}{\text{O}}}CO\overset{\text{O}}{\overset{\text{O}}{\text{O}}}NH$, respectively. The i.r. spectrum exhibited major absorptions at 3260 (broad, N-H), 1675 (strong, C=O) and 1180 (strong, P=O) cm$^{-1}$. Scheme 9 shows possible mechanisms for the formation of (42) and (43).
In contrast with the reaction of the 2-azidoketone with the
cyclic phosphonites, that with the corresponding acyclic phosphorus
(111) reagent (44) led to the intermediacy of a four co-ordinate phosphorus
species which absorbed at 16 p. p. m. Whilst the solution remained
colourless, the very slow evolution of nitrogen together with the fast rate
of disappearance of the starting PIII reagent, suggested the absorption
might be due to an intermediate triazene (45, R1=Ph, R2=Me). On standing,
this species gradually changed into the pentaco-ordinate phosphorus product
(46, R1=Ph, R=Me) as shown by the appearance of an absorption at -44
p. p. m. The corresponding reaction with triethyl phosphite also afforded
a four-co-ordinate intermediate (31, P =0, 6 p. p. m.) which was presumably
the triazine (45, R=Ph, R1=OEt, R2=Et). The gradual replacement of
this signal by one at -56 p. p. m. indicated the formation of the aminooxyphosphorane (46, R1=OEt, R2=Et, R=Ph).

\[
\text{PhP(OMe)2} \quad \begin{array}{c}
\begin{array}{c}
\text{(R2O)2P} \\
\text{N} \\
\text{N} \\
\text{-CH-CPH}
\end{array}
\end{array} \\
\begin{array}{c}
\text{(R2O)2P} \\
\text{N} \\
\text{N} \\
\text{-CH-CPH}
\end{array}
\]

(44) (45) (46)

For the reaction of 1-phenyl-2-azidoethan-1-one (37, R=H)
with methyl diphenyl phosphinite, 31 P n. m. r. investigations revealed
the initial and quantitative formation of a species resonating at -38.8
p. p. m. This was identified as the phosphorane (40, R=H) on the
basis of its negative chemical shift relative to phosphoric acid.
As expected, the phosphorane was less stable than its more conjugated
counterpart (40, R=Ph). 31 P N. m. r. spectroscopy showed
that, on standing in solution, the $P^V$ species underwent facile decomposition to give a plethora of phosphorus-containing products. This could arise from a combination of facile hydrolysis and ring-opening of the phosphorane to give $P^{IV}$ isomers. Attempts to isolate the phosphorane by addition of dry petroleum ether to the reaction mixture gave an oil whose $^31P$ n.m.r. spectrum indicated the presence of a number of decomposition and/or hydrolysis products.

$^31P$ N.m.r. spectra of a solution of the same azide treated with dimethyl phenylphosphonite (44) showed a major absorption at 15 p.p.m. which was attributed to the triazine (45, $R=H$, $R^1=Ph$, $R^2=Me$) together with a minor absorption of -40 p.p.m. which was assigned to the pentacoordinate phosphorane (46, $R=H$, $R^1=Ph$, $R^2=Me$). On standing the $P^V$ species became the major component of the reaction mixture, but it appeared to undergo some decomposition and/or hydrolysis as indicated by the appearance of a number of other phosphorus resonances.

$^31P$ N.m.r. spectroscopy also showed that the azide reacted with triethyl phosphite to give a triazine (45, $R=H$, $R^1=OEt$, $R^2=Et$), ($^31P$ δ 0.6 p.p.m.) which lost nitrogen to give the phosphorane (46, $R=H$, $R^1=OEt$, $R^2=Et$) ($^31P$ δ -52 p.p.m.). As in the other cases the latter compound subsequently underwent some rearrangement and/or hydrolysis to form $P^{IV}$ species.

(iii) Conclusions

The reaction of 2-azido ketones with tervalent phosphorus reagents to give amino-oxyphosphoranes of type (20, n=2 or 3) is a specific example of a general synthesis of pentaco-ordinate phosphoranes
(48) from bisfunctional azides (47, Z=O or N). The scope of this reaction which has been explored in this laboratory is summarized in Table 3.

Scheme 10

Table 3

<table>
<thead>
<tr>
<th>Starting azide</th>
<th>P^{III} reagent</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar(\text{O})</td>
<td>PhP</td>
<td>Ar(\text{O})</td>
</tr>
<tr>
<td>R,N(\text{3})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph(\text{N})</td>
<td>PhP</td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N,(\text{N})</td>
<td>PhP</td>
<td></td>
</tr>
<tr>
<td>Ph(\text{N})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar(\text{NH})</td>
<td>PhP</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R(\text{1})OH</td>
<td>P(OR)_3</td>
<td></td>
</tr>
<tr>
<td>R(\text{2}),N(\text{3})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH_2(\text{N})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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In general, the reaction occurs under very mild, neutral conditions and unlike some other methods, there are no side products. The starting materials are usually readily available and yields are good-to-quantitative. In the specific case of (20, n=2 or 3), the high yield, mild conditions and ease of isolation of the product are important factors in the success of the synthesis since this type of phosphorane is difficult to handle. Scheme 11 outlines another possible route to such compounds.

Scheme 11

This involves an extension of Trippett’s method which has been used to prepare several phosphoranes by addition of 1,2-diols, amines and thiols to tervalent phosphorus compounds. However, in this instance, the method has the disadvantage that the amino ketones undergo ready condensation to dihydropyrazines. A second possible route to (20) is an adaptation (Scheme 12) of Schmidpeter and Luber’s preparation of phosphoranes from N-acyl-N’-phenylhydrazines and dichlorophosphines (Scheme 13). This procedure also suffers from the same disadvantage.

as Trippett’s method.
The foregoing reactions of tervalent phosphorus compounds with bisfunctional azides (Table 3) are obviously related to the known addition of Z-H groups (Z=O or N) to the P=X bond (X=C, N or O) to form $P^V$ species. Several examples of this type of reaction have been discussed in the Introduction, p. 108. Of particular relevance is Stegman's $^{94,95,97}$ reaction of an iminophosphorazene (49) bearing an ortho-hydroxy group as shown in Scheme 14.

![Scheme 14](image)

In keeping with Stegman's observation, the formation of pentaco-ordinate phosphoranes (48) from the reaction of bisfunctional azides with tervalent phosphorus reagents is assumed to proceed via the intermediacy of an iminophosphorane (50) followed by intramolecular addition of the Z-H group to the P=N bond. As discussed earlier, in the case of azido ketones, initial formation of iminophosphorane is not observed. Instead, 31 P n.m.r. spectroscopy suggests the amino-oxyphosphorane is formed directly from the triazine by nitrogen extrusion.
Fig. 7 $^1$H N.m.r. spectrum of (62).
(b) Formation of an Iminophosphorane from 1-Phenylphosphorinan

In the reactions of the 2-azido ketones (18, R=H or Ph, Ar=Ph, p-MeOC₆H₄, p-PhC₆H₄ or p-BrC₆H₄) with tervalent phosphorus reagents, only one isolable iminophosphorane was obtained. In this instance, treatment of 1,2-diphenyl-2-azidoethan-1-one (10) with 1-phenylphosphorinan (51) gave a good yield of colourless crystals which were identified as the iminophosphorane (52) on the basis of spectroscopic evidence. Thus, the characteristic $^31P$ chemical shift at 18.3 p.p.m. ruled out a $P^V$ structure as in the case of the product from the reaction of the azide with phosphonites, and indicated the compound to be a $P^{IV}$ species viz. (52). This conclusion was supported by the $^1H$ n.m.r. spectrum of the product which is reproduced in Fig.7. It should be noted that the ring methylene and aromatic protons appear as a ten proton multiplet at 0.90-2.40 p.p.m. and a fifteen proton multiplet at 6.78-8.10 p.p.m., respectively. The characteristic doublet ($1H, J = 21$Hz) at 4.29 p.p.m. is assigned to the methine protons; interestingly, the latter does not undergo exchange with $D_2O$. The i.r. spectrum of the product exhibits a band at 1640 cm$^{-1}$ due to the C=O stretch.

This reaction contrasts with the formation of a pentaco-ordinate phosphorane from the reaction of the same azide with 2-phenyl-1,3,2-dioxaphosphorinan (19, $n=3$). This difference can be explained on the basis of electronic effects arising from the replacement of carbon by oxygen in the tervalent
phosphorus reagent. This should lead to an enhanced electrophilicity at phosphorus, and consequently favour collapse of the iminophosphorane (53) to the $P^V$ product.

![Diagram of molecular structure](attachment:structure.png)

(c) Reactions proceeding with Decomposition of the Resultant Phosphorane.

In a number of cases it was not possible to isolate either a pentaco-ordinate phosphorane or an iminophosphorane from the reaction of 2-azido ketones with the tervalent phosphorus compound. In general, an intermediate $P^{IV}$ and/or $P^V$ species was observed by $^{31}P$ n.m.r. spectroscopy, but this subsequently decomposed to give the oxide of the tervalent phosphorus reagent and a non-containing phosphorus product which was usually the pyrazine. For example, reaction of 1, 2-diphenyl-2-azidoethan-1-one (10), with triphenylphosphine in benzene at room temperature resulted in the slow evolution of nitrogen and the formation of two phosphorus-containing species with $^{31}P$ chemical shifts at +10.0 p.p.m. and -49 p.p.m. in the ratio of 3:6. The former absorption, which was assigned to the triazine (54), disappeared on standing whilst the latter absorption, which was attributed to the pentaco-ordinate phosphorane (55), showed a corresponding increase in intensity. After 3 days the spectrum also exhibited other absorptions at 18.0 and 25.1 p.p.m. which were assigned to the iminophosphorane (56) and triphenylphosphine oxide, respectively.
Attempts to isolate and purify the phosphorane (55) resulted in oily mixtures contaminated with varying amounts of triphenylphosphine oxide, 2, 3, 5, 6-tetraphenylpyrazine (17) and iminophosphorane. Similar results were obtained from the corresponding reaction with 1-phenylphospholon as discussed on p. 186.

These observations suggest that a $P^V$ species is formed initially but that it undergoes ring-opening to an iminophosphorane which then decomposes by an intermolecular Wittig reaction as shown in Scheme 15. As might be expected, higher reaction temperatures favoured both the ring opening of (55) and the decomposition of the iminophosphorane (56). Thus, on heating in benzene for 14 h, (55) was completely converted into triphenylphosphine oxide and the iminophosphorane (56) which was identified by the presence in the $^1$H n.m.r. spectrum of a doublet at 4.65 p.p.m. ($J_{HP} = 19$Hz).
The reaction of the same azide with diethylphenylphosphine was more complex and gave rise to at least six different phosphorus-containing products with $^{31}$P chemical shifts between +29 and +44 p.p.m. No pentaco-ordinate species were observed.

The reaction of 1-phenyl-2-azidoethan-1-one (6, $R^1 = \text{Ph}, R^2 = \text{H}$) with both 1-phenylphospholan and 1-phenylphosphorinan in benzene at room temperature gave good yields of 2,5-diphenylpyrazine (58, $R^1 = \text{Ph}, R^2 = \text{H}$) and the corresponding phosphine oxide (59, $n=2$ and 3). In the case of 1-phenylphospholan, the reaction was complete after thirty minutes and the only detectable intermediate by $^{31}$P n.m.r. spectroscopy was a $P^V$ species giving rise to a minor absorption at -33 p.p.m. By contrast no pentaco-ordinate species could be detected in the corresponding reaction with the 1-phenylphosphorinan. Instead, $^{31}$P n.m.r. studies revealed the presence of two absorptions at +26 and +32 p.p.m. which were attributed to (60, $x=0$ and 2).

