A Study of the Reactions
of t-Butyl Phosphorus Compounds

by

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THESIS

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STATEMENT

The experimental work described in this thesis has been carried out by the author in the laboratories of the Department of Chemistry of the University of Leicester and of Albright and Wilson (MFG) Ltd. between October 1968 and April 1971.

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

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Signed:

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E.M.S.
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Where t-butyl or phenyl ethylene phosphonothioite have been referred to, please read ethylene t-butyl or phenylphosphonothioite.
ABSTRACT.

The preparation and reactions of mono- and di-t-butyl phosphorus (III) compounds have been investigated in order to assess the importance of steric factors in nucleophilic and electrophilic reactions at tervalent phosphorus. In general, while the nucleophilic properties were unaffected by the presence of one or two t-butyl groups, di-t-butyl phosphorus (III) compounds are resistant to attack by all but the smallest nucleophiles. Four co-ordinate phosphorus bearing two t-butyl groups is also resistant to nucleophilic attack and several compounds of extraordinary stability have been obtained, e.g. di-t-butyldimethylphenoxyphosphonium iodide and benzyl-di-t-butyldiphenoxyphosphonium bromide.

A series of t-butyl oxyphosphoranes has been prepared and the variable temperature $^1$H n.m.r. spectra of these compounds have been investigated. The t-butyl group preferentially occupies the equatorial position. Phosphoranes derived from ethylene phosphonothioites decompose readily to give thiiran and phosphonate or phosphinate esters.

A synthesis of t-butylphosphine involving the acid catalysed addition of phosphine to isobutylene has been developed and the reactions of this phosphine investigated. The primary oxide and sulphide were prepared and characterized. t-Butylphosphine reacts with only one molecule of a variety of carbonyl compounds to give stable secondary phosphine oxides.
INTRODUCTION

There have been many reports in the literature of sterically hindered organophosphorus compounds and many proposals of steric interference in their reactions.

One of the early examples of a sterically hindered organophosphorus compound is 'Boyd's Chloride' (1) formed from triphenylcarbinol and phosphorus trichloride\(^1\). The structure originally assigned to the compound was (2) as alcohols normally form phosphites

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

with phosphorus trichloride. However as the compound is not attacked by boiling water or by aqueous sodium hydroxide, (1) must be the correct structure. It is, however, attacked by alcoholic potassium hydroxide to give triphenylmethylphosphinic acid.

Steric hindrance is also thought\(^2\) to account for the sluggish reactivity of a somewhat similar phosphinic chloride (3) towards nucleophiles:

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

In the synthesis of sterically hindered phosphorus compounds, it is almost impossible to attach more than two highly branched groups to the phosphorus atom. Thus highly branched Grignard reagents react
with phosphorus trichloride to give only the mono- or disubstituted product, depending on the reaction conditions.

The reactions of phosphonic dichlorides such as t-butylphosphonic dichloride with t-butylmagnesium chloride are very sluggish\(^3\) and similarly, the phosphoroamidic dichloride (4) reacts with only one mole of Grignard reagent (5) to give the highly hindered acid chloride (6):

\[
\begin{align*}
\text{Et}_2N-\text{POCl}_2 + \text{Me}_2\text{CH-CMe}_2\text{MgCl} & \quad \text{(4) (5)} \\
\text{Me}_2\text{CH-CMe}_2\text{P(OH)}\text{NET}_2 & \quad \text{1) HCl/ROH/H}_2\text{O,} \quad 23h \\
& \quad \text{2) NaOH} \\
& \quad \text{3) steam distil} \\
\end{align*}
\]

The acid chloride (6) is reported\(^4\) as being difficult to hydrolyze and, in fact, it is claimed that the partially hydrolyzed product (7) could be steam distilled out of the aqueous alkaline solution.

Use can be made of the step-wise reaction of sterically hindered Grignard reagents with phosphorus trichloride in the preparation of t-butyldichlorophosphine and di-t-butyldichlorophosphine in the pure state\(^5\), the yield of the latter being about 30\% due to a reduction reaction which gives di-t-butyldiphosphine\(^6\).

However, Hoffmann and Schellenbeck\(^6\) have prepared tri-t-butyldiphosphine by the reaction of chlorodi-t-butyldiphosphine with t-butyllithium. This compound reacts normally towards methyl iodide and sulphur although it does not form the usual coloured adduct with carbon disulphide.
Alkylphosphonous dichlorides can also be prepared by the reduction of the corresponding alkyltrichlorophosphonium tetrachloroaluminate in a donor solvent which co-ordinates with the aluminium chloride, thus preventing it complexing with the alkylphosphonous dichloride:

\[ RCl + PCl_3 + AlCl_3 \rightarrow (RPCl_3)^+ (AlCl_4)^- \rightarrow RCl_2 \]

Isopropylphosphonous dichloride can be successfully prepared in this way, by using either antimony or aluminium in diethyl phthalate but the method failed when \( R = \text{t-Bu} \). When t-butyl chloride was used, two complexes, \((\text{t-BuPCl}_3)^+ (Al_2Cl_7)^-\) and \((\text{t-BuPCl}_3)^+ (AlCl_4)^-\), were formed whose reduction was not achieved by aluminium or red phosphorus. The failure of these attempts to reduce the t-butylchloride-phosphorus trichloride-aluminium chloride complexes provides evidence as to the mechanism of the reductions. The t-butyl group might prevent reduction either because of its greater electron releasing power or because of its bulk. However, as two isopropyl groups are more electron releasing than one t-butyl group and since diisopropyl dichlorophosphonium tetrachloroaluminate can be reduced with antimony or zinc in diethyl phthalate, the non-reduction of the t-butyl complexes must be due to steric hindrance to the approaching reducing agent. The reduction can be envisaged as a transfer of a pair of electrons from the metal to a) the chlorine atom or b) the phosphorus atom. Since the peripheral chlorine atoms would be unhindered relative to the central phosphorus atom, it appears that attack must take place at the phosphorus atom.

The effect of a t-butyl group attached to phosphorus in
diminishing the ease with which reactions occur at the phosphorus atom has been previously noted in connection with the nucleophilic replacement of the chlorine atoms of t-butylphosphonic dichloride. It has been noted that the hydrolysis of t-butylphosphonous dichloride to the phosphonous acid is neither rapid nor exothermic in contrast with the analogous reactions of other alkylphosphonous dichlorides. Similarly the reaction of t-butylphosphonous dichloride with ethanol, which for phosphorus trichloride is vigorous, requires boiling under reflux with an excess of alcohol to give monoethyl t-butylphosphonite. Reaction of the dichloride with ethanol in the presence of a tertiary amine, however, proceeds gently without external heating.

Again, the effect of bulky groups attached to phosphorus can be seen in the rates of hydrolysis of various P(IV) halides and esters. For example, diisopropylphosphinyl chloride is hydrolyzed in aqueous acetone nearly seven hundred times as slowly as dipropylphosphinyl chloride. This, together with the fact that the diisopropyl compound exhibits a lower activation energy than the dipropyl compound, is probably indicative of steric hindrance.

Trippett and Hawes have shown that in RP(O)OEt (R = tBu), one t-butyl group attached to phosphorus produces little steric hindrance to attack by hydroxyl at phosphorus. When R = iPr the rate of hydrolysis is only seven times faster than when R = tBu. However, a sharp decrease in the rate of hydrolysis is observed in the esters R_2P(O)OEt, where R = iPr and tBu; the isopropyl ester hydrolysing some five hundred times faster than the t-butyl ester. This steric hindrance is also observed
in the reaction of dialkylphosphinyldihalides with methanolic sodium methoxide, which usually goes exothermically while di-t-butylphosphinyldichloride remains essentially unchanged after 24 h reflux.

A similar situation is found in the alkaline hydrolysis of t-butylphosphonium salts. Thus the salt (37; R = tBu) is hydrolysed about fifty times more slowly than salt (37; R = Me) to give the expected products, toluene and t-butyldiphenylphosphine oxide. The salt (38) is extremely resistant to alkaline hydrolysis, and after 11 days in 90% ethanolic N-sodium hydroxide at 100°C, 21% of the salt was recovered unchanged. The major phosphorus-containing product was benzyl-t-butylphenyolphosphine.

The reason for this retardation by two t-butyl groups might be twofold, a) that two t-butyl groups are difficult to accommodate in a pentacovalent intermediate or b) that when only one t-butyl is attached to phosphorus, attack by the hydroxyl anion could occur at the side opposite to the t-butyl group (39) to give a trigonal bipyramidal intermediate (40). In this case, there would be little steric hindrance to attack.
By 'Pseudo-rotation' (see second section) the ethoxyl anion in (40) could be lost from an apical position of a second trigonal bipyramidal intermediate (41). When a second t-butyl group is attached to phosphorus, attack has to occur adjacent to one of the t-butyl groups and steric hindrance will therefore be encountered:

![Reaction Diagram](image)

In the transition state (42) leading to the intermediate (43), the angle θ is less than 90° and so, despite the fact that the P-C bond length is 1.87 Å, substantial hindrance from the "equatorial" t-butyl group will be apparent at this point.

Resistance to both hydrolysis and oxidation by organophosphorus compounds possessing substantial steric hindrance can be illustrated by the reactions of (45) which is prepared from 2,4,6-tri-t-butylbenzene, phosphorus trichloride and aluminium chloride:\^[17]

![Reactions](image)
Attempts to oxidize (46) with alkaline hydrogen peroxide or chlorine were not successful, as shown by complete recovery of unchanged starting material. A substitution product (47) which in itself is extremely stable, was obtained in small yield (15%) from attempted oxidation of (46) with alkaline potassium ferricyanide. It is interesting to note that the corresponding phenyl analogue of (47) decomposes into tetraphenylcyclotetraphosphine, phenylphosphine and phenylphosphinic acid on standing at room temperature. Using alkaline permanganate as an oxidizing agent for compound (46) strikingly illustrates the difficulty in oxidizing the phosphorus-hydrogen bond in this compound. The phosphorus-chlorine bond is hydrolyzed, but the P-H bond remains intact. Also one t-butyl group is oxidized to a carboxyl function; which is not a well documented type of reaction:

\[ \begin{align*}
\text{Cl} & \quad \text{t-Bu} \\
\text{O} = \text{P-H} & \quad \text{t-Bu} \\
\text{K\textsubscript{3}MnO\textsubscript{4}} & \quad \text{t-Bu}
\end{align*} \]

Steric hindrance does appear to be the main factor here, but inductive effects could play an important role. For example, the stability towards oxidizing agents of secondary phosphine oxides increases markedly with increasing methyl substitution in the ring: 

\( (2,3,6-\text{Me}_3\text{C}_6\text{H}_2)\text{P(O)}\text{H} \) oxidized in 30 mins by \( \text{OH/Fe(CN)\textsubscript{3}^-} @ 80^\circ\text{C-90^\circC} \)
(2,3,5,6 - Me₄C₆H₂)₂P(O)H oxidized in 2 h by OH/Fe(CN)₆³⁻ @ 80-90°C

Kosolapoff et al. have shown that in the reaction of R'POCl₂
with Grignard reagents, the normal products, i.e., R'R''₂P = 0 are found,
where R'' comes from the Grignard reagent. On increasing the bulk of
the group on the Grignard reagent e.g. iPr, the expected product is
obtained, only in somewhat lower yield. The reaction is found to be
severely inhibited if the Grignard reagent carries a radical such as
t-butyl and compounds such as R'BuP(O)H, amongst others, are found:

RP(O)Cl₂ + tBuMgCl (excess) → R'BuP(O)H + tBu₂RP = 0
(48) (49)

Compounds of type (51) could have been formed by oxidation of compounds
of type (48) or by hydrolysis of R'BuP(O)Cl, a normal product of such
a reaction. The yield of compound (48) is increased with increasing
chain length of R. The yield of product (49) is very low and product
(50) is explained, possibly, by dimerization of the radical R'BuP=0
formed by the abstraction of a chlorine atom from R'BuP(O)Cl. These
results show that the attachment of two tertiary alkyl groups to
phosphorus is hindered but not prohibited by the bulk of the groups.

Kosolapoff et al. found little steric hindrance to the reaction
of 2,6-dialkylphenols with phosphoryl chloride except when bulky groups
were present. t-Butyl substituted phenols, although not promoting
C-phosphorylation as planned, underwent, in the presence of a Friedel-Crafts catalyst, either dealkylation or rearrangement of the ortho alkyl groups. C-phosphorylation always occurred.

Kosolapoff and Brown\textsuperscript{22} have found that using a series of sterically hindered aliphatic Grignard reagents in the following scheme;

\begin{equation}
R'MgX + (RO)\_2P(0)Cl \rightarrow (RO)\_2P(0)R' + MgXCl
\end{equation}

resulted in none of the desired product (52) being formed when $R'$ = t-butyl or t-amyl and only small amounts being formed when $R'$ = s-butyl or i-propyl. When they reacted phosphoryl chloride with three moles of t-butyl magnesium chloride in an effort to prepare the tertiary phosphine oxide, they obtained only di-t-butyl phosphinic chloride (33%) and di-t-butyl phosphine oxide, previously obtained\textsuperscript{23} as a minor product from the reaction of white phosphorus with t-butyl chloride in the presence of aluminium chloride.

Glamkowski et al\textsuperscript{24} have made use of the large size of the t-butyl group as a blocking group in their synthesis of phosphonomycin.
It can be seen from the foregoing discussion that sterically hindered phosphorus compounds have unusual chemical properties. The initial aim of this work was to make a study of these compounds so as to see what effects two t-butyl groups would have on the chemistry of the phosphorus atom.

Chloro-di-t-butylphosphine (53) reacts readily with sulphur to give the phosphinothioic chloride. Scherer and Schieder have described the reaction of (53) with ammonia to give amino-di-t-butylphosphine and methylamine to give di-t-butylmethylaminophosphine but no reaction occurred with diethylamine, even after 19 h under reflux, or with piperidine after 19 h under reflux.

Water hydrolyses (53) to the very unreactive di-t-butylphosphine oxide (54) with difficulty; it requires 12h reflux in aqueous benzene, compared to the violent reaction of chlorodiphenylphosphine with water. Miller, on reacting diphenylphosphine oxide (55) with aqueous sodium hydroxide obtained diphenylphosphine and sodium diphenylphosphinate, while Campbell and Stevens obtained diphenylphosphinic acid and hydrogen gas from refluxing (55) with alcoholic sodium hydroxide. The oxide (54) remains unchanged by treatment with aqueous or alcoholic alkali, and is also unchanged when heated to 100° for 2 h. Diphenylphosphine oxide when treated with methanolic sodium methoxide followed by a carbonyl or unsaturated compound forms a series of adducts.
e.g. with benzaldehyde (55) forms diphenyl-(α-hydroxybenzyl)phosphine oxide.

\[
\text{Ph}_2P = \text{H} + \text{CHO} \xrightarrow{\text{MeOH/MeO}^-} \text{Ph}_2P = \text{CHO}
\]

The oxide (54) proved unreactive under the same conditions with benzaldehyde, acetone and chloral. With MeO⁻/MeOH, as the base, the unreactivity is probably due to a series of equilibria being set up, i.e.

\[
\begin{align*}
\text{Bu}_2P^- + \text{CHO} & \rightleftharpoons \text{Bu}_2P = \text{CHO} \\
\text{MeO}^-/\text{MeOH} & \\
\text{Bu}_2PH & \xrightarrow{\text{BuLi}} \text{Bu}_2P^-\text{Li}^+ + \text{CHO} \rightleftharpoons \text{Bu}_2P = \text{CHO}
\end{align*}
\]

which lie in favour of the starting materials, but when butyl-lithium is used, the equilibrium lies completely to the right because the lithium salt of the oxide is formed irreversibly.

Atmospheric oxygen inserts quite readily into the P-H bond of (54) to form the phosphinic acid \(\text{Bu}_2P(\text{O})\text{OH}\).

If the metalated oxide (54) is subsequently treated with benzoyl chloride, benzoyl di-t-butyolphosphine oxide is obtained. This is one of the few authentic examples of acyl or aroylphosphine oxides. Trippett et al. attempted the reaction of sodium diphenylphosphinate and benzoyl chloride and obtained complex addition products formed by reaction of diphenylphosphinyl anion at the highly reactive carbonyl group of the intermediary aroylphosphine oxide, which, followed by rearrangement, forms
Compound (56) can then react with a further molecule of benzoyl chloride to give \( \phi - C - P\phi_2 \). This process is presumably prevented by steric effects in the t-butyl compound, since benzoyl di-t-butylphosphine oxide did not react with the di-t-butylphosphinyl-anion.