Pyrazines (58, $R^1 = \text{Ph}, R^2 = \text{H}$; $R^1 = \text{p-MeOC}_6\text{H}_4, R^2 = \text{H}$; $R^1 = (\text{CH}_3)_2\text{CH}, R^2 = \text{H}$; and $R^1 = (\text{CH}_2)_4$) have been previously prepared by Zbiral and Stroh from the Staudinger reaction of 2-azido ketones (6) with triphenylphosphine in boiling benzene. Re-examination of this reaction at room temperature in the case of (6; $R^1 = \text{Ph}, R^2 = \text{H}$) by $^{31}$P n.m.r. spectroscopy showed the absence of
a PT species as a detectable intermediate. Instead, two absorptions were observed at 10.0 and 8.0 p.p.m. which were tentatively assigned to the triazine and iminophosphorane. These intermediates rapidly decomposed to give good yields of 2,5-diphenylpyrazine and triphenylphosphine oxide. By contrast, the corresponding reaction of 1,2-diphenyl-2-azidoethan-1-one (6, R1=R2=Ph) did afford a PT intermediate (see p. 213). This is in accord with other observations150 that conjugation of the double bond with aryl groups favours PT relative to PTIV formation.

The reactions of 2-azidocyclohexanone (6, R1, R2 = -(CH2)-) with the cyclic reagents (61, X=0, n=2 and 3; X=CH2, n=2) in benzene at room temperature were also examined by 31P n.m.r. spectroscopy. The reaction with 1-phenylphospholan was rapid and complete conversion into the phospholan oxide occurred within fifteen minutes of mixing the reagents. No intermediates could be detected. For the corresponding reaction with 2-phenyl-1,3,2-dioxaphosphorinan, there was initial formation of a PTIV intermediate with a characteristic absorption at 0.6 p.p.m. This absorption was assigned to a triazine, which slowly lost nitrogen, to give a PT species (31Pδ = -44 p.p.m.), presumably the amino-oxyphosphorane (62, n=3). The phosphorane gradually decomposed over a period of 48 h to afford 2-phenyl-1,3,2-dioxaphosphorinan oxide. As expected, the reaction with the corresponding five-membered cyclic reagent, 2-phenyl-1,3,2-dioxaphospholan (61, X=0, n=2) did not give a
Table 4

Phosphoranes from the reaction of 2-azido oximes and $P^{III}$ reagents.

<table>
<thead>
<tr>
<th>Phosphorane (65)</th>
<th>Yield (%)</th>
<th>$^{31}P$ (ppm)</th>
<th>m.p. ($^\circ$C)</th>
<th>Analysis</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) $Ar=Ph$, $R_3P=61a$</td>
<td>62</td>
<td>-37.0</td>
<td>133-135</td>
<td></td>
<td>60.6</td>
<td>5.4</td>
<td>8.8</td>
</tr>
<tr>
<td>b) $Ar=Ph$, $R_3P=61b$</td>
<td>69</td>
<td>-52.0</td>
<td>123-126</td>
<td></td>
<td>61.7</td>
<td>5.8</td>
<td>8.6</td>
</tr>
<tr>
<td>c) $Ar=Ph$, $R_3P=61c$</td>
<td>73</td>
<td>-33.0</td>
<td>107-112</td>
<td></td>
<td>69.4</td>
<td>6.8</td>
<td>9.0</td>
</tr>
<tr>
<td>d) $Ar=BrC_6H_4$, $R_3P=61a$</td>
<td>66</td>
<td>-36.9</td>
<td>153-160</td>
<td></td>
<td>48.7</td>
<td>4.0</td>
<td>7.0</td>
</tr>
<tr>
<td>e) $Ar=BrC_6H_4$, $R_3P=61b$</td>
<td>86</td>
<td>-51.9</td>
<td>104-106</td>
<td></td>
<td>50.2</td>
<td>4.55</td>
<td>6.5</td>
</tr>
<tr>
<td>f) $Ar=BrC_6H_4$, $R_3P=61c$</td>
<td>74</td>
<td>-33.0</td>
<td>90 (decomp)</td>
<td></td>
<td>55.25</td>
<td>5.1</td>
<td>6.9</td>
</tr>
<tr>
<td>g) $Ar=Ph$, $R_3P=64a$</td>
<td>15</td>
<td>-27.9</td>
<td>188 (decomp)</td>
<td></td>
<td>66.05</td>
<td>4.7</td>
<td>7.7</td>
</tr>
<tr>
<td>h) $Ar=Ph$, $R_3P=64b$</td>
<td>13</td>
<td>-33.3</td>
<td>174 (decomp)</td>
<td></td>
<td>54.4</td>
<td>3.7</td>
<td>6.1</td>
</tr>
<tr>
<td>i) $Ar=BrC_6H_4$, $R_3P=64a$</td>
<td>27</td>
<td>-33.6</td>
<td>185 (decomp)</td>
<td></td>
<td>54.4</td>
<td>3.7</td>
<td>6.1</td>
</tr>
<tr>
<td>j) $Ar=BrC_6H_4$, $R_3P=64b$</td>
<td>39</td>
<td>-33.1</td>
<td>175-177</td>
<td></td>
<td>57.9</td>
<td>5.0</td>
<td>5.5</td>
</tr>
</tbody>
</table>
detectable $P^V$ intermediate. Instead, the reaction resulted in the initial formation of a $P^V$ species with $^{31}P$ chemical shift at -28 p.p.m. which spontaneously decomposed to 2-phenyl-1, 3, 2-dioxaphospholan oxide. These observations concur with the results from the corresponding reactions with the azides ($6, R^1=Ph, R^2=H$ or $Ph$), i.e. small ring $P^{III}$ reagents containing $\alpha$-oxygens favour $P^V$ relative to $P^{IV}$ formation. Thus, the reaction of the azides ($6, R^1=Ph, R^2=H$ or $Ph$) with cyclic phosphonites ($61, X=0, n=2$ and 3) gave isolable amino-oxyphosphoranes (see Table 1), whereas that with 1-phenylphospholan led to the initial formation of $P^V$ species, which spontaneously decomposed. That the phosphoranes ($62$) derived from 2-azidocyclohexanone are unstable compared with those from ($6, R^1=Ph, R^2=H$ or $Ph$) can be attributed to the absence of any conjugation of the double bond with the aryl groups.

2. Reactions of 2-Azido Oximes with Tervalent Phosphorus Reagents.

(a) Formation of Pentaco-ordinate Phosphoranes.

(i) Preparation of spirophosphoranes from cyclic $P^{III}$ reagents.

In an extension to the foregoing reactions of 2-azido ketones, treatment of the corresponding 2-azido oximes ($63, Ar=Ph$ or $p$-BrC$_6$H$_4$) with cyclic phosphorus reagents ($61$ and $64$) in benzene or ether at room temperature, gave isolable quinquevalent phosphoranes which were assigned the structure ($65$) on the basis of spectroscopic data. The yields obtained, $^{31}P$ chemical shifts, melting points and elemental analysis are listed in Table 4.
The phosphoranes were colourless solids which were stable indefinitely in the absence of moisture. In the case of (66), the ease of hydrolysis was apparently related to ring size and the nature of the atom or groups (X=O or CH$_2$) directly bonded to phosphorus. Thus, in the course of handling the compounds, it was found that the order of stability towards hydrolysis was (66, X=O, n=2) > (66, X=O, n=3) > (66, X=CH$_2$, n=2); it is noteworthy that benzene solutions of the latter hydrolysed spontaneously on exposure to the atmosphere. In general, the phosphoranes derived from 2-azido oximes were more stable than their counterparts from 2-azido ketones and showed no tendency to ring-open to form betaines or iminophosphoranes. For example, 1-phenylphospholan reacted with the azido oxime (63, Ar=Ph or p-BrC$_6$H$_4$) to give an isolable P$^V$ product, whereas the corresponding reaction with 1,2-diphenyl-2-azidoethan-1-one gave a P$^V$ species (67, X=CH$_2$, n=2) which spontaneously decomposed to a pyrazine and 1-phenylphospholan oxide (see p. 187). From this evidence it would appear that the presence of an extra
Fig. 8 $^1$H N.m.r. spectrum of (65c). Inset: $^{31}$P decoupled CH$_2$NH.

Fig. 9 $^1$H N.m.r. spectrum of (65b).
heteroatom in the spiro system confers greater stability to the phosphoranes derived from the oximes.

The $^{31}$P n.m.r. spectra of the phosphoranes (65) showed the usual upfield absorptions relative to phosphoric acid for $P^V$ species. As in the case of the compounds obtained from the azido ketones, the phosphorus becomes deshielded by ca 15 p.p.m. as the ring size decreases from six to five atoms.

Figure 8 shows that the most distinctive feature of the $^1$H n.m.r. spectrum (CDCl$_3$) of the 1-phenylphospholan derivative (65c) is the doublet at 4.07 p.p.m. ($^{3}J_{HP} = 16$Hz) which was assigned to the methylene protons of the amino-oxy ring. Although no signal due to the amino proton is obvious, presumably because of line broadening, the i.r. spectra of all the phosphoranes (65) showed a distinct N-H stretch at ca 3,400 cm$^{-1}$. The complex multiplets, in Fig.8, at 61.20-2.00 and 7.20-7.90 p.p.m. were assigned to the phospholan and aryl protons, respectively.

The $^1$H n.m.r. spectra for the phosphoranes (65b) and (65a) in CDCl$_3$ are also recorded in Figures 9 and 10. The integration indicated that the broad multiplets at 3.3-4.2 p.p.m. (Fig. 10) and 2.9-4.4 p.p.m. (Fig. 9) are due to the protons of the OCH$_2$ groups of the dioxa ring together with the methylene and amino protons of the amino-oxy ring.

In the case of (65a), the spectrum in deuterodimethyl sulphoxide exhibited an NH resonance as a broad doublet at 5.14 p.p.m. ($^{2}J_{HP} = 18$Hz) as shown in Fig. 11. The multiplet at 1.5-2.0 p.p.m. in the spectrum of (65b) was assigned to the unique methylene protons at C-5 of the dioxaphosphorinan ring.
Fig. 10 $^1$H N.m.r. spectrum of (65a) in CDCl$_3$.

Fig. 11 $^1$H N.m.r. spectrum of (65a) in (CD$_3$)$_2$SO.
Inset: $^{31}$P decoupled NH.
Fig. 12 $^{13}$C N.m.r. spectrum of (65a). (*)CDCl$_3$
Fig. 12 illustrates the $^{13}$C n.m.r. spectrum for (65a). The doublet at 169.13 p.p.m. ($J_{CP} = 10$ Hz) and the singlet at 40.07 p.p.m. were assigned to the imino carbon and the methylene carbon derived from the azide, respectively. The singlet at 63.17 p.p.m. and the doublet at 58.56 p.p.m. ($J_{CP} = 28$ Hz) were assigned to the methylene carbons of the dioxaphospholan ring and showed that these carbons were non-equivalent.

Possible N-Oxide Structure?

As described earlier, the n.m.r. data of the products of the reaction of the azido oximes with tervalent phosphorus reagents are consistent with the structure (65). A possible mechanism for the formation of the latter is shown in Scheme 16 (path a). This involves addition of the O-H group to the P=N bond of an intermediate iminophosphorane. An alternative structure to (65), which is
consistent with the i.r. and n.m.r. spectroscopic data, can be formulated whereby attack of nitrogen instead of oxygen on the phosphonium centre (path b) leads to the N-oxide (68). It was not possible to distinguish unequivocally between these two structures due to difficulties in obtaining crystals suitable for X-ray diffraction studies. Nevertheless, other evidence provides strong support for (65) as the correct structure.

Thus, as mentioned earlier, there are ample precedents\textsuperscript{94-96,241} for the formation of pentaco-ordinate amino-oxyphosphoranes by intramolecular addition of an O-H group to a P=N bond. More recently, Nay\textsuperscript{299} in this laboratory has shown that an isolable pentaco-ordinate phosphorane (69) is formed by the reaction of benzohydroxamic acid with 2-phenyl-1, 3, 2-dioxaphospholan. In addition, other workers\textsuperscript{228,238} have reported that

![Scheme 17](image)

Strong evidence against the structure (68) has come from mass spectroscopy which showed no appreciable loss of oxygen as might be expected for a compound containing an N-oxide group.\textsuperscript{300}
Perhaps, the most conclusive evidence against the N-oxide structure is the reluctance of the products to undergo deoxygenation by phosphites and phosphonites even under forcing conditions. For example, the product of 2-phenyl-1,3,2-dioxaphospholan and 1-phenyl-2-azidoethan-1-one oxime remained substantially unchanged after heating in neat dimethyl phenylphosphonite at 120°C. This behaviour contrasts with that of other N-oxide phosphoranes such as (70)\(^{207,300}\) which can be readily deoxygenated with trimethyl and triethyl phosphite and dimethyl phenylphosphonate.\(^{300}\)

![Chemical Structure](image)

Further evidence against the N-oxide structure is provided by u.v. spectroscopy. The spectra of the N-oxides (70) exhibit a characteristic absorption at ca 275 nm. which is absent from those of the products obtained from the azido oximes.

Finally, it is worth noting that whilst the evidence indicates that the major product from the reaction of the 2-azido oximes with P\(^{\text{III}}\) reagents is not (68), \(^{31}\)P n.m.r. studies show that the latter may be present as a minor product in the reaction mixture. Thus, in the reaction of 1-phenyl-2-azidoethan-1-one with 2-phenyl-1,3,2-dioxaphospholan the spectra showed the presence of two P\(^{\text{V}}\) signals in the ratio 1:10. The major absorption at -39 p.p.m. corresponded to the isolated phosphorane (65a, Table 4) which precipitated out of solution. The other P\(^{\text{V}}\) species, which absorbed at -25 p.p.m., remained in solution, but decomposed gradually to a mixture of a P\(^{\text{IV}}\) species with a broad signal at +23 p.p.m. and 2-
phenyl-1, 3, 2-dioxaphospholan oxide ($^{31}\text{P} S = 34$). Likewise, in the corresponding reaction with 2-phenyl-1, 3, 2-dioxaphosphorinan, there was a major signal at -53 p.p.m. due to the isolated phosphorane (65b, Table 4) as well as a minor absorption at -42 p.p.m. A possible explanation for the formation of two phosphoranes is that the reaction leads initially to a $^\text{IV}$ intermediate which can exist in two forms, e.g. (71a) and (71b). The syn isomer (71a) in which the hydroxyl group points towards the $\text{P}=\text{N}$ bond leads to the isolated product (65), whereas the anti isomer (71b) in which the hydroxyl group points away from the $\text{P}=\text{N}$ bond gives rise to the $\text{N}$-oxide (68), which is apparently unstable.
(iii) Stereochemistry of the spirophosphoranes

The combined effects of the small ring, the relative apicophilicities of the ligands and the lone pair factor are consistent with the structures (72) and (73) as the lowest energy t. b. p. conformers for the phosphoranes derived from five-membered cyclic reagents (Table 4).

In the case of (72b), it seems likely that ring strain considerations override the equatorial tendencies of carbon, thus allowing the phospholan ring to occupy the strain-free a,e position as indicated. In addition, structures such as (72b) permit the amino-oxy ring to adopt the more favourable a,e boat conformation in which the lone pair on nitrogen occupies an equatorial position. In the same way, apicophilicity demands and the lone pair effect dictate that structure (74) is the most stable t. b. p. conformer for those phosphoranes derived from 2-phenyl-1,3,2-dioxaphosphorinan.
As in the case of the spirophosphoranes prepared from the azido ketones (see p. 200), some consideration must be given to possible s.p. conformations. Of these, ring strain considerations \(^{154,304}\) and element effects \(^{19,156,304}\) point to (75) as the most favourable, but on the basis of \(^{13}C\) n.m.r. data the latter appear less likely than the most favourable t.b.p.'s (72), (73) and (74). Thus, reference to Fig. 12 shows that for (65a), C-4' and C-5' have markedly different chemical shifts and phosphorus-carbon splitting constants. This non-equivalence is more consistent with the different a, e positions in the rigid t.b.p. (72a) than the dibasal arrangement in the s.p. (75a), even allowing for any effect of the different ligands cis to the OCH\(_2\) group. An attempt was made to determine if any ligand reorganisation occurred at higher temperatures using \(^{13}C\) n.m.r. spectroscopy. However the phosphorane (65a) was insufficiently soluble in solvents
### Table 5

Predicted Relative Energies of Isomers of Dioxaphospholans (kcal/mol⁻¹)

<table>
<thead>
<tr>
<th>(72a)</th>
<th>(75a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) element effects</td>
<td>(a) element effects</td>
</tr>
<tr>
<td>2 x apical O</td>
<td>2.6</td>
</tr>
<tr>
<td>1 x equatorial O</td>
<td>2.8</td>
</tr>
<tr>
<td>1 x equatorial N</td>
<td>2.2</td>
</tr>
<tr>
<td>1 x equatorial Ph</td>
<td>1.7</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>9.3</td>
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<table>
<thead>
<tr>
<th>(b) ring strain</th>
<th>(b) ring strain</th>
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<tr>
<td>dioxa ring</td>
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</tr>
<tr>
<td>(\varepsilon)</td>
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</tr>
<tr>
<td>ring strain</td>
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</tr>
<tr>
<td>Total</td>
<td>11.3</td>
</tr>
<tr>
<td>(\Delta)</td>
<td>7.0</td>
</tr>
<tr>
<td>Total</td>
<td>14.2</td>
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</tbody>
</table>

### Table 6

Predicted Relative Isomer Energies of Phosvholans (kcal/mol⁻¹)

<table>
<thead>
<tr>
<th>(72b)</th>
<th>(75b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) element effects (\varepsilon)</td>
<td>(a) element effects (\varepsilon)</td>
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<tr>
<td>1 apical O</td>
<td>1.3</td>
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<tr>
<td>1 apical C</td>
<td>7.0</td>
</tr>
<tr>
<td>1 equatorial N</td>
<td>2.2</td>
</tr>
<tr>
<td>1 equatorial C</td>
<td>0.0</td>
</tr>
<tr>
<td>1 equatorial Ph</td>
<td>1.7</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>12.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b) ring strain</th>
<th>(b) ring strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 membered ring</td>
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<tr>
<td>(\varepsilon)</td>
<td>12.2</td>
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<tr>
<td>Total</td>
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<tr>
<td>(\Delta)</td>
<td>7.0</td>
</tr>
<tr>
<td>Total</td>
<td>21.6</td>
</tr>
</tbody>
</table>
suitable for high temperature studies. Moreover, the compound appeared to decompose on heating.

Application of Holmes model also predicts that spirophosphoranes of the type (65a-j, Table 4) are more likely to exist as a t.b.p. structure in the ground state. As shown in Table 5, comparison of the relative energies of the most stable t.b.p. and s.p. forms of the dioxaphospholan derivative (65a) gives a difference of 8.1 kcal mol⁻¹ in favour of the former. Likewise, similar calculations for the corresponding six-membered dioxa derivative (65b) indicate the t.b.p. form (74) to be favoured over the s.p. form (75b) by 9.1 kcal mol⁻¹. Table 6 shows that, as expected replacement of oxygens in the dioxaphospholan derivative (65a) by carbon leads to the even greater stabilisation (12.4 kcal mol⁻¹) of the t.b.p. form (72b) relative to the s.p. form (75c).

Finally, it is worth noting that the relative energy difference between the t.b.p. and s.p. forms of the amino-oxyphosphoranes (65a and b) derived from azido oximes is larger than that for the corresponding derivatives (20, n=2 and 3) from azido ketones (see p. 202). This implies that the former are less distorted towards the s.p. form in accord with their greater ring size. 154, 304
(b) **Preparation of Iminophosphoranes**

The 2-azido oximes (63) reacted with phosphines in benzene at room temperature to afford isolable iminophosphoranes (76) which were identified by their downfield $^{31}\text{P}$ chemical shifts relative to phosphoric acid. Details are given in Table 7 together with yields, melting points and elemental analyses.

Table 7

<table>
<thead>
<tr>
<th>Iminophosphorane (76)</th>
<th>Yield (%)</th>
<th>$^{31}\text{P}$ (°C)</th>
<th>m.p. (°C)</th>
<th>Analysis</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Ar=Ph, R$_3$P=(i)</td>
<td>74</td>
<td>+17.6</td>
<td>146-148</td>
<td>76.1</td>
<td>5.7</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) Ar=p-BrC$_6$H$_4$, R$_3$P=(i)</td>
<td>94</td>
<td>+18.3</td>
<td>137</td>
<td>64.0</td>
<td>4.6</td>
<td>5.7</td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>c) Ar=Ph, R$_3$P=(ii)</td>
<td>30</td>
<td>+31.5</td>
<td>90</td>
<td>68.6</td>
<td>7.2</td>
<td>8.9</td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d) Ar=Ph, R$_3$P=(iii)</td>
<td>78</td>
<td>+19.3</td>
<td>155</td>
<td>70.1</td>
<td>7.1</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e) Ar=p-BrC$_6$H$_4$, R$_3$P=(iii)</td>
<td>94</td>
<td>+19.1</td>
<td>127-130</td>
<td>56.5</td>
<td>5.5</td>
<td>6.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

The iminophosphoranes obtained were colourless solids which were exceptionally stable apart from the one derived from diethylphenylphosphine. The latter decomposed slowly in the solid state, but rapidly in chloroform solution to give a plethora of unidentified phosphorus-containing products.
Fig. 13 $^1$H N.m.r. spectrum of (76b). Inset: $^{31}$P decoupled CH$_2$.
The $^1$H n.m.r. spectra of all the iminophosphoranes exhibited a characteristic two proton doublet in the region 4.2-4.5 p.p.m. ($J_{HP} = 14-18\text{Hz}$) which was assigned to the methylene protons of the nitrogen side chain. A typical spectrum is reproduced in Fig. 13. In this instance the twenty proton multiplet at 7.20-7.80 p.p.m. was attributed to the aromatic and OH protons on shaking with $D_2O$ the integration indicated the loss of one proton.

The i.r. spectra (nujol mulls) of all the phosphoranes showed a very broad absorption centred at ca 2500 cm$^{-1}$ which was indicative of strong hydrogen bonding. Solution spectra of the products could not be obtained owing to their low solubility.

A $^{31}$P n.m.r. study of the formation of the iminophosphoranes indicated the presence in the reaction mixture of a minor product which resonated at approximately 1-2 p.p.m. away from the signal due to the isolated iminophosphorane. This minor absorption could be due to another geometric isomer of the isolated iminophosphorane which differs in the orientation of the hydroxy group $^{318}$ e.g. (71a) and (71b). Attempts to isolate the minor

$\begin{array}{c}
\text{Ar} \\
\text{R}_3\text{P} \equiv \text{N} \\
\text{HO}
\end{array}$

(71a)

$\begin{array}{c}
\text{Ar} \\
\text{R}_3\text{P} \equiv \text{N} \\
\text{H} \equiv \text{O}
\end{array}$

(71b)

$\begin{array}{c}
\text{Ar} \\
\text{B}_2\text{P} \equiv \text{N} \\
\text{N} \equiv \text{OH}
\end{array}$
product from the mother liquor failed due to its apparent hydrolysis. In view of the i.r. data, it is possible that the isolated geometric isomer derives enhanced stability from intramolecular hydrogen bonding as in (77).

The formation of iminophosphoranes as described above contrasts strongly with the corresponding reactions with 1-phenylphospholan, 2-phenyl-1,3,2-dioxaphospholan and -1,3,2-dioxaphosphorinan. This difference can be attributed to a combination of electronic and small ring effects in the latter which promote formation. These aspects will be dealt with in greater detail in Section 4.