Abramov and D'yakanova\(^\text{32}\) have claimed that acylphosphine oxides can be prepared by reacting alkyl dialkylphosphinites with acetyl chloride:

\[
R_2POR' + CH_3COCl \rightarrow R_2P=COCH_3
\]

\[R = Et, \text{Pr}, \text{tPr}, \text{Bu}, \text{tBu}; R' = \text{Me}\]

while Kostyanovskii et al\(^\text{33}\) have prepared them from the addition of di-t-butylphosphine to keten or bis(trifluoromethyl)keten:

\[
t_{\text{Bu}_2\text{PH}} + CR_2 = C = O \rightarrow t_{\text{Bu}_2\text{PCOCHR}_2}
\]

\[R = H, \text{CF}_3\]

The final oxidation step seems to be in conflict with the work of Isslieb and Priebe\(^\text{34}\) who report that \( \phi_2\rightarrow CO\phi \) could not be isolated.
Chlorodi-t-butyolphosphine quaternizes with benzyl chloride at 100° to form the phosphorane \( \text{tBu}_2P(\text{CH}_2\text{O})\text{Cl}_2 \) (57) which reacts with water to give benzylidi-t-butyolphosphine oxide. In an effort to increase the yield of the reaction by heating the mixture to 120°, the main product, on aqueous work-up, was found to be t-butyldibenzylphosphine oxide. This was formed by the thermal elimination of isobutylene from (57), quaternization and subsequent decomposition of the resulting phosphorane.

\[
\begin{align*}
\text{tBu}_2\text{PCl} + \text{CH}_2\text{Cl} & \rightarrow \text{tBu}_2\text{P(0)}\text{Bu} + \text{PCl}_2 \\
\text{tBu}_2\text{P(0)}\text{Bu} + \text{H}_2\text{O} & \rightarrow \text{tBu}_2\text{P(0)} \text{Bu} \text{Cl}
\end{align*}
\]

This sequence was proven by heating the phosphorane (57), obtained by reacting di-t-butylichlorophosphine with benzyl chloride, to 120° and treating the residue with alkaline hydrogen peroxide. Benzyl-t-butylyphosphinic acid (59) was obtained which could only have come from the chlorophosphine (58). The chlorophosphorane (57) is ideally suited for the investigation of species such as \( \text{tBu}_2P = \text{CH}^\circ \) (60). This type of intermediate has been postulated in the mechanism of reaction of primary phosphines and carbonyl compounds. Hamer et al. have also suggested that such planar intermediates exist to account for the racemic products they obtain in the base reaction.
hydrolysis of

\[
\begin{array}{c}
\text{MeO} \\
\text{P} \\
\text{Cl} \\
\text{C-C}_6\text{H}_{11}\text{NH}
\end{array}
\]

The concept was to treat (57), prepared by reaction of chlorine gas on benzyl-di-t-butylphosphine, with base and hope that the two t-butyl groups would prevent nucleophilic attack at phosphorus thereby forcing the reaction to occur on one of the benzyl protons to produce (60):

\[
\begin{align*}
\text{t Bu}_2\text{PCH}_2\text{O} + \text{Cl}_2 & \rightarrow \text{t Bu}_2\text{O} \text{CH}_2\text{PCl}_2 \rightarrow \text{t Bu}_2\text{P} = \text{CHO} \\
(57) & \rightarrow (60)
\end{align*}
\]

If this intermediate (60) were formed it could subsequently react with deuteriомethanol to give a deuterated phosphine oxide (62).

The phosphorane (57), while not reacting with methanol, did give benzyl-di-t-butylphosphine oxide exothermically, on treatment with methanolic sodium methoxide. However, repeating in deuterated ethanolic sodium ethoxide did not lead to the formation of any deuterated phosphine oxide, as shown by n.m.r. spectroscopy and mass spectrometry. This, therefore, implies that the base has attacked the phosphorus atom quite readily. The reason must be due to the high nucleophilicity of the methoxyl anion relative to methanol.

Treatment of chlorodi-t-butylphosphine with sodium methoxide gives
methyl di-t-butyl phosphinite which undergoes a normal Arbusov reaction with methyl iodide to give di-t-butylmethylphosphine oxide.

An attempt was made to react (53) with sodium azide in order to produce azidodi-t-butylphosphine which on pyrolysis, it was hoped, would form the di-t-butylphosphinic nitride trimer or tetramer:\n
$$tBu_2PCl + NaN_3 \rightarrow tBu_2P-N_3 \rightarrow (tBu_2P-N)^+ + (tBu_2P-N)_3$$

which might have had high thermal and hydrolytic stability. However, the starting materials were recovered unchanged. Even t-butylchlorophenylphosphine did not react with sodium azide.

The reaction of (53) with sodium phenolate gives phenyl di-t-butylphosphinite (63) which reacts with sulphur to give the $\Phi$-phenyl phosphinothioate and hydrolyses to di-t-butylphosphine oxide on treatment with boiling water.

Chlorine in carbon tetrachloride reacts with (63) to form a chlorophosphorane $tBu_2(\Phi0)PCl_2$ which hydrolyses with water, but not methanol, to give phenyl di-t-butylphosphinate.

Quaternization of (63) with methyl iodide yields di-t-butyldimethylphenoxyphosphonium iodide (64), which was unaffected by boiling water or methanol. Considering (64) to be a type of Rydon Reagent, it is
remarkably stable. Rydon Reagents are extremely hydrolytically unstable and can be used, by reaction with alcohols, as preparative intermediates for alkyl halides. The corresponding benzyl (65) and $p$-nitrobenzyl (66) salts of (63) are equally as stable towards water and methanol, (66) being stable enough to undergo a Wittig olefin synthesis using methanolic sodium methoxide and benzaldehyde. The major products were phenyl di-t-butylphosphinate and $p$-nitrostilbene. Small quantities of di-t-butyl-$p$-nitrobenzylphosphine oxide, formed by loss of the phenyl group, were also isolated.

The salts (64, 65, 66) hydrolysed with aqueous alkali to give the corresponding tertiary phosphine oxides by loss of the phenyl group.

Hexyl and phenacyl bromides and ethylbromoacetate failed to quaternize with (63).

CONCLUSION

In conclusion, these results show that di-t-butyl derivatives of tervalent phosphorus are able to function as nucleophiles but are strongly resistant to attack by nucleophiles other than the smallest. They also confirm the reluctance of phosphorus to accommodate two $t$-butyl groups in a trigonal bipyramidal intermediate.
The first report of cyclic oxyphosphoranes was by Kukhtin who postulated their intermediacy in the reactions of trialkyl phosphites and diacetyl which yielded \( \alpha,\beta \)-unsaturated methyl phosphates via an alkyl group translocation reaction.

In 1960 Ramirez et al first started a detailed study of the reactions between trialkyl phosphites and \( \alpha \)-diketones.

1,3,2-Dioxaphospholens

Ramirez et al found that the unsaturated oxyphosphoranes or the 1,3,2-dioxaphospholens, e.g. (67) can be formed by reaction of phosphites, phosphonites or phosphinites with \( \alpha \)-diketones, e.g. diacetyl.

\[
\text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\
\text{O} \quad \text{O} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \\
+ (\text{RO})_3\text{P} \rightarrow \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \quad \text{Me} \\
\text{O} \quad \text{O} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \quad \text{OR} \\
(67) \quad (68)
\]

They have the useful property of combining with a second molecule of the diketone to form (68), which is a new approach to the formation of carbon-carbon single bonds in polyoxygenated compounds. With some \( \alpha \)-diketones and \( \alpha \)-ketoesters, the second step of this condensation is faster than the first, so only the 2:1-adducts are isolated. The adduct (67) is stable enough to undergo successive exchange of its methoxy groups for benzoxoxy groups on heating with benzyl alcohol at 100\(^\circ\)C.

The Structure of Oxyphosphoranes:

The structure of the oxyphosphoranes could be one of several
possibilities, e.g. with the \(1,3,2\)-dioxaphospholen (67) where the phosphite is trimethyl phosphite, any one of the following structures could be correct:

\[
\begin{align*}
\text{(69)} & & \text{(70)} \\
\text{(71)} & & \text{(72)} & & \text{(73)} & & \text{(74)}
\end{align*}
\]

The isomeric phosphates (73) and (74) must be considered since alkyl group translocation is known to occur in the reactions of trialkyl phosphites with \(\alpha\)-quinones. The i.r. spectrum of the adduct shows no carbonyl absorption which immediately eliminates structures (69), (71), (73). A structure similar to (70) such as (75), triphenylphosphineacylmethylene, has a carbonyl absorption at 6.5 \(\mu\) which is not apparent in the spectrum of the adduct

\[
\text{(75)}
\]
The i.r. spectrum of (74), which is a methyl phosphate ester is inconsistent with the spectrum of the adduct.

This leaves us with structure (72) which fits all the physical data. It gives rise to a relatively strong and polarized Raman line which confirms the presence of an olefinic carbon-carbon double bond.

Triphenyl phosphate has a large positive $^{31}\text{P}$ n.m.r. shift compared with triphenyl phosphite, i.e., $\delta = +17$ ppm and -26 ppm respectively. This is true for a series of other esters and as the oxyphosphoranes have, in general, large positive $^{31}\text{P}$ n.m.r. shifts it can be concluded that the structure is the pentaco-ordinate cyclic structure (72). It has been shown by electron diffraction and X-ray crystallographic studies that pentaco-ordinate phosphoranes exist as trigonal bipyramids with two apical and three equatorial bonds. This structure has been found for all phosphoranes studied and is assumed for all pentaco-ordinate phosphorus compounds.

The $^1\text{H}$ n.m.r. spectrum agrees with structure (72) by showing a doublet due to the methoxy groups whose chemical shift is upfield from trimethyl phosphate and a singlet arising from the methyl groups attached to the carbon having the correct chemical shift for methyl groups attached to a double bond. The presence of one doublet due to the three methoxy groups means these groups occupy positions in the molecule which are readily interchangeable (see later section on pseudo-rotation).

1,3,2-Dioxaphospholans:

The 1,3,2-dioxaphospholans can be prepared, as 1:2-adducts, from trialkyl phosphites and suitably activated monocarbonyl compounds such as
a- and p-nitrobenzaldehyde, hexafluoroacetone, phthalaldehydes and fluorenone. These reactions lead to oxyphosphoranes such as (76) and (77).

\[
\begin{align*}
(76) & & (77)
\end{align*}
\]

The reactions between simple aliphatic aldehydes (2 moles) and trialkyl phosphites yield yet another type of oxyphosphorane; the 1,4,2-dioxaphospholans.

\[
(RO)_3P + C_2H_5CHO \xrightarrow{20^\circ \text{ slow}} (RO)_3P\xrightarrow{20^\circ \text{ fast}} (RO)_3P + CH_2\xrightarrow{EtCHO} (78)
\]

The 1:1 adduct (78) cannot be isolated because it reacts more rapidly
with a second molecule of the aldehyde to form the 2:1 adduct (79).
The condensation of aliphatic aldehydes with phosphites does not involve
deoxygenation or alkyl group translocation at the 1:1 or 1:2 stages,
since these processes are prevented by the formation of the cyclic
oxyphosphorane.

1,3-Oxaphospholans:
The 1,3-oxaphospholans (80) are the initial products from the
reaction of phosphites or aminophosphines with dimethylketen at -75°C.

\[
\text{Me}_2\text{C}=\text{C}=\text{O}+\text{R}_3\text{P} \rightarrow \text{Me}_2\text{C}=\text{C}=\text{O}+\text{R}_3\text{P}
\]

(80)

Compounds of type (80) have highly polarized carbon-phosphorus bonds.

1,2-Oxaphospholens:
Whereas transdibenzylethylene with phosphites does not form any
detectable intermediate that can be regarded as an oxyphosphorane\(^{49,51}\),
equimolar amounts of benzylideneacetylacetone and trialkyl phosphites or
dialkyl alkylphosphonites react at 20°C to form the crystalline 1,2-
oxaphospholen (81)\(^{52,53}\).
More recently Denney et al.\textsuperscript{54} have prepared a series of oxyphosphoranes from cyclic phosphites and diethylperoxide.

**Mechanisms of adduct formation:**

Kukhtin and his co-workers\textsuperscript{39,55,56} have proposed several mechanisms for the reaction of trialkyl phosphites with \(\alpha\)-diketones and \(\alpha\)-quinones. They have suggested several types of structures for the intermediates and for what they regard as the final products of these reactions. First\textsuperscript{39}, they proposed an attack by phosphorus on the carbonyl carbon, followed by a re-arrangement to a five-membered cyclic pentaerythrophorane analogous to that suggested by Ramirez et al.\textsuperscript{57,58} and by Birum and Dever.\textsuperscript{59}

This intermediate was said to re-arrange to a stable enol ether phosphate. Later\textsuperscript{55}, they abandoned the five-membered pentaerythrophorane structure in favour of one having a three-membered ring with pentacovalent phosphorus, 

\[(\text{RO})_3\text{P} + \overset{\text{O}}{\text{C}} - \overset{\text{O}}{\text{C}} - \overset{\text{O}}{\text{C}} - \overset{\text{O}}{\text{C}} - \overset{\text{O}}{\text{C}}\]

The mechanism now proposed by Ramirez et al.\textsuperscript{60,61} and by other workers\textsuperscript{62} involves nucleophilic attack of phosphorus on the carbonyl oxygen followed by cyclization of the zwitterion, as shown
However, Ogata and Yamashita, who seem to be the only group to have done a kinetic study on this type of reaction, prefer the mechanism by which nucleophilic attack of the phosphorus atom occurs on the carbonyl carbon.

\[
\begin{align*}
\text{(RO)}_3P : & \quad \text{fast} \\
\text{C} &= \text{C} = 0 \\
\end{align*}
\]

The reaction rates of benzil and trimethyl phosphite were measured by u.v. spectrophotometry in a series of solvents. The reaction was also studied over a temperature range of 15° and the energy and entropy of activation were calculated to be 8.41 kilocalories/mole and -47.5 e.u. respectively. A change in the solvent showed an increase in the rate constant with increase in dielectric constant of the solvent. The effect of changing the substituents of the phosphite was for the rate to increase with increasing nucleophilicity of the phosphite, but with (s-BuO)_3P a lowered rate was observed due to steric factors. Ogata and Yamashita found that acid catalysed the reaction and the reason they postulated for this was that the acid activated the carbonyl group by making the carbonyl carbon more amenable to attack, as follows:

\[
\begin{align*}
\text{(RO)}_3P : & \quad \text{fast} \\
\text{C} &= \text{C} = 0 \\
\end{align*}
\]
U.v. spectrophotometry showed evidence for the presence of hydrogen bonding to benzil. Conversely, they found that strong base inhibited the reaction, which they justified by saying that the carbonyl group was being deactivated.

The fact that dimethylaniline had virtually no effect, suggests that only strong bases can retard the reaction, and that the rate inhibition is not due to neutralization of any mineral acid which might have been present. This acceleration-retardation behaviour is in contrast to the formally analogous Diels-Alder reaction, where both trimethylamine and trichloroacetic acid have an accelerating effect.\(^{64}\)

**Stability of Phosphoranes:**

The stability of oxyphosphoranes varies considerably and it seems that stabilization comes from two main sources, a) the presence of electronegative substituents, which prefer to occupy apical positions and b) the presence of a four or five membered ring. This may be because the small ring partly offsets crowding difficulties in the quinquevalent state, or because the ring is less strained when spanning an apical-equatorial position of a trigonal bipyramid than when it contains a
tetrahedral phosphorus.

The normal decomposition product of a phosphorane is a tetrahedral phosphorus compound, but the presence of a ring prevents this process from occurring and so imparts considerable stability. In some cases sufficient stability can be imparted so as to allow stable phosphoranes to exist even though the apical positions are occupied by carbon functions.

The reaction between α-diketones and trivalent phosphorus compounds need not necessarily give pentaco-ordinate adducts, in some cases open dipolar species are formed, and these are distinguished by their negative \( ^{31}\text{P} \) shifts. This is, to some extent, dependent on the electronegativity of the substituents. Trimethyl phosphite forms the stable oxyphosphoranes (68,76,77) and (82,83),

![Diagram of oxyphosphoranes](82)

![Diagram of oxyphosphoranes](83)

while tris(dimethylamino)phosphine forms only zwitterions (84) and (85) with phenantraquinone and hexafluoroacetone.

![Diagram of zwitterions](84)

![Diagram of zwitterions](85)
This is due, in part, to the lower electronegativity of the nitrogen and in part to the larger steric requirements of the dialkylamino groups versus the alkoxy groups.

These effects can also be illustrated by the adducts of the \( \alpha \)-diketone, benzil. The trimethyl phosphate adduct is very stable whereas the adduct (86) formed with a cyclic aminophosphine is much less stable,

![Diagram](image)

and the adduct from the reaction of benzil and tris(dimethylamino)phosphine can be isolated in two crystalline forms, the metastable open dipolar form (87) and the stable oxyphosphorane (88).
In solution these are in equilibrium, the position of the equilibrium depending on the polarity of the solvent.

Stabilization of oxyphosphoranes by introduction of small rings can be exemplified by the oxyphosphorane (89) which reacts with one and two molecules of catechol to form oxyphosphoranes (90) and (91) which are of increasing stability.

Reetz and Powers have shown that tris(dimethylamino)phosphine yields a bicyclophosphorane (92) with 2-aminoethanol whereas a trivalent phosphorus compound (93) is obtained from the phosphine and 3-aminopropanol.

If N-substituted 2-aminoethanols are used then the trivalent and pentavalent species are found to be in equilibrium.
Catechol $^{68,69}$ and $\alpha$-aminophenol$^{70,71}$ have also been shown to give stable phosphoranes with tris(dimethylamino)phosphine. The phosphite ester of ethylene glycol$^{72}$ has been shown to exist as a pentaco-ordinate specie (95), by i.r. and $^{31}$P,$^{1}$H n.m.r.$^{73}$ rather than in the trivalent form (94).

This unexpected result can be explained by the enhanced stability offered to a phosphorane by two five-membered rings.

In contrast Bestmann et al.$^{74,75}$ have prepared phosphoranes containing one oxygen and four carbon functions attached to phosphorus. These phosphoranes were prepared by the action of cyclohexene oxide, styrene oxide and phenyl cyanate with cyclopropyldenetriphenylphosphorane.
These phosphoranes are stable enough to be distilled and their stability is due to the five-membered and spiro rings.

Hellwinkel\textsuperscript{76} has made an extensive study of the bisbiphenylene-phosphoranes (96) and has found that these compounds are quite stable even with carbon functions occupying apical positions.

In a study by Ramirez et al\textsuperscript{77} of the adducts between tertiary phosphines and hexafluoroacetone, it was found that the oxyphosphorane (97) was formed initially but it thermally rearranges to the oxyphosphetane (98), which is stabilized by the four membered ring occupying an apical-equatorial position and also by the oxygen functions being apical.
Pseudorotation in Pentaco-ordinate Phosphoranes

Pseudorotation in a pentaco-ordinate phosphorane is a process of ligand re-organization such that one trigonal bipyramid is converted to another trigonal bipyramid via a square pyramid intermediate.