The isolation of stable iminophosphoranes from the reaction of 2-azido oximes (63) differs markedly from the case of the corresponding 2-azido ketones. For example, reaction of triphenylphosphine with 1-phenyl-2-azidoethan-1-one oxime in benzene at room temperature affords a stable iminophosphorane (76a). By contrast the corresponding reaction of 1-phenyl-2-azidoethan-1-one gave good yields of 2,5-diphenylpyrazine and triphenylphosphine oxide presumably via the intermolecular Wittig reaction of an intermediate iminophosphorane (see p. 214).

(c) Reactions proceeding with Decomposition of the Resultant Phosphorane.

The preparation of isolable pentaco-ordinate phosphoranes by the reaction of 2-azido oximes with 2-phenyl-1,3,2-dioxaphospholan and -dioxaphosphorinan could not be extended to acyclic phosphites, phosphonites or phosphinates. Instead, $^{31}$P n.m.r. spectroscopy showed that the reactions afforded several phosphorus-containing compounds,
some of which have not been identified. Initially, the major product from the reaction of 1-phenyl-2-azidoethan-1-one oxime (63, Ar=Ph) with methyl diphenylyphosphinite was a $P^V$ species as indicated by an upfield absorption at -51 p.p.m. However, on standing, the phosphorane decomposed to give methyl diphenylyphosphinate and several other phosphorus-containing products with characteristic $P^{IV}$ absorptions.

Spectra of the corresponding reaction with dimethyl phenylphosphonite initially showed a major signal at -52 p.p.m., indicative of the formation of a $P^V$ species, together with several absorptions centred at 40 and 22 p.p.m. After 24 h, the signal assigned to the $P^V$ species had disappeared. By contrast the corresponding reaction with triethyl phosphite failed to give a detectable $P^V$ species. In this instance, $^{31}\text{P n.m.r.}$ spectroscopy indicated the formation of several different products all of which absorbed in the $P^{IV}$ region.

The plethora of products obtained from the reaction of 2-azido oximes with these organophosphorus (III) reagents can be rationalised on the basis of the facile hydrolysis of the initially formed phosphoranes (78, $R_1^1=R_3^3=\text{Ph}$, $R_2^2=\text{Me}$; $R_1^1=\text{OMe}$, $R_2^2=\text{Me}$, $R_3^3=\text{Ph}$; and $R_1^1=R_3^3=\text{OEt}$,

R$^2$=Et) leading to several phosphoryl compounds e.g. (79)-(82).

Another possible explanation is that, for such alkoxy-containing $P^V$ species (78), the ring-opened isomers (83) and (85) which are formed
by fission of the P-O and N bonds respectively, can undergo intramolecular and/or intermolecular attack of the anion on the alkoxy groups. These Arbuzov-type reactions can lead to several phosphorus containing species such as (84) and (86). This rationalisation is supported by the observation that increasing the number of alkoxy groups in the starting P\textsuperscript{III} reagents leads to increasing instability of the resultant phosphorane (78).

3. **Reactions of 1-Phenyl-2-azidoethan-1-one O-Methyl Oxime with Tervalent Phosphorus Reagents.**

The O-methyl oxime (87) was reacted with organophosphorus(III) reagents to observe the effect on phosphorane formation of blocking intramolecular addition of the O-H group to the P=N bond. While this effectively prevents attack by oxygen, it allows attack by the oxime nitrogen which might lead to a diaza phosphorane such as (89).

![Chemical structure](image)

A $^31$P n.m.r. study of the reaction between the azide (87) and 2-phenyl-1,3,2-dioxaphospholan in dry benzene at room temperature, indicated a slow and complex reaction. Two P\textsuperscript{IV} absorptions were
observed at 25 and 12 p. p. m., which were attributed to a triazine and iminophosphorane. After 24 hours these signals had disappeared and were replaced by that of a $\text{P}^\text{V}$ species, whose major resonance was at $\text{-60.7 p. p. m.}$. Repetition of the reaction on a synthetic scale afforded a good yield of the $\text{P}^\text{V}$ product which crystallised from benzene/light petroleum as colourless crystals. The solid was very resistant to hydrolysis and also soluble in common organic solvents.

Although the elemental analysis was consistent with the diaza phosphorane (92), the i.r. spectrum, both in the solid state and in solution, showed no N-H stretch absorption as would be expected for such a structure. However, on the basis of spectroscopic data, the
Fig. 14 $^1$H N.m.r. spectrum of (93): a) non-decoupled and b) $^{31}$P decoupled spectrum.
product was identified as the 1,3,4,2-diazadiphosphetidene (93) which is formed by dimerisation of the iminophosphorane (91).

Convincing evidence for the dimeric structure was obtained from the $^1$H n.m.r. spectrum which is reproduced in Fig. 14. The most significant feature is a triplet at 4.38 p.p.m. due to the amino methylene protons which are split by phosphorus ($J_{HP}$=28Hz). The singlet at 3.92 p.p.m. was attributed to the methoxy protons which are not coupled to phosphorus. Another interesting feature is the broad multiplet at 2.8-4.0 p.p.m. due to the dioxa ring protons, indicating that these protons are non-equivalent (see p.192).

The noise-decoupled $^{13}$C n.m.r. spectrum is reproduced in Figure 15. The signals at 162, 61.6, 58.9 and 40.1 p.p.m. were assigned to the imino, methoxy, amino and dioxaphospholan carbons respectively. The off-resonance decoupled spectrum is reproduced in Figure 16 and confirms the assignment of the above signals. Thus the imino, methoxy, amino and dioxaphospholan carbons resonate as the expected singlet, quartet, triplet and triplet respectively.

Further evidence in support of structure (93) was obtained from the mass spectrum which showed a small molecular ion at m/e 660 with a larger peak at m/e 330 due to the monomer.

On the basis of apicophilicity demands and the small ring effect, the most likely arrangement of the ligands around phosphorus is that represented by the t.b.p. (94), in which all the rings span a, e
Fig. 15 $^{13}\text{C N.m.r.}$ spectrum of (93) (noise - decoupled).

Fig. 16 $^{13}\text{C N.m.r.}$ spectrum of (93) (off-resonance decoupled).
Crystals of the dimer (93) have been submitted for X-ray structural analysis. The X-ray structure of the diazadi-phosphetidine (95) has been reported and shows the expected t.b.p. with a trigonal planar nitrogen.

![Chemical structure](image)

It is of some interest that the $^{31}$P n.m.r. spectrum (CDCl$_3$) of the dimer exhibited three absorptions: a major one at -55.6 p.p.m. and two minor ones at -48.7 and -55.0 p.p.m. in the ratio of 10:1:1. This multiplicity of signals can be rationalised in terms of geometric isomers arising from different orientations of the oxime methoxy group (see p.228).

Another feasible explanation for these signals is that, at least in solution, the dimer exists as two stereoisomers represented by (94) and (96).
In marked contrast to the foregoing reaction, that with the corresponding six-membered cyclic reagent, 2-phenyl-1,3,2-dioxaphosphorinan afforded a $P^{IV}$ species (98) rather than a pentaco-ordinate species. Careful monitoring of the reaction by $^{31}$P and $^{31}$H n.m.r. spectroscopy showed the formation of an intermediate triazene (97), $^{31}$Pδ = 0.1 p.p.m., which gradually lost nitrogen over a period over twenty-four hours to give the iminophosphorane (98) ($^{31}$Pδ 11.4 p.p.m.). Subsequent attempts to isolate this product afforded a gum which hydrolysed rapidly to 2-phenyl-1,3,2-dioxaphosphorinan oxide, and the identity of the iminophosphorane was confirmed by n.m.r. spectroscopy. Thus, the $^{31}$P n.m.r. spectrum showed the characteristic downfield
Fig. 17 $^1$H N.m.r. spectrum of (98).
absorption relative to phosphoric acid whilst the $^1$H n.m.r. spectrum, which is reproduced in Fig. 17 exhibited an expected doublet at 4.81 ($J_{HP} = 28$Hz), due to the amino methylene protons. It is worth noting that a similar $J_{HP}$ value was observed for the dimer (93).

The azide reacted with other tervalent phosphorus reagents to form iminophosphoranes which showed no tendency to dimerise. Thus, addition of equimolar amounts of the azide to dry benzene or deuterochloroform solutions of 1-phenylphospholan, 1-phenylphosphorinan and triphenylphosphine, at room temperature, led to vigorous evolution of nitrogen with the formation of $P^{IV}$ species with $^31P$ at 34.7, 10.0 and 7.1 p.p.m. respectively. This contrasts with the isolation of the $P^V$ species (93) from the reaction of 2-phenyl-1,3,2-dioxaphospholan. This difference can be rationalised on the basis of small ring and electronic factors which favour $P^V$ formation in the dioxaphospholan case. These aspects will be dealt with in the next section in greater detail.

Reactions of Bisfunctional Azides with Tervalent Phosphorus Reagents: Conclusions

The results from the foregoing investigations indicate that the reaction of bisfunctional azides such as 2-azido ketones or oximes with a tervalent phosphorus reagent can lead to the formation of a $P^{IV}$ species, i.e. an iminophosphorane (99), a pentaco-ordinate phosphorane (100) and/or an iminophosphorane dimer (101). Table 8 lists the phosphorus
TABLE 8

Phosphorus Species observed in the Reactions of Bisfunctional Azides with Tervalent Phosphorus Reagents.

<table>
<thead>
<tr>
<th>$R_3P$</th>
<th>Azide</th>
<th>PhCCHPhN$_3$</th>
<th>PhCCH$_2$N$_3$</th>
<th>PhCCH$_2$N$_3$</th>
<th>PhCCH$_2$N$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="PhP" /></td>
<td>$P^V$</td>
<td>$P^V$</td>
<td>$P^V$</td>
<td>$P^V$</td>
<td>Dimer</td>
</tr>
<tr>
<td><img src="image" alt="PhP" /></td>
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<td>$P^V$</td>
<td>$P^{IV}$</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="PhP" /></td>
<td>$P^V \rightarrow P^{IV} \rightarrow P=O$</td>
<td>$P=O$</td>
<td>$P^V$</td>
<td>$P^{IV}$</td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="PhP" /></td>
<td>$P^{IV}$</td>
<td>$P=O$</td>
<td>$P^{IV}$</td>
<td>$P^{IV}$</td>
<td></td>
</tr>
<tr>
<td>PhPEt$_2$</td>
<td>$P^{IV}$ decomp prods</td>
<td>$P^{IV}$ decomp prods</td>
<td>$P^{IV}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ph$_3P$</td>
<td>$P^V &amp; P^{IV} \rightarrow P=O$</td>
<td>$P^{IV} \rightarrow P=O$</td>
<td>$P^{IV}$</td>
<td>$P^{IV}$</td>
<td></td>
</tr>
<tr>
<td>Ph$_2$POMe</td>
<td>$P^V$</td>
<td>$P^V$</td>
<td>$P^V$</td>
<td>→decomp. prod</td>
<td></td>
</tr>
<tr>
<td>PhP(OMe)$_2$</td>
<td>$P^V$</td>
<td>$P^V$</td>
<td>$P^V$</td>
<td>→decomp. prod</td>
<td></td>
</tr>
<tr>
<td>P(OEt)$_3$</td>
<td>$P^V$</td>
<td>$P^V$</td>
<td>$P^{IV}$</td>
<td>decomp. prod</td>
<td></td>
</tr>
<tr>
<td>Et$_2$NP</td>
<td>$P^V$</td>
<td>$P^V &amp; P^{IV}$</td>
<td>$P^{IV}$</td>
<td>decomp. prod</td>
<td>decomp. prod</td>
</tr>
</tbody>
</table>
species observed in the reactions of 1,2-diphenyl and 1-phenyl-2-azidoethan-1-one, and 1-phenyl-2-azidoethan-1-one oxime and its O-methyl derivative with a variety of $P^{\text{III}}$ reagents at room temperature in benzene. It should be noted that in some cases the $P^{\text{IV}}$ or $P^{\text{V}}$ species decomposes, sometimes rapidly, to form the oxide of the starting $P^{\text{III}}$ reagent.

The reactions of Table 8 are obviously related to the Staudinger reaction, the mechanism of which has been extensively investigated (see p. 11). It is generally accepted that the first step is nucleophilic attack by phosphorus at the terminal nitrogen of the azide to form a triazene (103) which, in a second step, decomposes via a four-centre cyclic species (104) to give an iminophosphorane (Scheme 19).
In the present investigation $^1$H and $^{31}$P n.m.r. evidence was obtained for initial triazene formation in the reaction of 1-phenyl-2-azidoethan-1-one O-methyl oxime with 2-phenyl-1,3,2-dioxaphosphorinan (see p.236). $^{31}$P N.m.r. spectroscopy also confirmed the presence of a triazene in the reaction of 2-azido cyclohexan-1-one with 2-phenyl-1,3,2-dioxaphosphorinan (see p.215) and of the azido ketones (10) and (102) with triethyl phosphite and dimethyl phenylphosphonite (see p.206,207) In all cases, subsequent evolution of nitrogen occurred to give an iminophosphorane and/or a $^V$ species as shown by n.m.r. spectroscopy.

The exact mode of formation of amino-oxyphosphoranes of general structure (105) from the reactions of 2-azido ketones with $^III$ reagents is not entirely clear. As discussed earlier (see p.210) this

$$\text{R}_1\text{C} - \text{CHR}_2 \quad \text{R}_3\text{P} \quad \text{O} \quad \text{N}_3$$

$$\text{R}_3\text{P} \quad \text{H}_1\text{P} \quad \text{O} \quad \text{R}_2 \quad \text{R}_1$$

(105)

type of reaction is believed to involve an iminophosphorane (106), which undergoes intramolecular addition of the O-H group to the P= N bond as shown in Scheme 20.

$$\text{N}_3 \quad \text{HO} \quad \text{R}_3\text{P} \quad \text{N} - \text{N} - \text{N} \quad \text{HO} \quad \text{R}_3\text{P} - \text{N} \quad \text{HO}$$

(106)
However, no evidence could be obtained to substantiate the intermediacy of an iminophosphorane (107) in the formation of amino-oxyphosphoranes from 2-azido ketones. For example, in the reaction

\[
\begin{align*}
\text{R}_3\text{P}^-\text{N}^-\text{CHR}^2\text{CR}^1 \quad &\leftrightarrow \quad \text{R}_3\text{P}^-\text{N}^-\text{CR}^2\text{CR}^1 \\
\text{(107a)} \quad &\rightarrow \quad \text{(107b)}
\end{align*}
\]

of 1,2-diphenyl-2-azidoethan-1-one with dimethyl phenylphosphonite, \(^{31}\text{P}\) n.m.r. spectroscopy showed the absence of any signals which could be assigned to an iminophosphorane. Instead, the disappearance of the triazene coincided with the simultaneous formation of the pentacoordinate phosphorane. It is possible, of course, that an iminophosphorane is involved but that it rearranges too quickly to be detected on the n.m.r. time scale. However there is some evidence which appears to contradict this interpretation. Thus, in the reaction of 1,2-diphenyl-2-azidoethan-1-one with triphenylphosphine, nitrogen was evolved and \(^{31}\text{P}\) n.m.r. spectroscopy indicated the formation of a \(\text{P}^\text{V}\) species which subsequently ring-opened to give a long-lived iminophosphorane (see p.212). In this instance an absorption attributed to an intermediate triazene was observed and, as in the previous cases, this appeared to lose nitrogen to give the \(\text{P}^\text{V}\) species directly. Similar studies of the reaction of the same azide with 1-phenylphospholan also indicated the formation of a \(\text{P}^\text{V}\) species followed by the rearrangement of the latter to an iminophosphorane which had not been previously detected in the reaction mixture (see p.186). In this instance, rapid evolution of nitrogen occurred leading to the instantaneous formation of the pentacoordinate phosphorane and the intermediate triazene was not detectable.
These results suggest that the triazene loses nitrogen to form the $P^V$ species directly. One possibility is that the triazene undergoes enolisation followed by loss of nitrogen (Scheme 21).

\[
R_3P-N\equiv N\equiv N-R^2H \rightleftharpoons R_3P-N\equiv N=O
\]

\[
N_2 + R_3P=O
\]

\[\text{Scheme 21}\]

In the related reaction of 2-azido oximes (108) with $P^{III}$ reagents to give amino-oxyphosphoranes (111), $^{31}$P n.m.r. spectroscopy showed the instantaneous formation of the $P^V$ species. No absorptions due to an intermediate triazene (109) or iminophosphorane (110) could be detected. Recently, Baccolini et al. $^{309}$ have reported similar observations concerning the formation of the $P^V$ systems (115) from the reaction of 2-azido phenols with the diazaphospholes (112). These authors assumed the reaction proceeded via the intermediacy of an iminophosphorane (114), but suggested that the exceptional stability of the
Scheme 22

\[
\begin{align*}
R_3P + R^1C=CHR^2 & \rightarrow R_3P=N=N=N
\end{align*}
\]

\[
\begin{align*}
\text{HON} & \text{N}^3 \\
(108) & \\
\text{HON} & \text{R}^1 \\
(109) & \\
\text{HON} & \text{R}^2 \\
(110) & \\
\text{HON} & \text{R}^1 \\
(111) & \\
\text{HON} & \text{R}^1 \\
(112) & \\
\text{HON} & \text{R}^2 \\
(113) & \\
\text{HON} & \text{R}^1 \\
(114) & \\
\text{HON} & \text{R}^1 \\
(115) & \\
\end{align*}
\]
spirophosphorane (114) led to its instantaneous cyclisation. In view of the stability of the amino-oxyphosphoranes (111) derived from 2-azido oximes (see p.217), it is possible that their formation may also proceed by the rapid collapse of an iminophosphorane (110) as shown in Scheme 22.

Reference to Table 8 also shows that the only iminophosphorane dimer (101) obtained was that from the reaction of 2-phenyl-1,3,2-dioxaphospholan with 1-phenyl-2-azidoethan-1-one O-methyl oxime (87) in which attack by oxygen is blocked. This suggests that, in their reaction with P_{III} reagents, bifunctional azides prefer to form P_{V} species by intramolecular rather than intermolecular cyclisation. The factors which promote the formation of the iminophosphorane dimer (101) will be discussed later (p.252)

**Factors influencing P_{V} vs. iminophosphorane formation**

Scheme 23 summarizes the observed pathways for the reaction of tervalent phosphorus reagent with bifunctional azides. In order to explain the nature of the phosphorus species formed, a number of factors have to be considered.
From the results in Table 8, it appears that the presence of electron-withdrawing groups in the tervalent phosphorus reagent favours P\textsuperscript{V} formation. For example, a comparison of the reaction of 1-phenyl-2-azidoethan-1-one oxime (116) with six membered cyclic phosphorus reagents (117) shows that 2-phenyl-1,3,2-dioxaphosphorinan (117, X=O) affords an amino-oxyphosphorane whereas 1-phenylphosphorinan (117, X=CH\textsubscript{2}) gives an iminophosphorane, i.e., a P\textsuperscript{IV} species.
A similar effect is also observed in the acyclic series; \( \text{PhPEt}_2 \), \( \text{Ph}_3\text{P} \), \( \text{Ph}_2\text{POMe} \), \( \text{PhP(OMe)}_2 \), \( \text{P(OEt)}_3 \). Thus, with 1,2-diphenyl-2-azidoethan-1-one, diethyl phenylphosphine gave a mixture of \( P^{IV} \) species, triphenylphosphine gave a \( P^V \) species, which subsequently ring opened to an iminophosphorane, and the phosphinite, phosphonite and phosphite formed pentaco-ordinate phosphoranes. The same trend also occurred with 1-phenyl-2-azidoethan-1-one oxime, but the reactions with alkoxy-containing phosphorus reagents were complicated by the decomposition of the resultant phosphorane.

A possible rationale for these results is that the presence of electron-withdrawing groups at phosphorus increases its electropositivity and thus makes it more susceptible to nucleophilic attack by oxygen. Irrespective of the mode of formation of the \( P^V \) species (see Scheme 23), this will favour ring closure. Similar arguments show that any tendency of the \( P^V \) species to ring-open to the iminophosphorane will be reduced by the presence of electron-withdrawing groups.

(b) Small ring effect

Reference to Table 8 shows that incorporation of phosphorus into a small ring favours the formation of a \( P^V \) species. This appears to be the major factor influencing \( P^V \) formation and can override unfavourable electronic effects at phosphorus. This is clearly demonstrated by a comparison of the reaction of 1-phenyl-2-azidoethan-1-one oxime with the following \( P^{III} \) reagents:

\[
\begin{array}{c}
\text{PhP} \\
\text{PhP} \\
\text{PhPEt}_2
\end{array}
\]
Thus, a pentaco-ordinate phosphorane was obtained from the five-membered ring reagent, whereas its acyclic analogue and the six-membered ring reagent gave rise to iminophosphoranes. Since the electronic situation at phosphorus is virtually the same in all cases, it seems reasonable to conclude that the formation of a $P^V$ species in the case of 1-phenylphospholan is due to the presence of a small ring. This effect is also manifested in the reactions of 1,2-diphenyl-2-azidoethan-1-one and can be attributed to several factors, which are outlined below.

Firstly, the presence of a small ring partly reduces the molecular crowding which is inherent in the $P^V$ state as shown by X-ray data (see p.76). This is in keeping with the observed stability of pentaco-ordinate phosphoranes which lie in the order: spirocyclic > monocyclic > acyclic.  

Secondly, consideration of ring-strain arguments suggests that the iminophosphorane (118a) should be less favoured than its $P^V$ isomer (118b) in which the ring can span the strain-free a, e position. This is in accord

\[
\begin{align*}
(118a) & \quad X = O \text{ or } CH_2 \\
(118b) & \quad \text{Ph}
\end{align*}
\]

with several observations which show that inclusion of phosphorus into a small ring leads to an acceleration in the rate of nucleophilic attack at tetrahedral phosphorus relative to acyclic analogues. For example, in the classic study of this phenomenon, Westheimer and co-workers observed that certain cyclic phosphorus esters underwent acid hydrolysis $10^8$ times faster than their acyclic analogues. These results were attributed mainly to a relief of ring strain on going to a t. b. p. intermediate.
Support for the view that "small ring" iminophosphoranes such as (118a) are strained has come from X-ray data of N-(4-methoxy-2-nitrophenyl)-imino-1,2,5-triphenylphosphole (119). The observed bond angle $C_4P_1C_1$ of the phosphole ring is $94^\circ$ which is much closer to the $90^\circ$ a.e angle of a t.b.p. than the tetrahedral value of $109^\circ$. The exocyclic bond angle $N_1P_1C_{17}$ is fairly close to $109.5^\circ$ and shows that phosphorus is tetrahedrally co-ordinated. There must, therefore be a considerable amount of angle strain present in the phosphole ring.

Turnbolm and Katz have also shown that ring strain has a profound effect on ylide stability and that when the strain becomes very great as in the homocubyl system (120), a stable pentaco-ordinate phosphorane (121) is formed in preference to the ylide (122).