The process of pseudorotation was first invoked to explain some apparent anomalies in the $^{19}$F n.m.r. spectra of various fluorophosphoranes. Though the structure of pentafluorophosphorane was known to be trigonal bipyramidal, only one type of fluorine was indicated in the n.m.r. spectrum.

More recent work by Muetterties and Schmutzler on a wide range of substituted fluorophosphoranes has shown some similar anomalies. Methyltetrafluorophosphorane, where the methyl group is in an equatorial position of a trigonal bipyramid, showed only one type of fluorine at room temperature. Likewise, diethylaminotetrafluorophosphorane showed only one type of fluorine at room temperature. This is due to rapid equilibration of the fluorine atoms by pseudorotation. However, on cooling, the process of pseudorotation is slowed down and eventually stopped; at which point the $^{19}$F n.m.r. spectrum indicated the presence of two types of fluorine atoms.

From these observations and others, Muetterties and Schmutzler
suggested that the electronegative groups prefer to occupy the apical positions. Theoretical calculations agree with this hypothesis and indicate that the equatorial bonds have more electronegative character than the apical bonds, so the more electronegative groups will occupy the bond with more electropositive character.

When pseudorotation is applied to alkoxyphosphoranes that contain a five-membered ring, there are two preference rules which apply:
1) alkyl groups preferentially occupy equatorial positions, while oxygen atoms preferentially occupy apical positions and 2) five-membered rings preferentially occupy one apical and one equatorial position, so as to minimize ring strain.

**Pseudorotation in Oxyphosphoranes**

The $^1$H n.m.r. spectra of a number of oxyphosphoranes (57, 82; $R = \text{Me, Ph}$) have been examined in the temperature range -60° to +30°. In all cases the three methoxy groups attached to phosphorus give only one doublet, which is due to $P - H$ coupling. The data suggest that the methoxy groups are undergoing positional exchange among apical and equatorial positions. Pseudorotation can be invoked to explain the observed spectra.

Considering the 1,2-oxaphospholen formed from benzylideneacetylacetone and trimethyl phosphate\(^{91, 92}\) (99).
The preferred configuration of this adduct is (99) because the element with the lowest electronegativity, carbon, should tend to occupy an equatorial position\(^{84,93}\). The \(^1\)H n.m.r. spectrum is found to be temperature dependent and at \(-65^\circ\) the three methoxy groups are clearly different i.e. the trigonal bipyramid is "frozen" in the time scale of the n.m.r. whereas the room temperature spectrum shows only one doublet for these protons\(^{92,52}\).

When pseudorotation is applied to (99) using the starred methoxy group as a pivot, the trigonal bipyramid (100) is obtained; now there is a phospholene carbon occupying an apical position which is unfavourable on electronegativity grounds\(^{84,93}\). This accounts for the appearance of a barrier to pseudorotation which is sufficiently high to permit observation of the three methoxy groups at \(-65^\circ\).

If the ring carbon of (99) were used as a pivot, that carbon remains in an equatorial position, and the ring would have to span an angle of \(120^\circ\) in a diequatorial position. This would be accompanied by considerable ring strain\(^{94,95}\), and so would not be expected to occur. The \(^1\)H n.m.r. signals due to the acetyl and methyl groups attached to the phospholene ring of (99) coalesce into a singlet at about \(+125^\circ\). This change is reversible and is due to an opening of the ring to form the dipolar ion (101)

\[
\begin{align*}
\text{Me} & \quad \text{H} & \quad \text{OMe} \\
\text{Me} & \quad \text{C} & \quad \text{Ph} & \quad \text{OMe} & \quad \text{OMe}
\end{align*}
\]
Dimethyl phenylphosphonite reacts with benzylideneacetylacetone to form the following diastereomeric 1,2-oxaphospholenes (102) and (103) which differ in the configuration at the phosphorus.

\[
\begin{align*}
\text{MeCO} & \quad \text{OMe} \\
\text{Ph} & \quad \text{OMe} \\
\text{H} & \quad \phi
\end{align*}
\]

(102) (103) (104)

Each diastereomer consists of a pair of enantiomers. In (102) the phenyl in the ring and the phenyl at phosphorus are trans while in (103) they are cis.

The $^1$H n.m.r. spectrum is again found to be temperature dependent. The bipyramids (102) and (103) are "frozen" below $-20^\circ$. Although the $^1$H signals of the two equatorial methoxy groups (one from each isomer) are observable, the apical methoxy groups cannot be resolved.

These observations are accommodated by pseudorotation. One pseudorotation of (102) using the phenyl-phosphorus bond as a pivot places the ring carbon in an apical position and exchanges the methoxy groups, but leaves the phenyl ring in an equatorial position. This does not result in conversion of (102) in (103). A second pseudorotation places a phenyl in an apical position; two additional pseudorotations are required to convert (102) into (103) in this manner. The choice of the ring carbon as pivot requires the expansion of the C - P - O
angle from 90° to 120° and placement of a phenyl in an apical position simultaneously.

At about 0°, positional exchange among methoxy groups of each isomer is noted, but there is no isomerization of (102) into (103). The spectrum is similar up to about 40°, but at 52° positional exchange of the phenyl rings and of the methoxy groups at phosphorus seems to become important. This exchange is reflected in the coalescence of the doublets due to the methoxy groups and also in the coalescence of the singlets due to the two acetyl groups. At about 70°, the phosphorus-oxygen bond of the ring of (102) and (103) breaks leading to an equilibrium of the cyclic structure with the dipolar ion (104). The signals due to the acetyl and methyl groups coalesce at about + 125°, where the dipolar ion (104) is being observed exclusively. In this last stage the methyls become magnetically equivalent but the methoxy groups do not. All these changes are reversible.
DISCUSSION

The problem which concerns us here is, first, whether pentaco-ordinate adducts can be prepared containing one or two t-butyl groups and secondly, what position the t-butyl group will adopt in such structures when in competition with highly electronegative functions such as methoxy groups.

Throughout organophosphorus chemistry it is assumed that electronegative groups prefer apical positions in the pentaco-ordinate intermediate. It is on these grounds that one would predict that the t-butyl group would prefer to be in an equatorial position but on steric grounds it is very difficult to determine which position, apical or equatorial, would be least sterically demanding.

Concerning the first problem; attempts at preparing pentaco-ordinate adducts from benzylidene-t-butylphosphine (105) and phenanthraquinone, and from methyl (106) or phenyl (63) di-t-butylphosphinite and diacetyl, resulted in deoxygenation of the ketones giving the corresponding phosphine oxide and phosphinates respectively. This is presumably because of the strain or steric crowding that would occur in the phosphoranes. That compounds (63) (105) and (106) are good de-oxygenating agents was shown by the high yields of carbazole isolated from their reactions with 2-nitrodiphenyl.98

The same type of reaction occurs when diphenyl t-butylphosphonite (107) reacts with diacetyl. This contrasts with the formation of adduct (108) from diphenyl phenylphosphonite and diacetyl52.
While (107) seems incapable of forming pentaco-ordinate species it reacts normally with sulphur to give diphenyl t-butylyphosphonothioate and quaternizes with methyl iodide and benzyl bromide to form the very stable Rydon reagent-type salts (109) and (110) (see first section)

\[
\begin{align*}
\text{PhO} & \quad + \quad \text{tBu} \\
\text{PhO} & \quad \quad \quad \text{I}^{-} \\
\text{PhO} & \quad \quad \quad \quad \text{Me}
\end{align*}
\]

(109)

\[
\begin{align*}
\text{PhO} & \quad + \quad \text{tBu} \\
\text{PhO} & \quad \quad \quad \text{Br}^{-} \\
\text{PhO} & \quad \quad \quad \quad \text{CH}_{2}\text{Ph}
\end{align*}
\]

(110)

Assuming that the non-formation of an adduct with diacetyl by (107) was because of the bulky phenyl groups, o-phenylene t-butylyphosphonite was prepared. This phosphonite, while reacting normally with sulphur to give rise to o-phenylene t-butylyphosphonothioate and with methyl iodide to form an unstable methiodide, did form an air stable, crystalline adduct (111) with diacetyl which was purified by crystallization.

\[
\begin{align*}
\text{PhO} & \quad + \quad \text{tBu} \\
\text{PhO} & \quad \quad \quad \text{Me}
\end{align*}
\]

(111) \[ \delta^{31} \text{P} + 19 \text{ p.p.m.} \]
This therefore establishes that a route to relatively stable pentaco-ordinate adducts carrying t-butyl groups is available.

The second problem involves the preparation of a relatively stable adduct which contains a t-butyl group, and also some other electronegative group that would give rise to an easily interpretable $^1$H n.m.r. spectrum. Diethyl t-butylphosphonite (112) was considered a suitable compound. Due to initial difficulties in the preparation of (112) from t-butyl-dichlorophosphine and ethanol, a replacement reaction between t-butylbis(diethylamino)phosphine (113) and ethanol was attempted, but this proved unsuccessful. This was presumably because the t-butyl group prevented access of the nucleophile, ethanol, to the phosphorus. The aminophosphine (113) was prepared from bis(diethylamino)chlorophosphine and t-butyl-lithium. Compound (112) was eventually prepared from sodium ethoxide and t-butyldichlorophosphine and it was found to yield the stable adducts (114) and (115) with diacetyl and benzylideneacetylmethone.

\[ \text{EtO} \quad \text{EtO} \quad \text{Me} \quad \text{Me} \]
\[ \text{EtO} \quad \text{t-Bu} \quad \text{EtO} \quad \text{Me} \quad \text{Me} \]

(114) $\delta^{31}$P + 6 p.p.m.  (115) $\delta^{31}$P + 4 p.p.m.

The $^1$H n.m.r. spectra of (114) and (115) were found to be independent of temperature over the range $-60^\circ$ to $+25^\circ$.

Hydrolysis of (115) with one mole of water yielded the corresponding $\beta$-keto phosphinate ester (116),
which showed a strong carbonyl absorption at 1695 cm\(^{-1}\) supporting the keto form (116) as opposed to the enol form (116a).

In order to simplify the n.m.r. spectra further, dimethyl t-butylphosphonite (117) was prepared in the same manner as for (112) and stable adducts (118) and (119) were again formed analogous to (114) and (115).

The methyl derivative of (116) was obtained on hydrolysis of (119) with one mole of water.

The adduct (119) was designed so that the t-butyl group could be "placed" in the pentaco-ordinate structure; assuming the ring to occupy an apical-equatorial position, then the methoxy groups would be free to occupy whatever position they preferred. Which position each group adopted
was to be observed by low temperature n.m.r. It was expected that as the
temperature was lowered, there would come a point where the pseudorotation
would be stopped and the adduct would be "frozen" in one configuration
so that if, e.g. the t-butyl group occupied an equatorial position,
two different methoxy absorptions would be observed, one apical and one
equatorial, whereas if the t-butyl group preferred an apical position
one methoxy absorption would be visible because the methoxy groups would
be magnetically equivalent.

The room temperature n.m.r. spectrum of (119) consists of a doublet
at 8.8 τ, due to the t-butyl group being split by phosphorus, and two
singlets at 8.2 τ and 7.5 τ corresponding to the methyl and acetyl groups
attached to the double bond respectively. The apical methoxy group
gives a doublet at 6.9 τ and the doublet at 6.3 τ corresponds to the
equatorial methoxy group. The benzylic protons appear as a doublet at 5.8 τ.
The spectrum shows the methoxy groups to be magnetically non-equivalent
as a result of the asymmetric carbon centre in the ring. This implies
that there could be either, extremely rapid pseudorotation between the
isomers (120; R = tBu) and (120a; R = tBu),

![Diagram](image-url)
which could not be stopped, even at -90\(^\circ\) in deuteriomethylene chloride or, that there is only one detectable isomer presumably (120a; R=\(^t^\)Bu) because of steric effects. The latter situation, by analogy with (121) (see later) from which two isomorphic oxides (121a and 121b) were isolated would involve both isomers of (120) being formed initially.

\[
\begin{align*}
\text{O} & \quad \text{tBu} \\
\text{P} & \quad \text{O} \\
\text{CH} & \quad \text{COMe} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

\begin{align*}
\text{O} & \quad \text{tBu} \\
\text{P} & \quad \text{O} \\
\text{C} & \quad \text{COMe} \\
\text{H} & \quad \text{Ph}
\end{align*}

\(31^p\text{P} - 10\, \text{p.p.m.}\)

The behaviour of adduct (120) is in contrast with the corresponding dimethyl phenylphosphonite adduct\(^{52,96,97}\) in which pseudorotation to equilibrate the isomers (120; R = \emptyset) and (120a; R = \emptyset) is inhibited at -20\(^\circ\). This is probably connected with the relative populations of the isomers, which, in the phenyl case, is 3:1 in favour of the trans isomer while in the t-butyl case only the trans isomer exists.

On raising the temperature to 50\(^\circ\), no change in the spectrum occurs, but at 75\(^\circ\) a new doublet at 7.7 \(\tau\) starts appearing which is due to the benzylidenecetylacetone.
At 100°, this doublet has increased in size and the singlets due to the methyl and acetyl groups attached to the ring have decreased considerably, whilst a new methoxy peak is just appearing at 6.35 which is caused by the methoxy groups of the phosphonite (117). A singlet appears for the two methyl groups at 150° which reflects the formation of the zwitterion (122). Throughout these temperature changes, the benzylic proton peaks remained unaltered.

These processes seem, to some extent, reversible as all the original peaks are apparent on returning the sample to room temperature but some permanent decomposition does occur.

The behaviour of the adduct (119) is in contrast with that of the phenyl analogue of Ramirez et al. 50,96,97 where complete coalescence of the methyl singlets occurs at 52° and the open dipolar ion forms at approximately 125°. Throughout these elevated temperature n.m.r. studies there seems to be no evidence of any decomposition of the adduct into its starting materials.

It seems, therefore, that the methoxy groups in (120) will never become equivalent 91 because of the constraints on pseudorotation by the
ring always lying apical-equatorial and of the asymmetry of the ring carbon atom. The simplest way to overcome this problem is to study compounds where the asymmetry has been removed. Phosphoranes can be prepared from trimethyl phosphite and methyl vinyl ketone but attempts to prepare a phosphorane from dimethyl t-butylphosphonite and the ketone were unsuccessful, presumably because the adduct was too unstable to isolate, even at -70°C.

However, the stable adduct (123) from methylenedioxynbenzoin and dimethyl t-butylphosphonite has no asymmetric carbon centre.

The room temperature n.m.r. spectrum of (123) is as follows:

- a t-butyl doublet at 8.7 ppm, a doublet at 6.9 ppm due to the ring methylene protons, a methoxy group doublet at 6.4 ppm and a phenyl multiplet at 2.8 ppm.

The spectrum was found to be temperature dependent and on lowering the temperature of the probe to -10°C, the methoxy group doublet coalesced into a single broad band and at -25°C, this band had separated into two doublets at 6.43 ppm and 6.27 ppm i.e. pseudorotation had been slowed down sufficiently for the methoxy groups to become distinguishable. This
demonstrates that, whatever its kinetic preference$^{101}$, the t-buty1
group is thermodynamically more stable in the equatorial position of
a trigonal bipyramidal phosphorane when in competition with methoxy groups.
The behaviour of (123) is exactly similar to that of the phenyl analogue(124).

![Chemical Structure](image)

(124) $\delta^{31}P + 6 \text{ p.p.m.}$

**The Ethylene Phosphonothioites**

Phenyl ethylene phosphonothioite was prepared in order that its
adduct (125) with diacetyl could be investigated with respect to the
relative electronegativities of sulphur and oxygen in a pentaco-ordinate
phosphorane. This was attempted by looking at the $^1H$ n.m.r. of the methyl
absorptions of (125). If there is a considerable difference in
electronegativities of sulphur and oxygen then a low temperature n.m.r.
study should show the pseudorotation process slowing down giving rise to
two different methyl signals. If, however, the electronegativities are
of similar magnitude then only one methyl signal would be observed.

The n.m.r. spectrum at room temperature showed two signals for the
methyl groups. This can be explained by examining the limited
pseudorotation processes which can occur in this phosphorane.
It can be seen that the starred methyl group is linked to an equatorial sulphur in (125) and to an apical sulphur in (125a) which results in the methyl groups always being different.

The t-butyl analogue (126) was prepared in the hope that a low temperature n.m.r. study would show different t-butyl groups, however only one was apparent all the way down to -60°.

The reason for this could be that the equilibrium might be such that a small change in the equilibrium constant might only show a small, if not invisible, amount of the other form. The equilibrium remained unaltered at elevated temperatures. It was noticed that, at about 100°, the two singlets corresponding to the methyl groups collapsed into a singlet at 7.85°C and multiplets from the methylene protons of the ring were replaced by a singlet at 7.65°C. This is because the phosphorane is eliminating thiiran to form the corresponding phosphonate ester (127).
A similar type of elimination has been postulated by Hamer, Ramirez et al.\textsuperscript{103} and Denney et al.\textsuperscript{104} who found that the oxyphosphorane (128) decomposed at room temperature to tetramethylethylene oxide and triethyl phosphate.

It was found that all the adducts formed from the ethylene phosphonothioites (R = \textsuperscript{t}Bu or Ph) and diacetyl, benzylideneacetone or phenanthraquinone underwent this reaction to give the corresponding phosphonite or phosphinate esters.
The ethylene phosphonothioites (R=Ph or tBu), while reacting with sulphur to give the corresponding ethylene phosphonothiolothioates, quaternize with methyl iodide to give methides (129) which have two possible sites of attack in the subsequent Arbusov reaction.

\[
\begin{align*}
\text{ICH}_2\text{CH}_2\text{S} & \quad \text{ICH}_2\text{CH}_2\text{O} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

That the attack occurred to give (130) was established by mass spectrometry of the product and of the phosphinic acid obtained by hydrolysis with methanolic sodium hydroxide.