In some cases, a third factor contributing to the small ring effect is the possibility of pseudorotation in the $P^V$ species. Hudson and Brown have suggested that at least part of the acceleration observed for nucleophilic attack at phosphorus in cyclic phosphoryl compounds is due to an increase in entropy in the transition state associated with a "loosening of the pseudorotational motion" of the ring on passing from the four to the five co-ordinate state.
(c) The phospholan effect

The tendency of 1-phenylphospholane to form a pentaco-ordinate phosphorane rather than an iminophosphorane in reactions with bisfunctional azides can also be attributed to the so-called 'phospholan effect,' first reported by Aksnes and co-workers to account for the much faster hydrolysis of methyl-1-phenylphospholanium iodide (5) than the corresponding six-membered ring compound and its open-chain analogues. Molecular models showed that rotation of the phenyl and methyl groups in the five membered ring compound was severely restricted due to eclipsing
with the ring $\alpha$-hydrogen atoms, whereas in the phosphorinan compounds with a chair configuration, the eclipsing was much less critical. The models also showed no eclipsing in the t. b. p. $P^V$ intermediates postulated for the reaction. Consequently, relief of strain was greater for the phospholan than the phosphorinan compounds and the former hydrolysed at a much faster rate. The same phenomenon was also found to occur in the decomposition of $N$-benzoyliminophosphoranes to benzonitriles.\(^{301f}\)

In view of these results the 'phospholan effect' cannot be ignored when considering the nature of the products formed in the reactions of bisfunctional azides with dialkylphenylphosphines. Indeed, reference to molecular models shows a greater degree of eclipsing between the ring protons and the phenyl group in (123, $n=2$) than in (123, $n=3$).

\[
\begin{align*}
\text{(CH}_2\text{)}_n & \quad P & \quad N & \quad \text{CH}_2 & \quad \text{CAR} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{Ph} & \quad X \\
\text{(123, } X = O \text{ or NOH)}
\end{align*}
\]

(d) Other factors

Although the above effects account for the nature of the phosphorus species obtained, there are some other factors which could influence $P^V$ formation e. g. the type of OH group involved in the intramolecular cyclisation, the size of the new ring formed, the apicophilicities of the ligands at phosphorus and steric effects at phosphorus i. e. the ease of approach of oxygen. Reference to Table 8 shows that, for these reactions, it is not possible to determine the exact influence of some of these factors since they were not studied in isolation. Nonetheless, whilst these may
be contributing factors they are certainly not as important as the small ring effect. Thus, the observation that both 2-azido oximes and 2-azido ketones can give rise to \( P^V \) species with the same \( P^{\text{III}} \) reagents indicates that the nature of the OH group is not critical. This observation also suggests that the size (five or six) of the new ring does not influence \( P^V \) formation since the azido oximes lead to six-membered ring amino-oxyphosphoranes (65) whereas the azido ketones give rise to five-membered cyclic species (105). This contrasts with the marked effect of the presence of a small ring in the starting \( P^{\text{III}} \) reagent. However, the systems (105) and (65) are not homologues and it is possible that the latter gains additional stability from the presence of the extra heteroatom in the ring. The formation of pentaco-ordinate phosphoranes of type (65c)

suggests apicophilicity is not a deciding factor since carbon occupies an unfavourable apical position. Support for this view is provided by the observation that all the phosphoranes (124; \( R^1 = R^2 = R^3 = \text{OEt}, \ R^1 = R^2 = \text{OMe}, \ R^3 = \text{Ph}, \ R^1 = \text{OMe}, \ R^2 = R^3 = \text{Ph} \) can exist. If apicophilicity is the deciding factor, \( P^V \) formation will be observed only in those instances when the positions of the ligands are in accord with their apicophilicities. The
formation of all these phosphoranes also suggests that steric effects at phosphorus are not important for this system.

In summary, the predominant formation of pentaco-ordinate phosphoranes from the reaction of bifunctional azides with small ring tervalent phosphorus reagents can be rationalised on the basis of ring strain, steric, and/or entropy considerations. Such arguments show that where possible, the product from these cyclic reagents will exist preferentially in the $P^V$ rather than the $P^{IV}$ state. For six-membered ring and acyclic phosphorus reagents, the major factor in determining the mode of reaction appears to be the electronic situation at phosphorus. From Table 8 it is clear that replacement of carbon by oxygen in the cyclic phosphorus reagent favours $P^V$ formation. These results are consistent with observations concerning the $P^V$ Ramirez adducts (125a, $Y=OR$, $NR_2$, $CR_3$) which can exist in equilibrium with the betaine (125b).

The derivatives of small ring tervalent phosphorus reagents existed as the $P^V$ species (125a). Increasing the electronegativity of the ligands at phosphorus also led to increasing tendencies to form (125a) (page 78).
Factors influencing dimerisation of the iminophosphorane

The results outlined in Table 8 suggest that intramolecular cyclisation is the preferred mode of \( P^V \) formation for the reaction of tervalent phosphorus reagents with bisfunctional azides which contain an actual or potential O-H group. In an attempt to block this mode of reaction, it was found that 2-phenyl-1,3,2-dioxaphospholan reacted with the O-methyl oxime (87) to give the \( P^V \) diazadiphosphetidine (93) apparently via the dimerisation of an iminophosphorane which could be detected by \( ^{31} \)P n.m.r. spectroscopy. The same azide also reacted with 2-phenyl-1,3,2-dioxaphosphorinan and 1-phenylphospholan to form iminophosphoranes which did not dimerise. The dimerisation of an iminophosphorane derived from 2-phenyl-1,3,2-dioxaphospholan had not been previously reported.

The dimerisation of iminophosphoranes is well established for derivatives in which the ylidic nitrogen is sufficiently basic and when there are strongly electron-withdrawing groups such as chlorine at phosphorus, e.g. (126, \( R=\text{Me} \)). The ease of dimerisation of (126) is attributed to the degree of stabilisation afforded the diazaphosphetidine by contribution to the structure of cannonical forms such as (127). The presence of bulky groups at nitrogen can prevent cyclisation but electronic considerations appear to be more important. Schmidpeter and Ebeling have isolated the diazaphosphetidine (128, \( X=\text{Cl, CH}_3 \) or \( N(\text{CH}_3)_2 \)) from the reaction of acetohydrazide with

\[
\begin{align*}
\text{Cl}_3\text{P} \equiv \text{NR} + & \quad \text{Cl}_3\text{P} \equiv \text{NR} \quad \text{Cl}_3\text{P} \equiv \text{NR} \\
\text{Cl}_3\text{P} \equiv \text{NR} \quad \text{R}_N - \text{PCl}_3 & \quad \text{R}_N - \text{PCl}_3 & \quad \text{R}_N - \text{PCl}_3 \\
\text{(128)} & \quad \text{(127)}
\end{align*}
\]
trichlorophosphoranes. In this instance the dimerisation appears to be

\[
\begin{align*}
X_2PCl_3 & \xrightarrow{-3HCl} \text{(128)} \\
+ & \\
2 \text{MeCNHNH}_2 & \xrightarrow{\text{O}_2 2\text{MeCNHNH}_2} \text{Me}^+ \text{OCl}^{-}
\end{align*}
\]

connected with phosphorus becoming the member of a small ring since cyclic phosphazenes with six or more atoms in the ring showed no tendency to dimerise.  

It has also been observed that inclusion of the P=N function in a small ring favours dimerisation of the iminophosphorane. For example, the 1, 3, 2\textsuperscript{5}-benzoxazaphosphole derivative (129, R=Et) exists as the dimer.

Recently it has been reported that the reaction of aryl azides with cyclic tervalent phosphorus reagents can lead to the formation of iminophosphorane dimers (132). Thus reaction of (130, R=F, OMe, OEt, OBu, OPh, SEt) gave (132) where (130, R=NEt\textsubscript{2}, NMe\textsubscript{2}, NBu\textsubscript{2}) afforded only monomeric iminophosphoranes.
In the present work it appears that the electronic situation at nitrogen is not the determining factor in the formation of the dimer \((93)\) from the reaction of 2-phenyl-1,3,2-dioxaphospholan with the O-methyl azido oxime \((87)\). In addition, the electronic influence of the substituents at phosphorus cannot be of overriding importance since the dioxophosphorinan derivative \((133, X=O, n=3)\) failed to dimerise. Similar observations can
also be made concerning the small ring effect since the phospholan derivative (131, $X=\text{CH}_2$, $n=2$) did not dimerise despite the presence of a five membered ring.

This suggests that the unique dimerisation of (133, $X=\text{O}$, $n=2$) is due to a combination of several factors. Firstly iminophosphoranes of the type (133) are expected to be quite basic since there is no possibility of reducing the negative charge on nitrogen by the inductive or resonance effects of the imino side chain. Secondly, the presence of two electronegative ligands at phosphorus results in an increased susceptibility of the phosphonium centre to nucleophilic attack. Moreover, from the foregoing discussion this also favours diazaphosphetidine formation. Thirdly, the presence of the five-membered ring favours the system changing from the $P^{\text{IV}}$ to the $P^{\text{V}}$ state due to the small ring effect which can be attributed to a combination of ring strain, crowding and/or entropy factors. Thus the formation of the diazaphosphetidine (93) is entirely consistent with the previous discussions on factors favouring $P^{\text{V}}$ vs $P^{\text{IV}}$ formation.
(a) **Thermal Decomposition**

When heated in boiling cumene, the phosphorane \((134, \text{R}=\text{H})\) decomposed to give 2,5-diphenylpyrazine \((139, \text{R}=\text{H})\) in high yield and 2-phenyl-1,3,2-dioxaphospholan oxide in almost quantitative yield (Scheme 25).

\[
\begin{align*}
\text{Path a:} & \quad \text{R} \quad \text{Ph} \\
\Rightarrow & \quad \text{R} \quad \text{Ph} \\
\text{Path b:} & \quad \text{R} \quad \text{Ph} \\
\end{align*}
\]
In the case of the phosphorane (134, R=Ph), thermolysis in benzene under reflux for three days resulted in quantitative formation of 2-phenyl-1,3,2-dioxaphospholan oxide together with low yields of 2,3,5,6-tetraphenylpyrazine (139, R=Ph). In addition the thermolysis afforded a colourless solid in 42% yield which appeared to decompose slowly to the pyrazine (139, R=Ph). The solid was tentatively identified as 2,5-dihydro-2,3,5,6-tetraphenylpyrazine (138, R=Ph) on the basis of its $^1$H n.m.r. spectrum which exhibited a multiplet at $8.0-7.0$ p.p.m. and a singlet at 5.05 assigned to the aromatic and C-2,5 protons, respectively.

A plausible mechanism for the formation of (139) is that the reaction proceeds via initial ring-opening of the phosphorane to give a betaine (136) which rearranges to an iminophosphorane (137). The latter then undergoes an intermolecular Wittig-type reaction to form the dihydro pyrazine (139) which is oxidised. Earlier work in this thesis has shown that pentaco-ordinate phosphoranes similar to (134) can ring-open to give an iminophosphorane which subsequently forms pyrazines (see p. 212). As noted earlier Zbiral and Stroh have reported that the reaction of 2-azido ketones with triphenylphosphine, in benzene under reflux, afforded pyrazines. These workers assumed the reaction involved the intermediciy of an iminophosphorane but did not report the presence of a pentaco-ordinate phosphorane.

It is noteworthy that the thermolysis did not afford an aziridine either by direct fragmentation of the phosphorane (path a) or by an intramolecular Wittig reaction of the intermediate iminophosphorane (path b). In this
connection it is relevant that thermolysis of the iminophosphorane (52)

\[
P = N - C\text{Ph} - C\text{Ph}
\]

in chlorobenzene at \(130^\circ\text{C}\) gave 2, 3, 5, 6-tetraphenylpyrazine (17) in 32\% yield together with 1-phenylphosphorinan oxide in quantitative yield. There was no evidence of the formation of the azirine (140). This suggests that the intermediate required for azirine formation from iminophosphoranes are too highly strained and that the ylides prefer to form pyrazines by a low energy intermolecular Wittig pathway.

A similar situation occurs in the decomposition of the related methylene phosphoranes (142). Griffin and Witshand have reported that treatment of the phosphonium salt (141, \(n=1\)) with phenyllithium gave the product of the intermolecular Wittig reaction viz the 1,4-diphenylcyclohexane rather than 1-phenylcyclopropene. However, in the case of the higher homologue (141, \(n=3\)), the product of the intramolecular Wittig reaction was obtained by Bieber and Eisman.

The Staudinger reaction has been used to prepare the less strained aziridines. For example, Ittah and co-workers have obtained 2,3-diphenylaziridine (143) by the reaction of 2-azido alcohols with triphenyl-
and tri-n-butyl-phosphine. The stereospecificity of the preparation and the isolation of a phosphonium hydroxide (144) in one instance indicated that the reaction proceeded by the formation of an iminophos-

![Scheme 26](image)

phorane which subsequently underwent intramolecular displacement (Scheme 26).
The thermal decomposition of the amino-oxyphosphoranes (65) derived from 2-azido oximes was also studied. In a typical case

\[
\begin{align*}
\text{heat} & \quad \rightarrow \\
\text{PhC≡N}
\end{align*}
\]

pyrolysis of (65a) at 150°C/0.1 mmHg in a melt gave as the major product benzonitrile in 55% yield. The phosphorus moiety was obtained as a mixture of at least five inseparable products with \(^{31}\)P chemical shifts at 56, 39.3, 39.8, 32.6, and 33.0 p.p.m. In the same way decomposition of the phosphoranes (65i) and (65j) t-butylbenzene under reflux gave

\[
\begin{align*}
\text{heat} & \quad \rightarrow \\
\text{ArC≡N}
\end{align*}
\]

4-bromobenzonitrile in 20 and 39% yields, respectively. Decomposition of (65j) under flash vacuum conditions, oven temperature 600°C led to the isolation of 4-bromobenzonitrile in 75% yield.

By analogy with the preceding decomposition of the phosphoranes (20a or c) it is feasible that the break-down of (65) involves ring-opening
to give an ylide (145) which fragments in the manner shown in Scheme 27.

\[
\begin{align*}
\text{other products} & \quad \xrightarrow{\text{R}_3\text{P} - \text{N} = \text{CH}_2} \quad \text{ArC} = \text{N} \\
\text{Scheme 27}
\end{align*}
\]

This pathway is related to the known conversion of certain amino oximes, e.g. α-dialkylamino oximes (146) into nitriles in the presence of proton and Lewis acids (Scheme 28).

\[
\begin{align*}
\text{RC} - \text{CH}_2 - \text{NR}_2 & \quad \xrightarrow{\text{N-OH}} \quad \text{RC} = \text{N} + \text{CH}_2 = \text{NR}_2 \\
\text{Scheme 28}
\end{align*}
\]

Another possible mechanism for the nitrile formation is a reteere-[2+2+2]cycloaddition reaction as shown in Scheme 29. Decomposition in

\[
\begin{align*}
\text{Scheme 29}
\end{align*}
\]

this way is in keeping with the six-membered ring structure (65) rather than the alternative N-oxide structure as discussed on p. 220.
(b) **Hydrolysis/alcoholysis**

Exposure of benzene solutions of the phosphoranes (20a or b) to the atmosphere resulted in the quantitative formation of the phosphoryl compounds (24, \( n=2 \) or 3) and moderate to low yields of 2, 3, 5, 6-tetraphenylpyrazine (17). Similar results were obtained by shaking benzene solutions of the phosphorane (65c) with water. These products can be explained by hydrolysis as shown in Scheme 30 to give the amino ketone (147) which then condenses to form the pyrazine apparently via the unstable dihydropyrazine (16).

In a similar manner, hydrolysis of the phosphorane (65c) gave quantitative yields of both the amino oxime (148) and 1-phenylphospholan oxide.
By comparison, the hydrolysis of the phosphoranes (20c) and (65a) was less straightforward, but treatment with ethanol or methanol at 60-70°C afforded the pyrazine (58a) and the amino-oxime (148) respectively in good yields.
In both cases, the phosphorus moiety was obtained as a colourless oil with $^{31}\text{P} \delta +18.9$ for that from ethanol and $^{31}\text{P} \delta +16.5$ for that from methanol. The oils were tentatively identified as the phosphonates (150, R=Me) and (150, R=Et) on the basis of their $^{31}\text{P}$ and $^1\text{H}$ n.m.r. spectroscopic data. The latter showed resonances characteristic of the phenyl, OR, and $(\text{CH}_2)_2\text{OH}$ protons.

Scheme 31 shows a plausible mechanism for the alcoholysis of (65). This involves attack by the alcohol to give a new $^\text{V}$ species which undergoes further ligand displacement to form the phosphoryl compound (150).

Scheme 31

A $^{31}\text{P}$ n.m.r. of the reaction in methanol showed the appearance of an intense but transient signal at -40 p.p.m. which was ascribed to (149).

A similar mechanism can be postulated for (20c).
Appendix I

Reactions of 2-Diazo Ketones with Tervalent Phosphorus

Reagents: Formation and Decomposition of Phosphinazines

Introduction

Diazo compounds react with tervalent phosphorus compounds to form phosphazines (151). \[ R_3P + RR'C\text{CN}_2 \rightarrow R_3P-N-N-\text{CR}^1R^2 \]

The reaction is fairly general; the phosphorus compound may be a phosphine or phosphite, and the diazo compound may be a diazoalkane, or a diazocyclopentadiene among others.

The chemical properties and n.m.r. data of phosphazines indicate that the major canonical form contribution to the structure of the molecule is (152). However, the presence of electron withdrawing groups on carbon e.g. \( R^1 = \text{COR}^3 \), results in delocalisation of charge from the \( \alpha \)-nitrogen.

Phosphazines are similar to iminophosphoranes in many respects. For example, they undergo protonation and alkylation on the \( \alpha \)-nitrogen. There are reports of phosphazines reacting with carbonyl compounds in a Wittig-type reaction to form azines as shown in Scheme 32. This reaction is particularly valuable for the synthesis of unsymmetrical azines.
It is known that 2-diazo ketones react with triphenylphosphine to give the expected phosphazine. For example, Staudinger and Lusher have reported in 1922 that treatment of azibenzil with triphenylphosphine affords the phosphinazine, \( \text{Ph}_3\text{P} = \text{N} - \text{N} = \text{C} \text{PhC(O)Ph} \), which on pyrolysis at 120\(^\circ\)C gave triphenylphosphine (30%), triphenylphosphine oxide (50%) and traces of benzonitrile.

It was decided to study the reactions of 2-diazo ketones (153) with cyclic phosphorus (111) reagents, in the hope that the presence of the small ring would favour intramolecular cyclisation and the formation of a strain-free P species (155) as shown in Scheme 33. Moreover, it was expected that there would be a strong driving force for such phosphorus...
to undergo a two-fold extrusion process involving loss of nitrogen and a phosphoryl compound, thus providing a potential synthesis of acetylenes. Trippett and others have already prepared stable acetylenes by the high temperature intramolecular Wittig reaction of β-ketoalkyldene-phosphoranes as shown in Scheme 34. An alternative synthesis of acetylenes

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{R}^1 \\
\text{O} & \quad \text{R}^2
\end{align*}
\rightarrow
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{R}^1 \\
\text{O} & \quad \text{R}^2
\end{align*}
\rightarrow
\begin{align*}
\text{Ph}_3\text{PO} + & \quad \text{R}^1\text{C}≡\text{CR}^2
\end{align*}

Scheme 34

from cyclic phosphazines would have the advantages of more readily available starting materials and lower decomposition temperatures thereby allowing the isolation of unstable acetylenes not available by Scheme 34. In this connection it is noteworthy that Cadogan et al. have shown that the 'strained' ylide (156), prepared from 1,2,5-triphenylphosphole and 1-diazoacenaphthen-2-one decomposes smoothly on thermolysis to give 7,10-diphenylfluoranthene (159). A possible explanation for the formation of (159) is that the reaction proceeds via the strain-free intermediate (157) to give 1,2-acenaphthyne which is trapped by 1,2,5-triphenylphosphole oxide (path b).
Preparation of Phosphinazines

In preliminary studies, $^{31}$P n.m.r. spectroscopy showed that the reaction of the 2-diazo ketone (153, $R^1 = R^2 = p$-t-Bu C$_6$H$_4$) with 2-phenyl-1,3,2-dioxaphospholan (154, $X = O$) proceeded extremely slowly. In benzene, the reaction was somewhat faster but gave rise to an unstable phosphazene ($^{31}$P = +50 p.p.m.). By comparison, reaction with 1-phenyl-phospholan (154, $X = CH_2$) occurred almost instantaneously and this reagent was chosen as the cyclic component for further studies.

On a preparative scale, treatment of the 2-diazo ketones (160) with
Table 9

\[
\begin{array}{ccc}
\text{Phosphinazine (161)} & \text{Yield (\%)} & \text{\[^{31}\text{P}\] m. p. (°C)} & \text{Analysis} \\
\hline
(a) Ar=Ph, R_3P=i & 50-80 & 55.4 & 103-107 (decomp) 74.3 5.9 7.4 \\
(b) Ar=Ph, R_3P=ii & 70-80 & 21.2 & 114-116 (decomp) 79.1 5.5 5.7 \\
(c) Ar=p-Bu^tC_6H_4, R_3P=i & 30-50 & 55.5 & 84-85 (decomp) 77.0 8.0 5.6 \\
(d) Ar=p-Bu^tC_6H_4, R_3P=iii & 54 & 44.8 & 104-106 (decomp) 75.9 10.0 5.2 \\
(e) Ar=p-Bu^tC_6H_4, R_3P=ii & 60 & 21.6 & 142-145 (decomp) 80.3 6.7 4.5 \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{PhP} & \text{Ph_3P} & \text{Bu_3P} \\
\text{(i)} & \text{(ii)} & \text{(iii)}
\end{array}
\]
phosphines in benzene at room temperature gave moderate-to-high yield of phosphinazines (161) whose yield, $^{31}$P chemical shifts, melting points and elemental analytical data are listed in Table 9. The phosphazines showed the expected positive phosphorus chemical shifts and were shielded by 5-8 p.p.m. relative to the corresponding phosphine oxides. The compounds were yellow solids, stable indefinitely in the absence of moisture. The cyclic phosphazines were far more susceptible to hydrolysis than their acyclic counterparts presumably because of the small ring effect (see p.183). Exposure of benzene solutions of the cyclic phosphinazines (161a or c) to air led to the quantitative formation of 1-phenylphospholan oxide and a hydrazone (163, Ar=Ph or p-Bu$_2$C$_6$H$_4$) presumably via the intermediate P$^+$ species (162).

\[
\begin{align*}
\text{ArC} & \equiv \text{C} \equiv \text{N} \equiv \text{N} \equiv \text{P} \\
\text{O} & \text{Ar} \\
(161a, c) & \xrightarrow{\text{H}_2\text{O}} \\
\text{Ph} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \\
\text{HO} & \\
\text{N} & \equiv \text{N} \equiv \text{C} \equiv \text{C} \equiv \text{Ar} \\
\text{H} & \\
\end{align*}
\]

\[
\begin{align*}
\text{ArC} & \equiv \text{C} \equiv \text{N} \equiv \text{NH}_2 \\
\text{O} & \text{Ar} \\
(163) & \\
\end{align*}
\]
Thermal Decomposition of Phosphinazines

The phosphinazines (161) were decomposed either neat or adsorbed onto sand at 125-135°C in vacuo using the Kugelrohr 'bulb-to-bulb' technique. The major identifiable products are recorded in Table 10. As indicated, the phosphorus moiety was usually recovered as a mixture of phosphine and phosphine oxide in a ca. 1:2 molar ratio. In all cases, no evidence could be obtained for the formation of an acetylene even from the small ring phosphinazines (161a) and (161c).