It is interesting to note that, adducts (121)(125)(126) and the phenyl analogue of (121), all have negative \( ^{31}\text{P} \) n.m.r. chemical shifts. This seems to be in contrast with the general assumption that all pentacoordinate phosphoranes have positive shifts. The negative shifts of these adducts, whose \( ^1\text{H} \) n.m.r. spectra are proof that the pentaco-ordinate structure exists and not the dipolar form, can be justified by correlating shifts and structures of known adducts. The substitution of a methoxy group by an ethylthio group in the following adduct,
makes the chemical shift less positive by approximately twenty parts per million. The replacement of an alkoxy group by an alkyl group has the same effect by the same amount; also increasing the number of rings attached to phosphorus tends to make the chemical shift of the phosphorane less positive. Taking these factors into account makes pentaco-ordinate phosphoranes with negative $^{31}\text{P}$ chemical shifts less unusual.

**CONCLUSION**

It has been shown that relatively stable oxyphosphoranes containing a t-butyl group attached to phosphorus can be readily prepared and that the t-butyl group is thermodynamically more stable in an equatorial position when in competition with methoxy groups. However the question of the energy barrier involved in putting sulphur apical in a trigonal bipyramidal intermediate has yet to be answered. Ultimately, this could be worked out from an X-ray crystallographic study.
INTRODUCTION

The methods for the preparation of phosphines, especially those of the primary and secondary type, were inadequate until 1952. This is reflected particularly in the small number of primary and secondary phosphines known at that time.

The most widely used method of preparing primary phosphines up to that time was the thermal disproportionation of phosphonous acids, prepared by hydrolysis of phosphonous dichlorides.

\[ \text{RP(O)(H)OH} \rightarrow \text{RPH}_2 + \text{RP(O)(OH)}_2 \]

However, with the introduction of lithium aluminium hydride as a reducing agent rapid progress was made in preparing these compounds. Since its first use by Horvat and Furst in the preparation of phenylphosphine from phenylphosphonous dichloride, a wide variety of organophosphorus compounds such as phosphonic dichlorides, phosphonous acids, dialkyl or aryl phosphonates, and dialkyl or aryl phosphonites have been reduced to the corresponding phosphines. Other reducing agents such as lithium hydride, lithium in tetrahydrofuran or a finely divided suspension of sodium in toluene followed by treatment with water, have been used with success.

One of the most economical methods for the preparation of phosphines is the addition of phosphine gas to olefins. Olefins in which the double bonds are activated by electrophilic substituents, such as acrylonitrile, add to phenylphosphine and diphenylphosphine at elevated temperatures without catalyst, to give tertiary phosphines. In general, however, addition of phosphines to olefins has been effected in the presence of acidic (methanesulphonic acid, benzenesulphonic acid,
Acid Catalysed Reaction of Phosphine and Olefins

The acid catalysed addition of phosphines to olefins probably proceeds by a carbonium ion mechanism. Tertiary olefins, which are known to form the most stable carbonium ions, give

\[ \text{R}_2\text{C} = \text{CH}^+ \xrightarrow{+\text{H}^+} \text{R}_2\text{C} - \text{CH}_3 \]

primary phosphines in high yield\(^{116}\). Furthermore tertiary olefins react selectively in the presence of secondary and primary olefins\(^ {117}\). A normal Markownikow addition takes place to yield a product with the phosphorus atom bonded to the tertiary carbon atom.

\[ \text{R}_2\text{C}^+ - \text{CH}_3 + \text{PH}_3 \xrightarrow{+\text{H}^+} \text{H}_3\text{P}^+ - \text{CR}_2\text{CH}_3 \xrightarrow{+\text{H}^+} \text{H}_2\text{P}^+ - \text{CR}_2\text{CH}_3 \]

In order to achieve a good conversion a nearly stoichiometric amount of catalyst is required, because the primary phosphine formed is a much stronger base than phosphine and will combine with the catalyst to form a phosphonium salt. Higher temperatures favour the conversion. The reaction stops after the first step and only minor amounts of dialkylphosphines are formed. No tertiary phosphines have been detected. These findings reflect the tendency of the monoalkylphosphine to exist\(^ {1+}\) as \(\text{RPH}_3\) in acidic media. Therefore the concentrations of free monoalkylphosphine and of the olefin cation are low and formation of the dialkylphosphine is slow.
Base Catalysed Reaction of Phosphine and Olefins.

Base catalysed addition of phosphines to olefins was first reported in the case of acrylonitrile\textsuperscript{118}. The highest yields of addition products were obtained when acrylonitrile, in conjunction with a separate aqueous potassium hydroxide catalyst phase, was employed as the reaction medium. The reaction probably proceeds either by a Michael addition of PH\textsubscript{2}, i.e.

\[
\begin{align*}
\text{PH}_3 + \text{OH} & \rightleftharpoons \text{PH}_2 + \text{H}_2\text{O} \\
\text{PH}_2 + \text{CH}_2 = \text{CHCN} & \rightarrow \text{H}_2\text{PCH}_2\text{CHCN} \\
\text{H}_2\text{PCH}_2\text{CHCN} + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{PCH}_2\text{CH}_2\text{CN} + \text{OH}
\end{align*}
\]

or, less probably, of PH\textsubscript{3}, i.e.

\[
\begin{align*}
\text{CH}_2 = \text{CHCN} & \rightleftharpoons \text{CH}_2 - \text{CHCN} \\
\text{CH}_2 - \text{CHCN} + \text{PH}_3 & \rightarrow \text{H}_3\text{PCH}_2\text{CHCN} \rightarrow \text{H}_2\text{PCH}_2\text{CH}_2\text{CN}
\end{align*}
\]

Although mixtures of primary, secondary and tertiary phosphines are always obtained in the cyanoethylation of phosphine, the degree of substitution can be controlled to a great degree by varying the ratio of phosphine to acrylonitrile present in the reaction mixture.

Free Radical Addition of Phosphines to Olefins

The free radical addition of phosphine to unsaturated compounds can be initiated by radiation, organic peroxides\textsuperscript{119,119a} and other free radical sources\textsuperscript{115,119a}. The reaction proceeds by a free radical chain mechanism as proposed by Kharasch and Mayo and

\[
\begin{align*}
\text{PH}_3 + R (\text{or h}) & \rightarrow \text{PH}_2 + RH \\
\text{PH}_2 + RCH = \text{CH}_2 & \rightarrow \text{H}_2\text{PCH}_2\text{CHR} \\
\text{H}_2\text{PCH}_2\text{CHR} + \text{PH}_3 & \rightarrow \text{H}_2\text{PCH}_2\text{CH}_2R + \text{PH}_2
\end{align*}
\]
produces primary, secondary and tertiary phosphines whose relative percentages depend on the mole ratio of phosphine to olefin and also on the steric requirements of the olefin.

**Reactions of Primary Phosphines**

**Oxidation**

Primary phosphines are easily oxidized and, in particular, those containing the lower aliphatic residues will ignite spontaneously in air. The uncontrolled oxidation yields phosphonous and phosphonic acids. Very recently, however, the lowest oxidation product of primary phosphines, the primary phosphine oxides, have been isolated.

\[
\begin{align*}
\text{O} \\
\text{RPH}_2
\end{align*}
\]

They were initially obtained in the reaction of phosphine gas with ketones (see later), and then, more directly, in the controlled oxidation of primary phosphines with stoichiometric amounts of hydrogen peroxide. Primary phosphine oxides are, in general, rather unstable. Only octylphosphine oxide has been isolated as a crystalline solid of limited stability. \(^{31}\)P n.m.r. spectra of primary phosphine oxides show the expected 1-2-1 triplet centred at -15 ppm with P-H coupling constant of about 28 ppm. Primary phosphine oxides are easily oxidized further to phosphonic acids.

\[
\begin{align*}
\text{O} \\
\text{RPH}_2 \xrightarrow{[\text{O}]} \text{RP(OH)}_2
\end{align*}
\]

**Reaction with Sulphur**

Extraordinarily little work seems to have been done on the
reaction of sulphur with primary phosphines. Kohler and Michaelis\textsuperscript{123} report that when phenylphosphine was heated with one equivalent of sulphur to 100\textdegree\, two products were obtained. One appeared to be phenylphosphine sulphide which is said to have the following structure analogous to the oxide.

\[
\begin{array}{c}
\text{S} \\
\text{Ph-PH}_2
\end{array}
\]

The other product, seems, in the light of more recent work on tetraalkydiphosphine monosulphides\textsuperscript{123a}, to be the monosulphide of tetraphenylcyclotetraphosphine.

\[
\begin{array}{c}
\text{Ph} \\
\text{P---P---P---Ph}
\end{array}
\quad
\begin{array}{c}
\text{Ph} \\
\text{P---P---P---P} \\
\text{S}
\end{array}
\]

**Metalation**

The metalation of primary phosphines can be effected by the free alkali metals\textsuperscript{124-126} such as sodium, lithium or potassium or by organoalkali metal compounds in inert solvents\textsuperscript{127}. The degree of substitution depends on the conditions used. The mono-substituted metal phosphides, \(\text{RHPM (M = Na, K)}\), as well as the disubstituted metal phosphides, \(\text{RPM}_2 (M = \text{Li,Na,K})\), have been prepared. Phenylphosphine reacts with Grignard reagents with substitution of the hydrogen atoms by the MgX group\textsuperscript{128}.

\[
\text{PhPH}_2 + 2\text{RMgX} \rightarrow \text{PhP(MgX)}_2 + 2\text{RH}
\]

**Reactions with Acid Halides**

Phenylphosphine, when treated with phosgene, yields phenylphosphonous
dichloride\(^{129}\). It is thought that the product is formed by action
of phosgene on the intermediate tetraphenylcyclotetraphosphine.

\[
\begin{align*}
\text{PhPH}_2 + \text{COCl}_2 & \rightarrow (\text{PhP})_4 + \text{CO} + \text{HCl} \\
& \downarrow \text{COCl}_2 \\
& \text{PhPCl}_2 + \text{CO}
\end{align*}
\]

Thionyl chloride has been reported to react with phenylphosphine in
benzene solution with the formation of phenylphosphonothioic dichloride.

**Reactions with Halogens**

Primary phosphines react vigorously with halogens and give,
in the uncontrolled reaction, alkyltetrahalophosphoranes (RPX\(^4\)). If,
however, the reaction is carried out with stoichiometric amounts of
a halogen in an inert solvent, then phosphonous dihalides are formed\.\(^{126}\).

\[
\text{RPH}_2 + 2X_2 \rightarrow \text{RPX}_2 + 2HX.
\]

**Phosphonium Salt Formation**

Primary phosphines are classed as weak bases and their salts,
formed with hydrogen iodide are decomposed by water. The addition products
of primary phosphines with alkyl halides are decomposed by alkali.

\[
\begin{align*}
\text{RPH}_2 + \text{R'}X & \rightarrow (\text{RR'}\text{PH}_2)^+ \text{X}^- \\
& \downarrow \text{OH} \\
& \text{RR'}\text{PH} + \text{H}_2\text{O} + \text{X}^{-}
\end{align*}
\]

This reaction has been used as a preparation of secondary phosphines.
Reactions of Primary Phosphines with Carbonyl Compounds

Aliphatic Aldehydes

In an early investigation by Messinger and Engels, organic solvents were generally employed as media for the reactions of phosphine with aldehydes; anhydrous hydrogen chloride or bromide was used as the catalyst. At present, this reaction is conducted mostly in aqueous concentrated hydrogen chloride solution. Under acidic conditions formaldehyde, acetaldehyde, propionaldehyde, heptanal and dodecanal react readily with phosphine to give tetrakis(1-hydroxyalkyl)phosphonium halides.

\[ 4RCHO + PH_3 + HX \rightarrow (RCHOH)_4P^X^- \]

Under these conditions dialdehydes and phosphine give spirocyclic phosphonium salts.

\[
\begin{align*}
\text{CHO} & \quad \text{(CH}_2\text{)}_n \quad \text{CHO} \\
\text{CHO} & \quad \text{H}^+ \\
\text{(CH}_2\text{)}_n & \quad \text{OH} \\
\text{CH} & \quad \text{OH} \\
\text{CH} & \quad \text{OH} \\
\text{Cl} & \quad \text{(CH}_2\text{)}_n \\
\end{align*}
\]

Primary phosphines, in which the donor properties of the phosphorus atoms are strongly decreased by substitution with electronegative groups, such as tetrafluoroethyl groups, give, when treated with formaldehyde in acidic solution, only tertiary phosphines.

\[ \text{CF}_2\text{HCF}_2PH_2 + HCHO \rightarrow \text{CHF}_2\text{CF}_2P(\text{CH}_2\text{OH})_2 \]

The use of metal salts accelerates the rate of reaction and in the absence...
of acid, tertiary phosphines are obtained

\[ 3\text{HCHO} + \text{PH}_3 \xrightarrow{\text{PtCl}_4} (\text{HOCH}_2)_3\text{P} \]

Other aldehydes and phosphine as well as primary phosphines produce tertiary hydroxy phosphines.

Chloral and dichloroacetaldehyde react with phosphine in aqueous hydrochloric acid forming bis(\(\beta\)-chloro-\(\alpha\)-hydroxyethyl)phosphines (133), (136,137)

\[ 2\text{C}2\text{HCl}_2\text{CHO} + \text{PH}_3 \xrightarrow{\text{H}^+} (\text{C}2\text{HCl}_2\text{CHOH})_2\text{PH} \]

(133)

\(R = \text{Cl, H}\)

but chloroacetaldehyde gives an amorphous solid of unknown constitution (132).

A different type of reaction occurs with \(\alpha\)-branched aldehydes and \(\alpha\)-chlo-roaldehydes. Isobutyroaldehyde and 2-ethylhexanal, when treated with phosphine in hydrochloric acid, produce secondary phosphines in which the phosphorus atom is part of a heterocyclic system of the 1,3-dioxa-5-phosphacyclohexane type (132,122), (134).

\[ \text{R}_1\text{R}_2\text{CHO} + \text{PH}_3 \xrightarrow{\text{H}^+} \text{R}_1\text{R}_2\text{CH} \]

(134)

\(R_1 = R_2 = \text{Me}; R_1 = \text{Et}, R_2 = \text{n-Bu}.

which behaves as an ordinary secondary phosphine.

**Aromatic Aldehydes**

The following structures (135) and (136) have been proposed for
the crystalline product obtained from benzaldehyde and phosphine

\[
\text{(PhCHOH)}_3P \quad \text{(PhCHOH)}_2\text{PCH}_2\text{Ph}
\]

(135) \quad (136)

Buckler\(^{138}\) put forward strong chemical and physical evidence for structure (136). The same structure has been used for the products obtained from \(\alpha\)-tolualdehyde and \(\alpha\)-chlorobenzaldehyde\(^{138}\). Besides compound (136), another minor product was isolated from the reaction of benzaldehyde and phosphine and it was found to have the cyclic structure (137) similar to that obtained from \(\alpha\)-branched aliphatic aldehydes and phosphine.

The yield of (137) can be increased if the reaction is carried out in acetonitrile containing a trace of acid.

Petrov et al\(^{139}\) report that benzaldehyde and phenylphosphine form a tertiary phosphine, phenylbis(\(\alpha\)-hydroxybenzyl)phosphine, if hydrogen chloride, water and methanol are used as a reaction medium. Propylphosphine, similarly, yielded with benzaldehyde in ether containing hydrogen chloride, propylbis(\(\alpha\)-hydroxybenzyl)phosphine\(^{140}\).

Ketones

In acidic solution simple ketones and phosphine yield a mixture of the corresponding primary and secondary phosphine oxides. The first
step apparently involves transfer of oxygen from carbon to phosphorus.

\[ R_1R_2C = O + PH_3 \rightarrow R_1R_2CHPH_2 \]

\[ R_1R_2CHPH_2 + R_1R_2C = O \leftarrow R_1R_2CHPH_2 \]

Trippett\textsuperscript{135a} suggested that the oxidation-reduction process proceeds by way of a carbonium ion adjacent to phosphorus, and in agreement with this Buckler and Epstein\textsuperscript{135} put forward the following mechanism for this step:

\[ R_1'CR_2 + PH_3 \leftarrow R_1R_2C \rightarrow PH_2 \rightarrow R_1R_2C \rightarrow PH_2 \]

\[ R_1R_2CH \rightarrow PH_2 \leftarrow R_1R_2CH \rightarrow PH \rightarrow R_1R_2C = PH \]

The workers\textsuperscript{142} supplied some supporting evidence for this mechanism from their work on secondary phosphines. With these, it is possible to isolate the hydroxy phosphines, which are assumed to be intermediate in the reactions of phosphine, and to show that these undergo oxygen transfer. Furthermore, since the hydroxy phosphines do not have a P-H bond, a hydride transfer mechanism which is possible for phosphine can be excluded.

\[ Ph_2PH + PhCHO \xrightarrow{\text{dil HCl}} Ph_2P \xrightarrow{\text{MeOH}} \quad \text{(138)} \]

\[ \xrightarrow{\text{Conc HCl}} Ph_2PCH_2Ph \quad \text{Conc HCl} \]

\[ \xrightarrow{\text{Conc HCl}} Ph_2PCH_2Ph \quad \text{Conc HCl} \]

\[ \xrightarrow{\text{Conc HCl}} Ph_2PCH_2Ph \quad \text{Conc HCl} \]
It was found that the tertiary phosphine (138) prepared, in quantitative yield, by adding a few drops of aqueous hydrochloric acid to a methanol solution of diphenylphosphine and benzaldehyde, produced the phosphine (139), in good yield, when heated in concentrated aqueous hydrochloric acid as had the secondary phosphine and aldehyde when treated under these conditions directly. This provides some evidence that hydroxy phosphines are precursors of the phosphine oxides; however, the possibility of dissociation followed by reaction by some other route cannot be excluded. It is largely steric effects of the groups on the ketone or phosphine, in the case of primary phosphines, that govern the extent to which primary phosphine oxides are formed in the reaction of phosphines and ketones.  