Table 10

<table>
<thead>
<tr>
<th>Phosphinazines (161)</th>
<th>Decompr. temp. °C</th>
<th>Products (%)</th>
<th>R₃P=O</th>
<th>R₃P</th>
<th>Ar₂CHC=N</th>
<th>ArC≡N</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) R₃P=(i), Ar=Ph</td>
<td>125-145</td>
<td>60-72</td>
<td>30-35</td>
<td>22</td>
<td>traces</td>
<td></td>
</tr>
<tr>
<td>(b) R₃P=(ii), Ar=Ph</td>
<td>130-135</td>
<td>53-67</td>
<td>32-43</td>
<td>10-15 traces</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(c) R₃P=(i), Ar=pBu₆C₆H₄</td>
<td>125</td>
<td>61</td>
<td>34</td>
<td>14</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>130*</td>
<td>66</td>
<td>34</td>
<td>11</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>125*</td>
<td>66</td>
<td>33</td>
<td>12</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>(d) R₃P=(ii), Ar=pBu₆C₆H₄</td>
<td>135</td>
<td>72</td>
<td>14</td>
<td>12</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>(e) R₃P=(iii), Ar=pBu₆C₆H₄</td>
<td>125</td>
<td>66</td>
<td>33</td>
<td>16</td>
<td>14</td>
<td></td>
</tr>
</tbody>
</table>

* in chlorobenzene under reflux
f in a melt with copper
For the phosphinazines (161a and 161b) the volatiles consisted of traces of benzonitrile, diphenylcyanomethane and the corresponding phosphine; 1-phenylphospholan oxide was also isolated from the derivative (161a).

The involatile residue was a tar from which few tractable products could be obtained. In the case of the triphenylphosphine derivative (161b), chromatography gave triphenylphosphine oxide in approx. 60% yield, and for (161a) trace amounts of 2, 3, 5, 6-tetraphenylpyrazine (17) and 2, 4, 5-triphenyloxazole (164), and less than 1% of an unidentified polar solid,

\[
\text{Ph} \quad \text{Ph} \\
\text{Ph} \quad \text{N} \quad \text{Ph} \\
\text{Ph} \\
\text{Ph}
\]

m.p. 182-182.5°C (colourless needles from ethanol), \( \nu_{\text{max}} \) 1700 cm\(^{-1}\) with an elemental analysis corresponding to \( \text{C}_{21}\text{H}_{15}\text{NO}_3 \) (\( M^+ = 329 \)). Small amounts (ca. 3%) of a yellow crystalline solid, m.p. 190-194°C, were also isolated and tentatively identified as the azine (165, Ar=Ph) mainly on the basis of mass spectral data which showed the expected molecular ion at m/e 416 and a base peak at m/e 105 corresponding to the stable acylium ion (166).

\[
\text{ArC} \equiv \text{N} \equiv \text{N} \equiv \text{C} \equiv \text{C} \equiv \text{Ar} \\
\text{O} \quad \text{Ar} \quad \text{Ar} \quad \text{O}
\]

By comparison, pyrolysis of the phosphinazines (161c-e) yielded p-t-butylbenzonitrile and the phosphine as the only volatile products, with
the exception of (161c) and (161e) which also gave the phosphine oxide. Examination of the residues from these decompositions by thin layer and high pressure liquid chromatography revealed the presence of a number of different products but only one major component which was isolated by repeated chromatography and recrystallisation from n-hexane as pale yellow crystals, m.p. 190-196°C, υmax 1670 cm⁻¹. Unfortunately, it proved impossible to obtain consistent elemental analysis of this compound, but spectroscopic evidence pointed to the azine (164, Ar = p-BuC₆H₄) as the correct structure. The only other identifiable products obtained by chromatography were di-p-t-butylphenylcyanomethane, and in the case of the derivative (161e), triphenylphosphine oxide.
\[
\text{Scheme 35}
\]
Discussion

The mechanism of the decomposition of the phosphinazines is unclear. That tars are obtained suggests the reactions involve reactive species such as carbenes and perhaps, even radicals. Scheme 35 outlines several possible mechanistic pathways, some of which are less likely than others. Thus, path (a) involving a pentaco-ordinate phosphorane (167) can probably be discounted since no acetylenes were found in the reaction products. This view is supported by $^3^1$P n.m.r. spectroscopy, which showed the absence of any signals due to $P^V$ species.

Path (b) involves dissociation of the phosphinazine into starting materials, a reaction that is well documented, especially in cases where electron-withdrawing groups are attached to nitrogen. In a second step the diazo ketone decomposes to give a carbene which is trapped by the phosphine to form an ylide (169). The latter then reacts with more diazo ketone to give an azine (165) in a manner typical of phosphonium, arsonium, and pyridinium ylides. While no evidence could be obtained for the intermediacy of an ylide, other workers have shown that the decomposition of phosphinazines can lead to their formation in certain cases. This procedure has been particularly successful in the synthesis of bisarylmethylenetriphenylphosphoranes.

Another pathway which is probably competitive with (b) is (c) in which the carbene undergoes a Wolf rearrangement to form a bisarylketene (170). In several cases, vacuum pyrolysis of the phosphinazines at high temperature gave a distillate with a characteristic red tinge and at 2230 cm$^{-1}$, attributable to a ketene. Rapid reaction of ketene
with undecomposed phosphinazine or phosphine probably accounts for the plethora of products observed in the reaction mixtures. In this connection, it is worth noting that diphenylketene reacts with phosphazines to give derivatives (172) of acetonitrile apparently by rearrangement of the mixed azine (171) as shown in Scheme 36.

\[
\begin{align*}
\text{Ph}_3\text{PO} + \text{Ph}_2\text{C} &\equiv \text{C} \equiv \text{O} \quad + \quad \text{Ph}_2\text{P} &\equiv \text{N} \equiv \text{N} &\equiv &\text{Y} \quad \rightarrow \quad + \\
\text{Ph}_2\text{C} &\equiv \text{N} \quad \downarrow \quad \text{Ph}_2\text{P} &\equiv \text{N} \equiv \text{N} &\equiv &\text{Y} \quad \rightarrow \\
&\text{Y} = \begin{array}{c}
\text{CHPh}
\end{array} \quad \text{and} \quad \text{CMe}_2
\end{align*}
\]

Scheme 36

The genesis of the cyanomethanes in the decomposition of the phosphinazines is unclear, but it is possible that they could arise from thermally-induced cleavage of the acetonitrile derivatives (173).

\[
\begin{align*}
\text{Ar}_2\text{C} &\equiv \text{N} \quad \downarrow \quad \text{Ar}_2\text{C} &\equiv \text{N} \equiv \text{C} &\equiv &\text{Ar} \quad \rightarrow \\
\text{Ar}_2\text{C} &\equiv \text{N} \equiv \text{C} &\equiv &\text{Ar} \quad \rightarrow \quad \text{Ar}_2\text{C} &\equiv \text{N}
\end{align*}
\]

In summary it is clear that the mode of reaction of tervalent phosphorus reagents with 2-diazo ketones is different from that with 2-azido ketones. As discussed earlier, the latter can give rise to either iminophosphoranes or pentaco-ordinate phosphoranes depending on the nature of the $\text{P}^{\text{III}}$ reagent. In particular, small ring $\text{P}^{\text{III}}$ reagents were found to favour $\text{P}^{\text{V}}$ formation. On the other hand, the corresponding reactions with 2-diazo ketones result in the formation of only $\text{P}^{\text{IV}}$ products. Moreover, the nature of the products obtained from the high temperature decomposition of these phosphinazines suggest that $\text{P}^{\text{V}}$ species are not formed even as transient species in these
reactions. The reasons for this dichotomy are not clear but several factors may be involved.

Firstly, it is possible that $P^V$ formation will be more favoured in the reactions with azido ketones (and oximes) due to the presence of a more nucleophilic oxygen and/or a more electrophilic phosphorus in the betaine intermediates (175) and (177). Clearly, the lack of any delocalisation of charge on nitrogen in (174 and 176, $x=0$ or 3), either by resonance or inductive effects, makes betaine formation by proton abstraction very likely. These betaines (175) and (177) would be expected to have more nucleophilic oxygens than the phosphinazines since in the former the negative charge is delocalised over only three atoms in the enolate and oximate anions, respectively. By contrast, in the phosphinazines (161), the negative charge is delocalised over at
least five atoms which results in a greatly reduced charge on oxygen. The possibility of some contribution to the phosphinazine structure by cannonical forms such as (178) in which the negative charge is delocalised into the aryl ring further reduces the likelihood of the oxygen being very nucleophilic. As a consequence, attack by oxygen at phosphorus to give a $P^V$ species is less likely in the reactions of diazo ketones.

Another important factor could be the orientation of the oxygen relative to the phosphonium centre. The most favourable orientation for intramolecular cyclisation is the cisoid form represented by (179) for the phosphinazines. It is possible that for steric reasons, the phosphinazines cannot obtain this configuration. In addition, the expected greater attraction between oxygen and phosphorus in the betaines (175) and (177) compared with (161) should increase the possibility of the former attaining the correct orientation for $P^V$ formation.

Finally, it is worth noting that the absence of a $P^V$ species in the high temperature reaction of the phosphinazines is not surprising in view of the presence of a relatively easy intramolecular decomposition pathway involving dissociation into phosphine and diazo compound.
Appendix II

Preparation of Phosphoryl Compounds from the Reaction of Tervalent Phosphorus Compounds with Lead Tetraacetate.

Scott\(^{31}\) has reported that the reaction of phospholes with lead tetraacetate gives excellent yields of phosphole oxides. Dimroth and Lerch\(^{333}\) have previously synthesised phosphates by the treatment of cyclic and acyclic phosphites with the same reagent.

For our purposes it was necessary to prepare authentic samples of several phosphoryl compounds. The lead tetraacetate oxidation has proved to be the most convenient method of producing these compounds. Addition of solid lead tetraacetate to a wide range of tervalent phosphorus gave excellent yields of the corresponding phosphoryl compounds. Table 11 lists the compounds prepared in this manner together with yields and \(^{31}\)P chemical shifts.

<table>
<thead>
<tr>
<th>(R_3P)</th>
<th>LTA</th>
<th>(R_3P=O)</th>
<th>Yields (%)</th>
<th>(^{31})P (\delta) (CDCl(_3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhP</td>
<td></td>
<td></td>
<td>88</td>
<td>36.8</td>
</tr>
<tr>
<td>PhP</td>
<td></td>
<td></td>
<td>95</td>
<td>14.8</td>
</tr>
<tr>
<td>(Et_2NP)</td>
<td></td>
<td></td>
<td>73</td>
<td>26.6</td>
</tr>
<tr>
<td>PhP</td>
<td></td>
<td></td>
<td>80</td>
<td>60.1</td>
</tr>
<tr>
<td>$R_3P=O$</td>
<td>Yields (%)</td>
<td>$^{31}P$ $\Delta (CDCl_3)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>-------------</td>
<td>--------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="PhP Me" /></td>
<td>83</td>
<td>61.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="PhP Me" /></td>
<td>88</td>
<td>57.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ph}_3P=O$</td>
<td>93</td>
<td>29.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Bu}^n_3P=O$</td>
<td>93</td>
<td>49.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ph PEt}_2$</td>
<td>83</td>
<td>44.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="PhP" /></td>
<td>99</td>
<td>26.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{PhP(OMe)}_2$</td>
<td>90</td>
<td>21.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ph POMe}$</td>
<td>99</td>
<td>33.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ph P OEt}$</td>
<td>97</td>
<td>31.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image" alt="PhP Ph" /></td>
<td>86</td>
<td>41.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{Ar P Ar}$</td>
<td>94</td>
<td>42.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\text{Ar} = \text{p-C}_6\text{H}_4\text{C}_6\text{H}_4$
Possibilities for future work on pentaco-ordinate phosphoranes.

The related phosphoranes containing the 1, 3, 2-dioxaphospholene group have found widespread applications in synthesis. Hence the amino-oxyphosphoranes derived from the 2-azido ketones should have synthetic potential. For example, by analogy with the known reactions of the related pentaoxyphosphoranes, amino-oxyphospholene oxides could possibly be prepared by the method outlined in Scheme 37, provided n
is sufficiently large. Similarly, the reaction of the phosphoranes with electrophiles e. g. carbonyl compounds provides a possible synthetic route to phosphoranes containing the amino-oxyphospholane ring (181) as shown in Scheme 38. This approach is analogous to the known conversion of pentaoxyphosphoranes containing 1,3,2-dioxaphospholene ring into 1,3,2-dioxaphospholans, (see p79).

Scheme 38
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