Diketones

Solutions of 2,4-pentanedione in aqueous 4-6N hydrochloric acid readily absorb phosphine and primary phosphines to give crystalline solids to which a trioxa-6-phosphoadamantane structure has been assigned (140).  

\[
\begin{align*}
2\text{MeCCH}_2\text{CMe} + \text{RPH}_2 & \rightarrow \text{MeO} - \text{C} - \text{MeP} - \text{R} \\
\end{align*}
\]

\( R = \text{H, }^1\text{Bu, }\text{C}_6\text{H}_{17}, \text{Ph, PhNHCO} \)  

\( (140) \)

The reaction product with phosphine \((R = \text{H})\) exhibited properties typical of a secondary phosphine.
**Isocyanates**

Phosphines react with isocyanates under mild conditions in benzene as solvent and in the presence of a basic catalyst to give carbamoylphosphines.

\[
R_x PH_{3-x} + (3 - x) PhNCO \rightarrow R_x P(\text{CONHPh})_{3-x}
\]

The fact that the intermediate mono- and dicarbamoylphosphines, \(RNHCO_{\text{Ph}}\) and \((RNHCO)_{2}\text{Ph}\), are never detected in the reaction of phosphine and isocyanates indicates that the intermediates are more reactive towards isocyanate than the phosphine. Apparently the nucleophilic reactivity of the phosphorus atom is increased by substitution of a carbamoyl group. Resonance of the type

\[
\text{RNH} - \text{PH} \leftrightarrow \text{RNH} = \text{PH}
\]

is probably not important in these compounds, since if it were one would expect to obtain monocarbamoyl derivatives. Attempts to react phosphine with phenylisothiocyanate, isocyanic and cyanic acids were unsuccessful. No reaction was observed.
DISCUSSION

The aim of this work was to synthesise t-butyIphosphine and to study its reactions to see how they differed from those of other primary phosphines.

All attempts at reducing t-butyIphosphonous dichloride, t-butyIphosphonous dibromide and dimethyl t-butyIphosphonate with sodium hydride, phenylsilane, diphenylsilane, trichlorosilane and polymethylhydrogensiloxane were unsuccessful.

It was then decided to prepare t-butyIphosphine by the acid catalysed addition of phosphine to isobutylene. Phosphine was generated in a similar manner as that employed by Rauhut et al in the base catalysed cyanoethylation of phosphine, by slowly adding an excess of water to a slurry of magnesium aluminium phosphide in petrol (100-120°). Petrol, as opposed to dioxan, was used, so that any solvent carried over from the generator would not freeze in the gas-bubbler situated in the reaction vessel, in which the temperature was -15°. Phosphine was dried by passing it through anhydrous calcium chloride tubes. Hoff and Hill found, in their studies of acid catalysed additions of phosphine to various olefins that methanesulphonic acid was the most efficient catalyst. But, if this acid was used then a mixture of petrol (100-120°) and diethyl ether had to be employed to prevent the catalyst from freezing. Obviously, efficient catalysis is impossible if the catalyst cannot be mixed intimately with the reactants. After neutralizing the acidic reaction mixture with sodium hydroxide, separation, drying, and distillation of the organic layer yielded (approx. 2%) t-butyIphosphine heavily contaminated with ether and low-boiling petrol fractions. The catalyst did not freeze in di-n-butyl ether at -15° and because of the high boiling
point of this solvent, it was hoped that a clean separation of the phosphine would result on distillation. However, t-butylphosphine (approx 2%) was obtained still containing considerable amounts of ether, even though a Vigreux column was used for the distillation. On changing the catalyst to an equimolar mixture of boron trifluoride and 85% phosphoric acid\textsuperscript{155} with petrol as solvent, the yield of t-butylphosphine rose to approximately 20%, but the petrol impurities still remained. Originally, the acidic reaction mixture was neutralized with sodium hydroxide, but this produced, with the phosphoric acid catalyst, partially soluble sodium salts which prevented separation of the organic layer. Ammonia solution (0.880) was subsequently used for neutralization and this gave ammonium salts which readily dissolved in the aqueous layer. Finally, a change to decalin as solvent gave almost pure t-butylphosphine in 30% yield, containing only small quantities of t-butanol as impurity. The pure phosphine, as shown by g.l.c., was obtained only after the reaction mixture was set aside overnight at room temperature. This allowed the unreacted isobutylene to evaporate so that it could not be hydrated, during neutralization, to form t-butanol. The yield of t-butylphosphine depends on how efficiently the heterogeneous mixture of reactants and catalyst is stirred and on how long the phosphine is passed into the mixture.

When 100% phosphoric acid was used as the catalyst, no t-butylphosphine was isolated.

t-Butylphosphine is a colourless liquid which is not spontaneously inflammable in air as are other primary phosphines\textsuperscript{120}. It quaternizes with methyl iodide to give an unstable methiodide and reacts with bromine to give t-butylphosphonous dibromide.
The primary sulphide, prepared by reacting equimolar amounts of sulphur and t-butylyphosphine, slowly reacts with atmospheric oxygen to form t-butylyphosphinothioate (141), presumably by oxidation and subsequent elimination of water.

\[
\begin{align*}
\text{tBuPH}_2 & \quad \text{O}_2 \quad \text{tBuP}_
\end{align*}
\]

The n.m.r. data of t-butylyphosphine sulphide indicate that it exists as the pentavalent (142) and not the trivalent form (143).

The primary phosphine sulphide seems to be the only product formed whereas sulphur and phenylphosphine in equimolar amounts, form the monosulphide of tetraphenylcyclotetraphosphine as well as the primary phosphine sulphide.

The oxides of primary phosphines are generally very unstable and are rarely isolated in the pure state. They are more stable in acidic solution, presumably in the protonated form. Controlled oxidation of t-butylyphosphine using an equivalent amount of hydrogen peroxide yields t-butylyphosphine oxide (144) which is sufficiently stable at room temperature in methanol solution to allow \(^1\text{H}\) and \(^{31}\text{p}\) n.m.r.
spectra to be recorded. The $^{31}\text{P}$ spectrum shows a 1-2-1 triplet centred at -8 p.p.m., with a $\text{P}-\text{H}$ coupling constant of about 29 p.p.m., and the $^1\text{H}$ spectrum shows a t-butyl doublet and another doublet, with a coupling constant of 458 Hz, for the protons attached to phosphorus. This indicates the "keto" form (145) exists rather than the "enol" form (146).

\[
\text{S} \quad \text{t-Bu-\text{PH}_2}
\]

(145)

The oxide (144) was characterized by the formation of t-butyl-($\alpha$-hydroxybenzyl)-phosphine oxide (147) from two moles of benzaldehyde under acidic conditions.

\[
\text{t-BuP\text{H}_2} + 2\text{CHO} \xrightarrow{\text{H}^+} \text{t-BuP-\text{CH}_2\text{O}}
\]

(144)

(147)

The disubstituted product is generally obtained in the reactions of other primary phosphines\textsuperscript{151}.

\[
\text{RPH}_2 + 2\text{CHO} \xrightarrow{\text{H}^+} \text{RP-\text{CH}_2\text{O}}
\]

$R = n-C_8\text{H}_{17}$; t-Bu

To ensure that (147) was obtained from the oxide (144) and not from the
unchanged phosphine, t-butylphosphine was reacted, under the same conditions, with two moles of benzaldehyde; this gives benzyl-t-butyl-(α-hydroxybenzyl)phosphine oxide (148).

\[
\text{tBuPH}_2 + 2\text{CHO} \xrightarrow{H^+} \text{tBuP} - \text{CH} = \text{OH}
\]

(148)

The oxide (144) was also characterized by cyanoethylation with two moles of acrylonitrile. This reaction gives t-butyldis(2-cyanoethyl)phosphine oxide (149).

\[
\text{tBuPH}_2 + 2\text{CH}_2 = \text{CHCN} \xrightarrow{\text{EtO}^-} \text{tBuP(CH}_2\text{CH}_2\text{CN})_2
\]

(144) (149)

Disubstitution is the normal reaction with other primary phosphine oxides. Uncontrolled oxidation of (144) yields, predominantly the phosphinic acid (150), characterized as its anilinium salt (151).

Metalation of (144) can be achieved using potassium metal, which is one of the reagents used for phenylphosphine, but sodamide in...
liquid ammonia was found to be more convenient. t-Butylmethylphosphine was prepared by adding methyl iodide to a suspension of $t^-$BuPH Na in liquid ammonia. However, metalation and subsequent treatment with 1,2-dichloroethane, in an effort to prepare t-butyphosphiran (152), was unsuccessful.

$$t^\text{-BuPH} + \text{ClCH}_2\text{CH}_2\text{Cl} \rightarrow t^\text{BuP}$$ (152)

Several substituted phoshrans $^{152}$ and phosphiran $^{153}$ itself have been isolated and it was hoped that the t-buty group would impart sufficient stability to the three membered ring to allow the chemistry of compound (152) to be studied.

The products derived from the reaction of carbonyl compounds with primary phosphines depend on a number of factors, e.g. the size of the substituents on the phosphine, the steric requirements of the carbonyl compound, and the pH and type of solvent in which the reaction takes place.

Whereas phenylphosphine treated with one or two molar equivalents of cyclohexanone gives (153)$^{135}$,

$$\text{PhPH}_2 + \text{C}_6\text{H}_{11}\text{CH}=\text{CH}_2 \rightarrow \text{PhP}$$ (153)

t-buty phosphine, with an excess of the ketone, forms only the monosubstituted product (154).

$$t^\text{BuPH}_2 + \text{C}_6\text{H}_{11}\text{CH}=\text{CH}_2 \rightarrow t^\text{BuP}$$ (154)
Phenylphosphine reacts stepwise with acetophenone giving the mono- and disubstituted phosphine oxides, (155,156),

\[
\begin{align*}
\text{(155)} & \quad \phi - \text{P} \quad \text{H} \\
\text{(156)} & \quad \phi - \text{C} \quad \text{OH} \\
\end{align*}
\]

however, t-butylphosphine with an excess of acetophenone gives the t-butyl analogue of (155) i.e. (157)

\[
\begin{align*}
t_{\text{Bu}}\text{PH}_2 + \phi \text{CCMe} + H^+ & \rightarrow t_{\text{Bu}}\text{P} \quad \text{CH}\phi \\
\end{align*}
\]

(157)

Compound (157) is a mixture of diastereoisomers which are separable by fractional crystallization and have characteristic n.m.r. spectra.

It was hoped that t-butylphosphine and chloroacetone would give (158), which on treatment with base would form the phosphinyl anion which

\[
\begin{align*}
t_{\text{Bu}}\text{P} \quad \text{CH}_2\text{Cl} \\
\end{align*}
\]

(158)

then might cyclize at the \(\beta\)-carbon atom to give a t-butylphosphiran oxide (159).
However, instead of (158), the product was \(\text{t-butyl-(x-methylvinyl)-phosphine oxide (160)},\) presumably formed by the elimination of hydrogen chloride from (158).

\[
\begin{align*}
\text{BuPH}_2 + \text{Me}_2\text{CO} & \overset{H^+}{\longrightarrow} \text{BuP(C\text{=CCH}_2\text{)}Me} + \text{MeCO} + \text{H}_2\text{O} \\
\text{(161)} & \quad \text{(162)}
\end{align*}
\]

which is rapidly oxidized on standing in air to give the phosphinic acid (152).

Very little work has been published on the reactions of primary or secondary phosphines with hexafluoroacetone. Stockel reports that secondary phosphines and hexafluoroacetone give a phosphinite and not a 1,3,2-dioxaphospholane.
It was found that the t-butylphosphine, with two moles of hexafluoroacetone gave the phosphinite (163), which was isolated as the phosphinate (164).

\[
\text{tBuPH}_2 + (\text{CF}_3)_2\text{CO} \rightarrow (\text{CF}_3)_2\text{C}^{-} \rightarrow (\text{CF}_3)_2\text{CH}^{-}\text{OPH}_2
\]

(164)

(163)

Succinaldehyde and t-butylphosphine react together, in the presence of acid, to give 1-t-butyl-2,5-dihydroxyporphalium chloride (165),

\[
t\text{BuPH}_2 + \text{CH}_2\text{CHO} + \text{H}^{+} \rightarrow \text{Cl}^{-}
\]

(165)

while with acetonylacetonon only tars were produced. No identifiable products were obtained from the reaction of t-butylphosphine and diacetyl with or without acid present. The reaction without acid was undertaken
to find out if a 1,3,2-dioxaphospholan could be obtained with two hydrogen atoms attached to phosphorus.

The secondary phosphine oxides of the type

\[
\begin{align*}
^{t}\text{Bu} \quad \text{P} \quad \text{R} \\
\text{H} \\
\end{align*}
\]

are remarkably stable towards any attempt at P-H bond fission.

Diphenylphosphine oxide has been shown by Miller\(^{26}\) to give diphenylphosphine and sodium diphenylphosphinate when refluxed with sodium hydroxide, while Campbell et al\(^{27}\) have found that diphenylphosphine, treated with an excess of alcoholic sodium hydroxide, forms diphenylphosphinic acid and hydrogen. The oxide (154) remained completely unchanged and one isomer of (157) gave a 98:2 ratio, i.e. 2% of the other isomer, when treated with alcoholic sodium hydroxide. Di-t-butylphosphine oxide (54) was also stable under these conditions. (54) also resisted any attempt at thermal disproportionation. t-Butylphosphine oxide treated with alcoholic sodium hydroxide yielded t-butylphosphinic acid which was characterized as its anilinium salt. Even when one isomer of (157) was photolyzed for 48 h in the presence of dibenzyl disulphide\(^{156}\), in order to see if the generated free radical would equilibrate to a mixture of isomers, there was no reaction and starting materials were recovered unchanged. Any thermal attempts at this reaction using di-t-butyl disulphide, were unsuccessful.

**CONCLUSION**

An adequate synthesis of t-butylphosphine has been developed. In
the reactions of this phosphine the bulk of the t-butyl group plays an important role in determining the extent of reaction and the stability of the products.
EXPERIMENTAL

INSTRUMENTATION

Infra red spectra were recorded on Perkin-Elmer 237 or 257 spectrometers.

$^1$H n.m.r. spectra were recorded on a Varian T-60, Varian A-60 or Varian DA-60 spectrometer in deuterochloroform or as neat liquids unless otherwise stated, with tetramethylsilane as internal standard. All $^{31}$P spectra are quoted in p.p.m. relative to 85% H$_3$PO$_4$.

Mass spectra were recorded on an A.E.I. M.S.9 instrument; in each case the mass peak is given first, followed by those of structural significance.

G.L.C. analyses were run on a Perkin-Elmer F.11 instrument using a 2 metre silicone gum rubber O.E. 120 column.

GENERAL DETAILS:

All reactions involving air-sensitive reactants or products were carried out under an atmosphere of dry oxygen-free nitrogen. Solvents were dried as follows:

Benzene, petrol and ether over sodium wire; dimethylformamide refluxed over calcium hydride and distilled; pyridine was refluxed over potassium hydroxide pellets and distilled; methanol and ethanol by their magnesium alkoxides and distillation; tetrahydrofuran was distilled from sodium wire onto sodium and distilled before use.

All liquid reagents were distilled before use.

The n-butyl and t-butyl-lithiums were used as a 2.5N solution in pentane as supplied by Aldrich Chemical Company.
The Preparation of Chloro-di-t-butylphosphine

Chloro-di-t-butylphosphine was prepared by the method of Voskuil and Arens. Yield 35% b.p. 50-54°/3mm; Literature b.p. 69-70°/10mm.

Preparation of Di-t-butylphosphinothioic Chloride

Sulphur (0.16g; 0.005 mol) was added to chloro-di-t-butylphosphine (0.9g; 0.005 mol) with gentle warming. A sudden exothermic reaction occurred. The residue gave di-t-butylphosphinothioic chloride, m.p. 18.20° (from petrol (60-80°), ν max. 1175, 1020, 935, 800 and 695 cm⁻¹, Σ 8.5 (d, JPH = 18Hz) (Found: C, 45.3; H, 8.8; P, 14.9. C₈H₁₉C₆PS requires C, 45.1; H, 8.5; P, 14.6%).

Preparation of Di-t-butylphosphine Oxide

Di-t-butylchlorophosphine (0.9g; 0.0055 mol), water (1 ml), and triethylamine (3.03g; 0.03 mol) were refluxed in benzene (100 ml) for 12 h; the mixture was then filtered. Evaporation of the filtrate and crystallization of the residue from petrol (60-80°) gave di-t-butylphosphine oxide (1.4g) m.p. 65-68°, ν max. 2280, 1150 cm⁻¹, Σ 3.2 (d, 2H, JPH = 498Hz), and 8.8 (d, 18H, JPH = 14Hz).

Preparation of Di-t-butyl-(α-hydroxybenzyl)-phosphine Oxide

Butyl-lithium (7.5 ml) was added to di-t-butylphosphine oxide (1.6g; 0.01 mol) in ether (30 ml). An immediate white precipitate was formed. Benzaldehyde (1.06g; 0.01 mol) was added to the suspension. After stirring at room temperature for 2 h, acidification, and ether extraction the residue gave di-t-butyl-(α-hydroxybenzyl)-phosphine oxide (2g, 75%), recrystallized from ether, m.p. 120-123°, ν max. 3400, 1455, 1130, 1050, 815, 775, 700 cm⁻¹, δD_DMSO/CDCl₃ 2.6 (5H, m), 3.6 (1H, d, JPH = 15Hz), 6.6 (1H, s), 8.6 (9H, d, JPH = 12Hz) and 9.0 (9H, d, JPH = 12Hz). (Found: C, 67.0; H, 9.6; P, 11.0. C₁₅H₂₅O₂P requires C, 67.2; H, 9.3; P, 11.6%).
Preparation of Benzoyldi-t-butyldichlorophosphorane

Chloro di-t-butyldichlorophosphorane (24.3g; 0.135 mol) and benzyl chloride (18g; 0.142 mol) were heated together at 100° for 5 h and then treated with water. Extraction with chloroform and chromatography of the extract on alumina gave benzoyldi-t-butyldichlorophosphorane oxide (0.9g), m.p. 115-117° (60-80 petrol), $\nu_{\text{max}}$ 1160, 1140, 820, 760 and 700 cm$^{-1}$, m/e 252, 195, 161 and 138, $\delta$ 2.8 (5H,m), 6.9 (2H,d, $\delta_{\text{pH}}$ 14HZ), and 8.8 (18H,d, $\delta_{\text{pH}}$ 14HZ) (Found: C, 71.3; H, 9.7; P, 12.6. C$_{15}$H$_{23}$O$_2$P requires C, 71.5; H, 9.9; P, 12.3%). The same experiment carried out at 120° gave, after chromatography, dibenzyl-t-butyldichlorophosphorane oxide (7.3g) m.p. 159-162° (60-80 petrol), $\nu_{\text{max}}$ 1475, 1372, 1225, 1128, 1035, 940, 830,
765, 700, m/e 286, 229, 195 and 104, δ 7.0 (4H, s), 7.0 (4H, d, J 12 Hz) and 9.0 (9H, d, J 16 Hz) (Found: C, 75.3; H, 8.1; P, 10.7. Requires C, 75.5; H, 8.1; P, 10.8%).

**Alkaline Hydrolysis of Benzyldi-t-butylichlorophosphine**

Benzyldi-t-butylichlorophosphorane (0.005 mol) was heated to 120° for 2.5 h. The residue was treated with alkaline hydrogen peroxide, and after acidification and extraction with chloroform it yielded benzyldi-t-butylyphosphinic acid (0.4 g), m.p. 168-171°, δ max. 3030, 3010, 1260, 1130, 970, 835, 780 and 700 cm⁻¹, m/e 212, 155, 121, δ 1.4 (1H, s), 2.8 (5H, s), 7.0 (2H, d, J 14 Hz) and 9.0 (9H, d, J 16 Hz)

(Found: C, 62.4; H, 7.94; P, 14.36. C₇₁₄₁₇O₂P requires C, 62.4; H, 8.0; P, 14.6%).

**Preparation of Benzyldi-t-butylyphosphine**

Benzyllithium (0.04 mol in toluene) was added to the chlorodi-t-butylyphosphine (3.2 g; 0.018 mol) in toluene (50 ml) and the solution was kept at 80° for 9.5 h. The cooled solution was washed with water and dried. Distillation gave benzyldi-t-butylyphosphine (40%), b.p. 126-130°/0.25 mm, δ max. 1600, 1500, 1480, 1390, 1370, 1170, 810, 760, and 700 cm⁻¹, δ 3.2 (5H, m), 7.5 (2H, d, J 2 Hz), and 9.2 (18H, d, J 12 Hz). The methiodide had m.p. 205° (decomp), δ 2.6 (5H, m), 5.8 (2H, d, J 14 Hz), 7.9 (3H, d, J 12 Hz), and 8.5 (18H, d, J 14 Hz)

(Found: C, 50.5; H, 7.5; P, 8.1. C₁₆₂₈₁₇P requires C, 50.8; H, 7.4; P, 8.2%).

**Reaction of Benzyldi-t-butylyphosphine with Chlorine**

Chlorine (0.006 mol) in carbon tetrachloride (8 ml) was added to benzyldi-t-butylyphosphine (1.1 g; 0.006 mol). On removing the solvent and treatment with methanolic methoxide or deuterated ethanolic ethoxide,
the residue yielded benzyl-di-t-butylphosphine oxide, identified by its i.r. and n.m.r. spectra.

**Reaction of Chlorodi-t-butylphosphine and Sodium Methoxide**

Sodium hydride (0.9g; 0.0366 mol) was added slowly to dry methanol (0.59; 0.0183 mol) in ether, then chlorodi-t-butylphosphine (3.3g; 0.0183 mol) in ether was added. After stirring at room temperature for 0.5h, distillation yielded methyl-di-t-butylphosphinite 2.5g b.p. 37-38°/2.5mm, \( \nu_{max} \) 1470, 1362, 1173, 1050, 1010, 805 and 720 cm\(^{-1}\), \( \tau \) 6.4 (3H,d, \( \Delta \) \( \nu_{PH} \) 12Hz) and \( \delta \) 8.9 (18H,d, \( \Delta \) \( \nu_{PH} \) 12Hz).

**Reaction of Methyl Di-t-butylphosphinite with Methyl Iodide**

Excess of methyl iodide was added slowly to methyl di-t-butylphosphinite cooled in ice. On removing the unreacted methyl iodide and distillation, di-t-butylmethylphosphine oxide was obtained quantitatively, b.p. 104° (bath temperature) /2.5mm, \( \nu_{max} \) 1480, 1315, 1290, 1165, 872, 815, 735 and 675 cm\(^{-1}\), \( \tau \) 8.6 (3H,d, \( \Delta \) \( \nu_{PH} \) 11Hz) and \( \delta \) 8.7 (18H,d, \( \Delta \) \( \nu_{PH} \) 14Hz) (Found: C, 61.0; H, 12.1; P, 17.4. \( \text{C}_{9}\text{H}_{21}\text{O} \) requires C, 61.5; H, 11.9; P, 17.6%).

**Reaction of Methyl Di-t-butylphosphinite with Sulphur**

Sulphur was added to methyl di-t-butylphosphinite (0.6g; 0.0034 mol) in dry benzene (1ml). On filtration and distillation \( \text{O-methyl-di-t-butylphosphinothioate} \) was obtained (80%), b.p. 107° (bath temperature) /4mm, m.p. 27-29°, \( \nu_{max} \) 1465, 1380, 1355, 1035, 1000, 800, 748 and 670 cm\(^{-1}\), \( \tau \) 6.4 (3H,d, \( \Delta \) \( \nu_{PH} \) 12Hz) and \( \delta \) 8.7 (18H,d, \( \Delta \) \( \nu_{PH} \) 15Hz) (Found: C, 52.3; H, 10.0; P, 15.1. \( \text{C}_{9}\text{H}_{21}\text{OPS} \) requires C, 52.0; H, 10.1; P, 14.9%).

**Preparation of Phenyl Di-t-butylphosphinite**

Chlorodi-t-butylphosphine (3.6g; 0.02 mol) was added slowly to sodium
phenolate (2.3g; 0.02 mol) in dimethylformamide (10ml) at room
temperature and the mixture was stirred at room temperature for 0.5h.
Distillation then gave phenyl di-t-butylphosphinite (50%) b.p.
92-95°/0.2mm., \( \nu_{\text{max}} \) 1230 and 870 cm\(^{-1} \), \( \tau \) 2.8 (5H,m) and 8.8 (18H,d,
\( \downarrow_{\text{PH}} \) 12Hz) (Found: C, 70.4; H, 9.7; P,12.9. \( \text{C}_{14} \text{H}_{23} \text{OP} \) requires C, 70.6;
H, 9.7; P, 13.0%).

Preparation of O-Phenyl Di-t-butylphosphinothioate

Sulphur (0.12g; 0.0037 mol) was added to phenyl di-t-butylphosphinite
(0.09g, 0.0037 mol) in benzene (5ml) to give an exothermic reaction.
Evaporation and crystallization of the residue from petrol (60-80°) gave
O-phenyl di-t-butylphosphinothioate, m.p. 53-54°, \( \nu_{\text{max}} \) 1590, 1390,
1370, 1200, 1160, 900, 810, 760, 730, 680 and 625 cm\(^{-1} \), \( \tau \) 2.7 (5H,s)
and 8.6 (18H,d,\( \downarrow_{\text{PH}} \) 14Hz) (Found: C, 62.4; H, 8.3; P,11.5. \( \text{C}_{14} \text{H}_{23} \text{OPS} \) requires
C, 62.2; H, 8.5; P, 11.5%).

Reaction of Phenyl Di-t-butylphosphinite with Chlorine

Chlorine (0.4g; 0.0055 mol) in carbon tetrachloride (8 ml) was added
to phenyl di-t-butylphosphinite (1g; 0.0042 mol) and the solution was
stirred at room temperature for 2h. Methanol (0.5 ml) was then added.
After a further 2 h the solution showed no phosphoryl absorption in the
i.r. spectrum. Solvent was removed and the crystalline residue was
treated with water and extracted with chloroform to give phenyl di-t-
butylphosphinite (87%), b.p. 130-140° (bath temperature) /0.2 mm., \( \nu_{\text{max}} \)
1600, 1200, 920, 820, 760, 730, 690 and 670 cm\(^{-1} \), \( \tau \) 2.8 (5H,m), and
8.8 (18H,d,\( \downarrow_{\text{PH}} \) 14Hz) (Found: C, 66.4; H, 9.9; P,12.2. \( \text{C}_{14} \text{H}_{23} \text{OP} \) requires
C, 66.2; H, 9.7; P, 12.2%).

Reaction of Phenyl Di-t-butylphosphinite with Methyl Iodide

Phenyl di-t-butylphosphinite (1g; 0.0042 mol) and methyl iodide were
set aside at room temperature overnight. The resulting solid gave
methylphenoxydi-t-butylphosphonium iodide, m.p. 218-218.5° (from chloroform-ethyl acetate), \( \nu \max 1600, 1590, 1210, 1170, 960, 900, 790, 770 \) and 700 cm\(^{-1}\), \( \tau 2.8 \) (5H, m), 7.4 (3H, d, 3 \( \rho H \)), and 8.3 (18H, d, 3 \( \rho H \)) (Found: C, 47.6; H, 6.7; P, 8.3. \( C_{15}H_{26}IOP \) requires C, 47.4; H, 6.8; P, 8.2%). The salt was unchanged after being refluxed overnight in aqueous solution.

**Reaction of Phenyl Di-t-butylphosphinite with Benzyl Bromide**

Phenyl di-t-butylphosphinite (1g; 0.0042 mol) and benzyl bromide (1g; 0.006 mol) were heated at 100° for 1 h. Crystallization from chloroform-ethyl acetate gave benzylphenoxy-di-t-butylphosphonium bromide, m.p. 189-192°, \( \nu \max 1595, 1585, 1205, 1160, 1075, 945, 815, 780, 760 \) and 695 cm\(^{-1}\), \( \tau 2.8 \) (10H, m), 5.9 (2H, d, 3 \( \rho H \)), and 8.4 (18H, d, 3 \( \rho H \)) in trifluoroacetic acid (Found: C, 61.3; H, 7.1; P, 7.8. \( C_{21}H_{29}BrO_{2}P \) requires C, 61.5; H, 7.3; P, 7.6%). The salt was unchanged when refluxed in water. Hydrolysis with 2N-sodium hydroxide for 3 days gave benzylid-di-t-butylphosphine oxide, m.p. and mixed m.p. 115-117°.

**Reaction of Phenyl Di-t-butylphosphinite with para-Nitrobenzyl Bromide**

Phenyl di-t-butylphosphinite (1g; 0.0042 mol) and p-nitrobenzyl bromide (1g; 0.0046 ml) were heated at 100° for 1 h. Crystallization from chloroform-ethyl acetate gave p-nitrobenzylphenoxydi-t-butylphosphonium bromide m.p. 197-198°, \( \nu \max 1600, 1585, 1510, 1340, 1210, 1180, 1165, 955, 760, \) and 690 cm\(^{-1}\), \( \tau 1.6 \) (m) (total 9H), 4.5 (2H, d, 3 \( \rho H \)), and 8.4 (18H, d, 3 \( \rho H \)) in trifluoroacetic acid (Found: C, 55.4; H, 6.4; P, 7.0. \( C_{21}H_{29}BrNO_{3}P \) requires C, 55.5; H, 6.4; P, 6.8%). The salt (128g; 0.0028 mol) and benzaldehyde (0.8g; 0.0075 ml) in methanol (10ml) in which sodium (0.07g; 0.003 g-atom) had been dissolved were kept at 60° for 24 h. Removal of solvent and chromatography of the residue on alumina gave 4-nitrostilbene (0.3g), m.p. 148-152°, phenyl di-t-butylphosphinate (0.3g) identified by i.r. and n.m.r. spectra, and p-nitrobenzylid-di-t-
butylphosphine oxide (0.113g) m.p. 198-200° (petrol), \( \nu \) max. 1600, 1510, 1340, 1150, 810 and 695 cm\(^{-1}\), \( \tau \) 1.9-2.4 (4H,m) 6.7 (2H,d, \( \delta \) 10Hz) and 8.7 (18H,d, \( \delta \) 14Hz), m/e 297, 240, 183 and 161 (Found: C, 60.4; H, 8.05; P, 9.9. \( \text{C}_{15}\text{H}_{24}\text{NO}_{3}\text{P} \) requires C, 60.5; H, 8.1; P, 10.05%). This oxide (88%) was also obtained on refluxing the salt in 2N-sodium hydroxide for 3h.

**Reaction of Phenyl Di-t-butylphosphinite with Benzyl-Lithium**

Benzyl-lithium (0.0025 mol) in toluene (6ml) was added slowly to phenyl di-t-butylphosphinite (0.85g; 0.0025 mol) in toluene (10 ml). Excess methyl iodide was added and the mixture was left stirring for 2h at room temperature. After washing the suspension with chloroform and evaporation, the residue yielded benzyl-di-t-butylmethylyphosphonium iodide (50%), m.p. 174-177°, \( \nu \) max. 1587, 1380, 1311, 1205, 1170, 1025, 960, 900, 810, 785, 770 and 695 cm\(^{-1}\), \( \tau \) 2.7 (5H,s), 5.8 (2H,d, \( \delta \) 14Hz), 7.9 (3H,d, \( \delta \) 14Hz) and 8.5 (18H,d, \( \delta \) 16Hz) (Found: C, 39.0; H, 9.3; P, 10.7. \( \text{C}_{10}\text{H}_{28}\text{IP} \) requires C, 39.2; H, 9.15; P, 10.1%).

**Attempted Reaction of Methyl Di-t-butylphosphinite with Diacetyl**

Diacetyl (0.40g; 0.0047 mol) was added to methyl di-t-butylphosphinite (0.82g; 0.0047 mol) and the mixture was stirred at room temperature for 1 h, and then stirred at 60° for an hour. N.m.r. analysis after each hour showed that a deoxygenation reaction forming methyl di-t-butylphosphinate was proceeding slowly. The same type of reaction occurred in the attempt to react phenyl di-t-butylphosphinite with diacetyl.

**Reaction of Benzyl-di-t-butylphosphine and 2-Nitro-Biphenyl**

Benzyl-di-t-butylphosphine (2.36g; 0.01 mol) and 2-nitro-biphenyl (0.5g; 0.0025 mol) were heated together at 200° for 24 h. After cooling,
excess methyl iodide in benzene was added to quaternize any unreacted phosphine. Hot filtration, to remove any benzyl di-t-butylmethylphosphonium iodide, followed by chromatography on alumina yielded carbazole (66%) identified by m.p. and mixed m.p. (25% benzene-petrol) and benzylid-t-butylphosphine oxide (60%), identified by i.r. and m.p. (100% benzene).

Preparation of t-Butyldichlorophosphine

T-Butyldichlorophosphine was prepared by the method of Voskuil and Arens.\(^5\)

Yield 40% b.p. 143-146°/760 mm, m.p. 50-51°, literature 145-150°/760, m.p. 49°.

Preparation of Diphenyl t-Butylphosphonite

T-Butyldichlorophosphine (4.8; 0.03 mol) in dry dimethylformamide was added slowly to sodium phenolate (7g; 0.06 mol) dissolved in dimethylformamide (35 ml). The mixture was stirred for 1 h at 80°. Distillation yielded diphenyl t-butylphosphonite (71%), b.p. 142-146°/1 mm., \(\lambda_{max}\) 1605, 1500, 1470, 1240, 1215, 1200, 1170, 1078, 910, 885, 865, 775, 725 and 700 cm\(^{-1}\), \(\tau\) 2.9 (10H, m) and 8.8 (9H, d, \(J_p = 14\) Hz).

Preparation of O,O-Diphenyl t-Butylphosphonothioate

Diphenyl t-butylphosphonite (1.3g; 0.005 mol), sulphur (0.32g; 0.01 mol) and anhydrous aluminium chloride (small crystal) were heated together at 100° for 12 h. Residue from ether extraction yielded O,O-diphenyl t-butylphosphonothioate on crystallization from petrol (60-80°) (90%), m.p. 52-55°, \(\lambda_{max}\) 1590, 1361, 1210, 1180, 1160, 1021, 920, 900, 823, 770, 735 and 685 cm\(^{-1}\), \(\tau\) 2.9 (10H, m) and 8.5 (9H, d, \(J_p = 18\) Hz) (Found: C, 72.9; H, 3.9; P, 11.9. C\(_{16}\)H\(_{10}\)PS requires C, 72.5; H, 3.87; P, 11.7%).

Reaction of Diphenyl t-Butylphosphonite with Methyl Iodide

Diphenyl t-butylphosphonite (2g; 0.0073 mol) was refluxed in methyl iodide for 3 days. Filtering yielded t-butylmethyldi-phenoxyporphosphonium iodide (73%), \(\lambda_{max}\) 1585, 1400, 1310, 1395, 1385, 1375, 1369, 1355, 1020, 970, 885, 800
778, 768 and 690 cm⁻¹, 2.6 (10H, m), 6.2 (3H, d, J = 18 Hz) and 8.2 (9H, d, J = 20 Hz) (Found: C, 49.0; H, 5.2; P, 7.3. C₁₁H₁₇O₂P requires C, 49.1; H, 5.3; P, 7.5%). Hydrolysis of this salt with 2N-sodium hydroxide gave on chromatography phenol and phenyl t-butyldimethylphosphinates, b.p. 130-135° (bath temperature)/0.4 m.m., 1570, 1430, 1250, 1025, 1015, 828 and 700 cm⁻¹, 2.9 (5H, s), 8.4 (3H, d, J = 12 Hz) and 8.6 (3H, d, J = 16 Hz) (Found: C, 62.9; H, 7.9; P, 14.2. C₁₇H₁₆O₃P requires C, 62.3; H, 8.1; P, 14.6%).

Reaction of Diphenyl t-Butylphosphonite with Benzyl Bromide

Diphenyl t-butylphosphonite (1.37 g; 0.005 mol) and benzyl bromide (0.86 g; 0.005 mol) were heated to 100° for 2.5 days. N.m.r. indicated the presence of benzyl-t-butyldi-phenoxyphosphonium bromide, but it was too difficult to purify. Hydrolysis, by refluxing it with N-sodium hydroxide for 48 h, removal of the solvents and extraction with methylene chloride, yielded benzyl t-butylphenoxyphosphine oxide (40%) which served to characterize the original salt, m.p. 69-73°, 1590, 1490, 1455, 1205, 915, 900, 828, 758 and 700 cm⁻¹, 2.85 (10H, m), 6.6 (2H, d, J = 14 Hz) and 8.63 (9H, d, J = 16 Hz) (Found: C, 70.8; H, 7.3; P, 10.6. C₁₁H₁₇O₂P requires C, 70.8; H, 7.3; P, 10.7%).

Reaction of Diphenyl t-Butylphosphonite with Diacetyl

Diphenyl t-butylphosphonite (1.37 g; 0.005 mol) and diacetyl (0.43 g; 0.005 mol) were stirred at room temperature for 1 h, n.m.r. showed no change. Then heated to reflux for 5 h. On cooling, crystals appeared, which were diphenyl t-butylphosphonate m.p. 132-133°, 1590, 1490, 1475, 1455, 1400, 1265, 1215, 1185, 1165, 920, 830, 765, 731 and 695 cm⁻¹, 2.8 (10H, m) and 8.6 (9H, d, J = 18 Hz) (Found C, 66.0; H, 6.8; P, 11.0. C₁₇H₁₉O₃P requires C, 66.2; H, 6.56; P, 10.7%)

Reaction of Diphenyl t-Butylphosphonite with Phenanthraquinone

Phenanthraquinone (1.04 g; 0.005 mol) and diphenyl t-butylphosphonite (1.37 g; 0.005 mol) were heated together for 9 h at 60°. The reaction
mixture was washed with dry hexane, in a dry-box, and evaporation of the supernatant liquor yielded diphenyl t-butylphosphonate (60%) which was identified by its ir. and n.m.r. spectra.

Preparation of o-Phenylene t-Butylphosphonite

Sodium hydride (4.8g; 0.1 mol-50% dispersion) was added slowly to catechol (11g; 0.1 mol) dissolved in ether. The suspension was refluxed for 1 h. t-Butyldichlorophosphine (7.95g; 0.05 mol), dissolved in ether (20 ml), was added and refluxing was continued for a further hour. Removal of solvents and distillation yielded o-phenylene t-butylphosphonite (50%), b.p. 68-72°/1 mm, \( \nu \) max. 1475, 1360, 1333, 1230, 1090, 1010, 830, 800, 740 and 710 cm\(^{-1} \), \( \tau \) 3.3 (4H, m) and 9.4 (9H, d, \( \delta \) 1.51 HZ).

Reaction of o-Phenylene t-Butylphosphonite with Sulphur

Sulphur (0.32g; 0.01 mol) and o-phenylene t-butylphosphonite (1.96g; 0.01 mol) were gently warmed together. An exothermic reaction took place and extraction of the residue with chloroform yielded o-phenylene t-butylphosphonothioate (75%), m.p. 65-62° (petrol 60-80°), \( \nu \) max. 1363, 1330, 1230, 1010, 865, 780, 740 and 720 cm\(^{-1} \), \( \tau \) 3 (4H, m) and 8.6 (9H, d, \( \delta \) 20 HZ) (Found: C, 51.0; H, 5.5; P, 13.0. \( \text{C}_{10} \text{H}_{13} \text{O}_{2} \text{PS requires C, 50.5; H, 5.7; P, 13.6%} \))

Reaction of o-Phenylene t-Butylphosphonite with Methyl Iodide

o-Phenylene t-butylphosphonite (0.49g; 0.0025 mol) and excess methyl iodide were refluxed in benzene for 12 h. Filtering yielded the hygroscopic t-butyl o-phenylene phosphonite methiodide m.p. 166-170°, \( \nu \) max. 1300, 1258, 1155, 1020, 950, 800 and 735 cm\(^{-1} \), \( \tau \) 3.4 (4H, s) 8.6 (3H, d, \( \delta \) 13 HZ) and 9.0 (9H, d, \( \delta \) 18 HZ). Hydrolysis of this salt with 2N-sodium hydroxide in ethanol, and chromatography on silica yielded catechol (50% ether-petrol) and t-butylmethylphosphinic acid (10% methanol-ether) characterized as its anilinium salt m.p. 124-127° (chloroform-ethylacetate).
$\nu_{\text{max}}$ 1630, 1600, 1580, 1560, 1360, 1150, 1115, 1030, 960, 820, 750 and 690 cm$^{-1}$, $\tau$ - 0.5 (3H,s), 2.8 (5H,m), 8.2 (3H,d, J$\text{P-H}$ 19Hz) and 8.9 (9H,d, J$\text{P-H}$ 18Hz) in trifluoroacetic acid. (Found: C, 55.3; H, 8.5; P, 12.6. C$_{11}$H$_{20}$O$_2$NP requires C, 55.2; H, 8.37; P, 12.9%)

**Reaction of o-Phenylene t-Butylphosphonite and Diacetyl**

Diacetyl (0.28g; 0.0033 mol) was added to o-phenylene t-butylphosphonite (0.6 g; 0.0033 mol) in methylene chloride (3mls). The mixture was refluxed for 2 h. Removal of the solvent and crystallization of the residue from petrol (40-60$^0$) yielded the adduct (111) (80%), m.p. 147-147.5$^0$, $\nu_{\text{max}}$ 3100, 3050, 1445, 1385, 1350, 1260, 1225, 1138, 1010, 992, 850, 815, 742 and 650 cm$^{-1}$, m/e 282, 212, 156, 139.

$\tau$ 3.2 (4H,m), 8.1 (6H,s) and 8.7 (9H,d, J 20Hz), $^{31}$P + 19 p.p.m. (Found: C, 60.0; H, 6.85; P, 10.8. C$_{14}$H$_{19}$O$_2$NP requires C, 59.5; H, 6.75; P, 11.0%)

**Preparation of Tris(diethylamino)phosphine**

Tris(diethylamino)phosphine was prepared by the method of Steubbe and Laukelma. Yield: 73% b.p. 107-111$^0$/3mm. Literature 120-122$^0$/10mm.

**Preparation of Chlorobis(diethylamino)phosphine**

Chlorobis(diethylamino)phosphine was prepared by the method of Noth and Vetter. Yield: 67% b.p. 100-106$^0$/7mm.

**Preparation of t-Butylbis(diethylamino)phosphine**

t-Butyl-lithium (70mls; 0.11 mol) was added slowly to chlorobis(diethylamino)phosphine (23.2g; 0.11 mol) in ether (30 ml) cooled in ice. The solution was stirred at room temperature for 1.5 h and distillation in vacuo yielded t-butylbis(diethylamino)phosphine, 56%, b.p. 116-123$^0$/4.15mm, $\nu_{\text{max}}$ 1460, 1370, 1288, 1185, 1010, 915, 900, 790 and 655 cm$^{-1}$, $\tau$ 7.0 (8H,m) and 9.1 (12H,t, J7Hz) and 9.1 (9H,d, J$\text{P-H}$ 14Hz)
Reaction of t-Butylbis(diethylamino)phosphine with Sulphur

Sulphur (0.16g; 0.005 mol) and a crystal of aluminium chloride were added to t-butylbis(diethylamino)phosphine (1g; 0.0043 mol).

After an exothermic reaction, the residue was washed with petrol, filtered; and distillation yielded t-butylphosphonothioic diethylamide (90%) b.p. 150° (bath temperature) /1.25 mm; \( \nu_{\text{max}} \) 1460, 1382, 1200, 1178, 1160, 1025, 940, 815, 800, 710, 685, and 655 cm\(^{-1}\), \( \tau \) 6.8 (7H,m) and 8.8 (21H,m) (Found: C, 44.8; H, 13.6; P, 14.0; requires C, 44.5; H, 13.4; P, 14.3%).

Reaction of t-Butylbis(diethylamino)phosphine with Methyl Iodide

t-Butylbis(diethylamino)phosphine (1.16g; 0.005 mol) was refluxed in methyl iodide for 24 h. The residue, after removal of the solvent, yielded an oil; t-butylbis(diethylamino)methylphosphonium iodide 67%, which eventually crystallized, m.p. 171-173°, \( \nu_{\text{max}} \) 1310, 1205, 1150, 1100, 1015, 960, 795 and 681 cm\(^{-1}\), \( \tau \) 6.8 (6H,m), 7.8 (3H,d, \( J_{\text{H,H}} \) 11Hz) and 8.6 (21H d on t,P-H, 16Hz, 36Hz) (Found: C, 41.4; H, 8.4; P, 8.2; N, 7.6. \( C_{15}H_{32}PN_2I \) requires C, 41.7; H, 8.5; P, 8.3; N, 7.4%).

Attempted Reaction of t-Butylbis(diethylamino)phosphine with Methanol

t-Butylbis(diethylamino)phosphine (1.16g; 0.005 mol) and methanol (1.6g; 0.05 mol) were added to a Carius tube under an atmosphere of dry oxygen free nitrogen and heated for 2 days at 120°. The N.m.r. spectrum of the product, after removal of the solvents, showed a very complex pattern and the starting phosphine was recovered in 50% yield.

Preparation of Diethyl t-Butylphosphonite

Sodium hydride (4.8g; 0.1 mol) was added slowly to ethanol (4.6g; 0.1 mol) in ether (10 ml). Then t-butyldichlorophosphine (7.95g; 0.05 mol) in
ether (30 mls), was added dropwise. After refluxing for 1 h and removal of the solvents, distillation yielded diethyl t-butyl phosphonite (26%) b.p. 46-50°/15mm, \( \nu \) max. 1480, 1390, 1368, 1253, 1220, 1100, 1030, 940, 835, 810, 750 cm\(^{-1}\), \( \tau \) 6.4 (4H,m), 9.0 (6H,d, J\(_{\text{p-H}}\) 7.5Hz) and 9.3 (9H,d, J\(_{\text{p-H}}\) 14Hz)

**Reaction of Diethyl t-Butylphosphonite with Methyl Iodide**

Diethyl t-butylphosphonite (1.58 g; 0.01 mol) was reacted with an excess of methyl iodide in benzene. Removal of the solvents and distillation yielded the hygroscopic, ethyl t-butylmethyl phosphinate 60% b.p. 80-84°/1.5mm, \( \nu \) max. 1480, 1392, 1364, 1300, 1240, 1200, 1040, 950,880, 825, 775, and 730 cm\(^{-1}\), \( m/e \) 164, 149, 119, 108, 76.0 (4H,m), 8.7 (3H,d, J\(_{\text{p-H}}\) 11Hz) 8.8 (3H,t, J\(_{\text{p-H}}\) 8Hz) and 8.9 (9H,d, J\(_{\text{p-H}}\) 16Hz) (Found: C, 50.8; H, 10.51; P,18.6.

\( C_{7}H_{17}O_{2}P \) requires C, 51.2; H, 10.35; P, 18.9%).

**Reaction of Diethyl t-Butylphosphonite with Sulphur**

Sulphur (0.5g; 0.0156 mol) was added to diethyl t-butylphosphonite (1.58g; 0.01 mol). Chromatography on alumina and elution with petrol yielded 0,0-diethyl t-butylphosphonothioate in 93% yield, b.p. 121-124°/2mm, \( \nu \) max. 1480,1460,1390, 1361,1160, 1040, 950,825, 775 and 690 cm\(^{-1}\), \( m/e \) 210,165,120,63,76.7 (4H,m), 8.7 (6H,t, J\(_{\text{p-H}}\) 6Hz) and 8.8 (9H,d, J\(_{\text{p-H}}\) 18Hz). (Found: C, 45.8; H, 9.09; P, 14.8. \( C_{7}H_{17}O_{2}PS \) requires C, 45.79; H,9.05; P,14.79%)

**Reaction of Diethyl t-Butylphosphonite and Diacetyl**

Diacetyl (0.86g; 0.01 mol) was added to diethyl t-butylphosphonite (1.78g; 0.01 mol) with stirring. After cooling the exothermic reaction, the mixture was warmed to 60° for 1.5 h. N.m.r. and i.r. spectroscopy showed that the adduct (114) was formed, \( \nu \) max. 1480, 1388, 1282, 1244, 1150,1100, 1060, 990,955, 920, 830, 815 and 730 cm\(^{-1}\), \( \tau \) 6.2(4H,m), 8.2 (5H,s) and 8.8 (6H,t, J\(_{\text{p-H}}\) 7Hz) and 8.8 (9H,d, J\(_{\text{p-H}}\) 18Hz) at room temperature, \(^{31}P + 6 p.p.m. \)
Reaction of Diethyl t-Butylphosphonite with Benzylidene Acetylacetone

Benzylidene acetylacetone (0.8g; 0.0042 mol) was added to diethyl t-butylphosphonite (0.75g; 0.042 mol). There was a slight exothermic reaction. The reactants were stirred for 55 h at room temperature. N.m.r. and i.r. spectroscopy showed that the adduct (115) was formed, ν max. 1655, 1560, 1370, 1320, 1145, 1100, 1060, 940, 820 and 700 cm⁻¹, C (at room temperature) 2.8 (5H,s), 5.8 (4H,m), 6.7 (1H,m), 7.5 (3H,s), 8.2 (3H,s), 8.8 (9H,d, J p-H 18HZ) and 9.0 (6H,t, 7HZ), 31p 4 p.p.m.
The adduct (115) reacted with one mole of water to give the corresponding 8-Diketone Phosphonate (116) mp 109-111°, ν max. 1723, 1695, 1195, 1145, 1035, 953, 825, 793, 758 and 705 cm⁻¹, m/e 367, 296, 293, 281, 239,2.8 (5H,m), 5.6 (3H,m), 7.7 (3H,s), 8.2 (3H,s), 8.7 (3H,t, 7HZ) and 8.9 (9H,d, J p-H 16HZ); Found: C, 63.6; H, 9.2; P, 8.9. CgH₀₁³O₅P requires C, 64.0; H, 8.0; P, 9.2%.
The Preparation of Dimethyl t-Butylphosphonite

Dimethyl t-butylphosphonite was prepared in the same manner as the diethyl derivative, Yield: 35%, bp. 86-90°/220 mm., ν max. 1460, 1390, 1360, 1260, 1100, 1050, 945, 840, 740 cm⁻¹, c6.6 (6H,d, J p-H 12HZ) and 9.4 (9H,d, J p-H 12HZ) 31p-196 p.p.m.

Reaction of Dimethyl t-Butylphosphonite with Methyl Iodide

t-Butylphosphonite (1.5g; 0.01 mol) was stirred with an excess of methyl iodide for 3 h. Removal of the solvents and distillation yielded methyl t-butylmethylphosphinate (79%), b.p. 120-122°/5mm., ν max. 1480, 1300, 1238, 1203, 1040, 885, 825, 785 and 730 cm⁻¹ and c6.3 (3H,d, J p-H 10HZ), 8.6 (3H,d, J p-H 12HZ) and 8.8 (9H,d, J p-H 14HZ) Found: C, 53.5; H, 11.0; P, 23.6. CgH₁₅O₅P requires C, 53.8; H, 11.2; P, 23.2%.)
Reaction of Dimethyl t-Butylphosphonite with Sulphur

Dimethyl t-butylphosphonite (1.5 g; 0.01 mol) was reacted with sulphur (0.5 g; 0.0156 mol). Chromatography on alumina and elution with petrol yielded 0,0-dimethyl t-butylphosphonothioate (75%) b.p. 98-101°/2.5 mm, \( \nu_{max} \) 1480, 1470, 1360, 1160, 1045, 930, 820, 760 and 702 cm\(^{-1}\), \( \tau \) 6.0 (6H, d, J = 12 Hz) and 9.0 (9H, d, J = 14 Hz) (Found: C, 40.0; H, 8.1; P, 17.5. \( C_{6}H_{10}O_{2}PS \) requires C, 39.6; H, 8.25; P, 17.1%).

Reaction of Dimethyl t-Butylphosphonite with Diacetyl

Dimethyl t-butylphosphonite (0.75 g; 0.005 mol) was added to diacetyl (0.43 g; 0.005 mol) and stirred for 2 h at room temperature. N.m.r. and i.r. spectroscopy showed that the adduct (118) was formed, \( \nu_{max} \) 1480, 1386, 1280, 1245, 1150, 1105, 1062, 991, 955, 920, 830, 815 and 730 cm\(^{-1}\), \( \tau \) 6.0 (6H, d, J = 12 Hz), 8.4 (6H, s) and 8.8 (9H, d, J = 14 Hz), \( 31P + 6 \) p.p.m.

Reaction of Dimethyl t-Butylphosphonite with Benzylidene Acetylacetone

Dimethyl t-butylphosphonite (0.75 g; 0.005 mol) was added to benzylidene acetylacetone (0.94 g; 0.005 mol). The reactants were stirred at room temperature for an hour and warmed to 50° for a further h. N.m.r. and i.r. spectroscopy showed that the adduct (119) was formed. \( \nu_{max} \) 1655, 1560, 1370, 1320, 1140, 1085, 1065, 940, 825, 700 cm\(^{-1}\), \( \tau \) 2.7 (5H, s), 5.8 (1H, d, J = 13 Hz), 6.3 (3H, d, J = 12 Hz), 6.8 (3H, d, J = 8 Hz), 7.4 (3H, s), 8.2 (3H, s) and 8.8 (9H, d, J = 18 Hz), \( 31P + 0.5 \) p.p.m. and + 7 p.p.m. (two isomers). The adduct (119) reacted with a mole of water to give the corresponding B-diketone phosphonate, mp. 126-129° (petrol 40-60°).

\( \nu_{max} \) 1695, 1227, 1197, 1180, 1045, 790, 764 and 705 cm\(^{-1}\), m/e 324, 293, 281, 267 and 223, \( \tau \) 2.6 (5H, m), 5.7 (2H, m), 6.4 (3H, d, J = 10 Hz), 7.8 (3H, s), 8.2 (3H, s),
9.2 (9H,d, J p-H 16Hz) (Found: C, 63.5; H, 7.3; P, 10.0; C17H26O4P requires C, 63.0; H, 7.7; P, 9.6%).

**Attempted reaction of Dimethyl t-Butylphosphonite and Methyl Vinylketone**

Methyl vinylketone (0.466g; 0.0066 mol) was added to dimethyl t-butylphosphonite (10g; 0.0066 mol) and after stirring for 1 h at room temperature, the reaction mixture was warmed to 40° for 1 h. The 1H m.m.r. spectrum was too complex for analysis. The reaction was repeated but the reactants were mixed and stirred at -40°, but the 1H m.m.r. was equally complex.

**Preparation of t-Butyl Ethylene Phosphonothioite**

Sodium hydride (4.8g; 0.2 mol) was added slowly to β-mercaptoethanol (3.9g; 0.05 mol) in dry ether (30 mls). The mixture was refluxed for 1.5 h and t-Butyldichlorophosphine (7.95g; 0.05 mol) in ether (30 mls) was added. After refluxing for 3.5 hr, distillation yielded t-butyl ethylene phosphonothioite (60%), b.p. 48-52°/0.5mm. \( \nu_{max} \) 1460, 1357, 1025, 1018, 934, 850, 798, and 710 cm\(^{-1}\), \( \tau 5.4 \) (1H, m), 6.0 (1H, m), 7.1 (2H, m) and 9.1 (9H, d, J p-H 13Hz) \( ^{31}P -174 \) ppm.

**Reaction of t-Butyl Ethylene Phosphonothioite with Sulphur**

Sulphur (0.256g; 0.008 mol) was added to t-butyl ethylene phosphonothioite (1.0g; 0.006 mol) together with a trace of aluminium chloride. An exothermic reaction occurred, and chromatography followed by elution with petrol yielded t-butyl ethylene phosphonothiolothioate, (72%) m.p. 94.5-97°, b.p. 145-149°/1.5 mm. \( \nu_{max} \) 1360, 1270, 1027, 1001, 940, 855, 788 and 680 cm\(^{-1}\), \( \tau 5.3 \) (2H, m), 6.5 (2H, m) and 8.6 (9H, d, J p-H 21Hz) (Found: C, 37.0; H, 7.4; P, 16.1. C\(_6\)H\(_{13}\)O\(_2\)S\(_2\) requires C, 36.8; H, 7.4; P, 15.8%).
Reaction of t-Butyl Ethylene Phosphonothioite with Methyl Iodide

t-Butyl ethylene phosphonothioite (1.64 g; 0.01 mol) was added to an excess of methyl iodide and warmed to 40° for 1 h. Removal of the solvents yielded 5-2-iodoethyl t-butylmethylphosphonothiolate which decomposed on distillation, \( \nu_{\text{max}} \) 1460, 1363, 1290, 1174, 1010, 870, 815 and 740 cm\(^{-1} \), \( m/e \) 306, 179, 151, 119, 16 (4H, m), 8.3 (3H, d, \( J_{\text{p-H}} \) 11 Hz) and 8.8 (9H, d, \( J_{\text{p-H}} \) 18 Hz).

Reaction of t-Butyl Ethylene Phosphonothioite with Diacetyl

Diacetyl (0.86 g; 0.01 mol) was added to t-butyl ethylene phosphonothioite (1.64 g; 0.01 mol) cooled with ice. Stirred at room temperature for 1 h. N.m.r. and i.r. spectroscopy showed that the adduct \( 126 \) had been formed. \( \nu_{\text{max}} \) 1490, 1435, 1400, 1270, 1235, 1150, 1055, 1000, 840, 820 and 680 cm\(^{-1} \), 5.6 (1H, m), 6.4 (1H, m), 7.2 (2H, m), 8.2 (3H, s), 8.3 (3H, s) and 8.7 (9H, d, \( J_{\text{p-H}} \) 20 Hz) 31p-24 p.p.m.

Thermolysis of the adduct (126)

The above adduct (6.25 g; 0.025 mol) was heated to 140°, a pale yellow liquid, thiiran (88%), was collected, b.p. 52-56°, literature 55-56°, \( \nu_{\text{max}} \) 1445, 1425, 1048, 940, 820 cm\(^{-1} \), 7.7 (s).

Thiiran (0.60; 0.0 mol) was reacted with an excess of methyl iodide by warming to 40° for 1 h and standing overnight. The thiiran methiodide was filtered off, (78%), m.p. 97-98°, \( \nu_{\text{max}} \) 1233, 1155, 1040, 1000 cm\(^{-1} \), 6.7 (3H, m) and 7.4 (4H, s).

The residue, from the thermolysis, yielded the cyclic phosphonate (127) (petrol 40-60°) mp 79-80°, \( \nu_{\text{max}} \) 1610, 1395, 1270, 1285, 1185, 1127, 995, 910, 860, 805 and 715 cm\(^{-1} \), \( m/e \) 190, 136, 133, 86, 108.1 (6H, s) and 8.7 (9H, d, \( J_{\text{p-H}} \) 18 Hz) (Found: C, 50.0; H, 7.6; P, 16.0. \( \text{C}_{8}\text{H}_{15}\text{O}_3\text{P} \) requires C, 50.5; H, 7.9; P, 16.3%).
Reaction of t-Butyl Ethylene Phosphonothioite with Benzylidene Acetylacetone

Benzylidene acetylacetone (1.88g; 0.01 mol) was added to cooled t-butyl ethylene phosphonothioite (1.64g; 0.01 mol) and stirred at 0°C for 1.5 h. The reactants set into a glass so after warming to room temperature, methylene chloride was added and stirring was continued for a further hour. N.m.r. and i.r. spectroscopy indicated that the adduct (121) was formed, \( \nu \) max. 1680, 1600, 1200, 1165, 1110, 1025, 1008, 928, 822, 793 and 700 cm\(^{-1}\), \( \tau \) (at room temperature) 2.7 (5H,s), 5.5(1H,m), 6.0 (4H,m), 7.6 (3H,s), 8.1 (3H,s), 8.6 (4.5H,d, J=20Hz) and 8.9 (4.5H,d, J=18Hz), \( ^{31} \) P = 10 p.p.m.

Thermolysis of adduct (121) at 120°C produced, thiran, identified by b.p., and m.p. of methiodide and a mixture of two isomeric cyclic phosphinates (121a) and (121b), which were separated by fractional crystallization from 50/50 cyclohexane-carbon tetrachloride, m.p. 173-175°C and 148-152°C, \( \nu \) max. 1680, 1695, 1290, 1250, 1208, 1165, 1110, 930, 922, 800 and 700 cm\(^{-1}\), \( \nu \) max. (solution in chloroform) 1700, 1600, 1250, 1145, 950 cm\(^{-1}\), \( \delta \) 292, 277, 235, 171, 154, 129, \( \tau \) 2.7(5H,s), 5.6 (1H,m), 7.5 (3H,d, J=2Hz), 8.1 (3H,s) and 8.7 (9H,d, J=16Hz), and 2.5 (5H,m), 5.2 (1H,m) 7.5 (3H,s), 8.0 (3H,s) and 9.0 (9H,d, J=16Hz), (Found: C, 64.7; 64.2; H, 7.25, 7.4; P, 11.2, 10.7. \( C_{16}H_{21}O_3P \) requires C, 65.8; H, 7.2; P, 10.6%).

Reaction of t-Butyl Ethylene Phosphonothioite with Phenanthraquinone

t-Butyl ethylene phosphonothioite (1.64g; 0.01 mol) was added to phenanthraquinone (2.08g; 0.01 mol) dissolved in methylene chloride (4 mls). The solution was stirred at room temperature for 4 h. N.m.r. spectroscopy showed that the adduct was formed, \( \delta \) 1.6(m), 2.0(m) and 2.4(m) (total 6H), 6.2 (2H,m), 7.2 (2H,m) and 8.6 (9H,d, J=22Hz). Thermolysis of adduct
at 100° for 3 h gave thirian and the corresponding cyclic phosphonate
m.p. 274-277, $\nu_{\max}$ 1277, 1050, 1025, 943, 850, 760, 750 and 693 cm$^{-1}$,
m/e 312, 256, 210, 180, 152,$\delta$ 1.8 (8H,m) and 8.6 (9H,d, $\beta$ H$^1$ 18Hz) (Found:
C, 70.8; H, 4.9; P, 9.66. C$_{16}$H$_{17}$O$_3$P requires C, 69.2; H, 5.4; P, 9.9%).

Preparation of Phenyl Ethylene Phosphonothioite

Dichlorophenylphosphine (17.9g; 0.1 mol) in ether (20ml) was added slowly
to p-mercaptoethanol (7.8g; 0.1 mol) and pyridine (15.4g; 0.2 mol) in ether
(40mls). The mixture was set aside for 1 h. after filtering off the
pyridinium chloride, distillation yielded phenyl ethylene phosphonothioite,
23%, b.p. 110-115°/1mm., $\nu_{\max}$ 1432, 1261, 1155, 1091, 994, 929, 743, 725 and
697 cm$^{-1}, \delta 2.7 (5H,s), 5.9 (2H,m) and 7.2 (2H,m).

Reaction of Phenyl Ethylene Phosphonothioite with Methyl Iodide

An excess of methyl iodide was added to phenyl ethylene phosphonothioite
(1.84g; 0.01 mol) in benzene (3ml). The mixture was stirred for 2 h.
Removal of the solvents yielded S-2-idoethyl phenylmethylphosphinothiolate,
$\nu_{\max}$ 1290,1240, 1195,1110, 875,740 and 690 cm$^{-1}, \delta 2.4 (5H,m), 5.7 (2H,m),
6.8 (2H,m) and 9.1 (3H,d, $\beta$ H$^1$ 12Hz). S-2-Iodoethyl phenylmethylphosphinothiolate
was treated with $\text{N}_2$-Sodium hydroxide, after removal of the solvents and
extraction with methylene chloride, chromatography on alumina yielded
methylphenylphosphinic acid (20% methanol-ether), $\nu_{\max}$ 1460,1440,1375,
1165, 1130, 975, 880, 778, 745 and 700 cm$^{-1}, m/e 128, 113, 51, \delta 2.6 (5H,m),
6.7 (1H,s) and 8.4 (3H,d, $\beta$ H$^1$ 14Hz)

Reaction of Phenyl Ethylene Phosphonothioite with Diacetyl

Diacetyl (0.43g; 0.005 mol) was added to cooled phenyl ethylene
phosphonothioite (0.92g; 0.005 mol). An exothermic reaction occurred
forming a white solid. N.m.r. and i.r. spectroscopy showed that the adduct
(125) was formed, \( \nu_{\text{max.}} \) 1528, 1510, 1438, 1318, 1280, 1190, 1110, 1040, 880, 860 and 740 cm\(^{-1}\); 2.4 (5H,m), 5.6 - 7.6 (4H,m) and 8.3 (3H,s), 8.4 (3H,s), 3.1 p.p.m. - 20 p.p.m.

**Thermolysis of Adduct (125)**

Adduct (125) (0.005 mol) was heated to 100° for 10 h, thiriran was collected and the residue yielded the corresponding cyclophosphonate (35%), \( \nu_{\text{max.}} \) 1620, 1283, 1185, 1128, 995, 910, 860, 805, 740, 670 cm\(^{-1}\); 2.4 (5H,m) and 8.0 (6H,s) (Found: C, 58.0; H, 5.2; P, 15.0. C\(_{12}\)H\(_{22}\)O\(_{3}\)P requires C, 57.2; H, 5.2; P, 14.7%).

**Reaction of Phenyl Ethylene Phophonothioite with Benzylidene Acetylacetone**

Benzylidene acetylacetone (0.98g; 0.005 mol) was added to phenyl ethylene phosphonothioite (0.97g; 0.005 mol) in methylene chloride. An exothermic reaction occurred. N.m.r. and i.r. spectroscopy showed that the adduct was formed, \( \nu_{\text{max.}} \) 1655, 1550, 1370, 1315, 1150, 1050, 940, 910, 800, 730 and 698 cm\(^{-1}\); 2.7 (1OH,m), 5.5 (lH,m), 5.8(m) and 6.3(m) (2H total), 6.7(m) and 7.1(m) (2H total), 7.6 (3H,d, J = 10Hz) and 8.1 (3H,s), 3.1 P-8 p.p.m. This adduct was thermolysed at 100° for 5 h. Thiriran was produced and the residue yielded the corresponding cyclic phosphinate, \( \nu_{\text{max.}} \) 1650, 1600, 1475, 1350, 1201, 1165, 1110, 930, 822, 795, 730, 700 cm\(^{-1}\); 2.8 (1OH,m), 5.3 (1H,d, J = 10Hz), 7.4 (3H,q, J = 2Hz) and 8.1 (3H,d, J = 5Hz) (Found: C, 69.8; H, 8.0; P, 13.8. C\(_{18}\)H\(_{17}\)O\(_3\)P requires C, 69.3; H, 7.8; P, 14.3%).

**Preparation of Methylenedioxbenzoin**

Methylenedioxbenzoin was prepared by the method of Fiesseilmann and Ribka in 81.5% yield, b.p. 120-125°/0.1 mm., literature: 67%, b.p. 124-127°/0.1 mm.
Reaction of Methyleneoxynbenzoin and Trimethyl Phosphite

Methyleneoxynbenzoin (2.08g; 0.01 mol) was added to trimethyl phosphite (1.24g; 0.01 mol) in methylene chloride. The mixture was set aside for 4 h at room temperature. After removal of solvents n.m.r. and i.r. spectroscopy showed that the adduct had been formed m.p. 58-60°, \( \gamma \) max. 1375, 1260, 1140, 1090, 1060, 933, 838, 810 and 795 cm\(^{-1}\), \( \tau \) 2.9 (10H,m), 6.4 (9H,d, \( \delta \) p-\( \text{H} \) 12Hz) and 6.9 (2H,d, \( \delta \) p-\( \text{H} \) 17Hz).

Reaction of Methyleneoxynbenzoin with Dimethyl t-Butylphosphonite

Methyleneoxynbenzoin (0.54g; 0.0025 mol) was added to dimethyl t-butylphosphonite (0.38g; 0.0025 mol). The reactants were stirred at room temperature for 4 h. N.m.r. and i.r. spectroscopy showed that the adduct (123) was formed, \( \gamma \) max. 1478, 1443, 1340, 1262, 1145, 1070, 930, 833, 755 and 695 cm\(^{-1}\), \( \tau \) 2.8 (10H,m), 6.4 (6H,d, \( \delta \) p-\( \text{H} \) 11Hz), 7.0 (2H,d, \( \delta \) p-\( \text{H} \) 15Hz) and 8.7 (9H,d, \( \delta \) p-\( \text{H} \) 18Hz), + 5 p.p.m.

Preparation of Dimethyl Phenylphosphonite

Dichlorophenylphosphine (8.95g; 0.05 mol) was added slowly to a mixture of methanol (3.2g; 0.1 mol) and pyridine (7.9g; 0.1 mol) in ether (20ml). The mixture was stirred for 2h. After filtering off the pyridinium chloride, distillation yielded dimethyl phenylphosphonite (60%), b.p. 75-76°/0.5mm., \( \gamma \) max. 1431, 1235, 1165, 1100, 1030, 840, 818 and 695 cm\(^{-1}\), \( \tau \) 2.5 (5H,m) and 6.4 (6H,d, \( \delta \) p-\( \text{H} \) 10Hz).

Reaction of Methyleneoxynbenzoin and Dimethyl Phenylphosphonite

Methyleneoxynbenzoin (0.62g; 0.003 mol) was added to dimethyl phenylphosphonite (0.425g; 0.003 mol). The reaction was set aside overnight. N.m.r. and i.r. spectroscopy showed the adduct (124) was formed \( \gamma \) max. 1490, 1444, 1268, 1157, 1120, 1070, 1048, 1032, 1015, 931, 825, 755 and 695 cm\(^{-1}\), \( \tau \) 2.8 (15H,m), 6.4 (5H,d, \( \delta \) p-\( \text{H} \) 12Hz) and 6.6 (2H,d, \( \delta \) p-\( \text{H} \) 16Hz), 31P + 6 p.p.m.
Preparation of t-Butylphosphine

Attempts at reducing t-butyl-di-chlorophosphine, dibromo-t-butylphosphine, and dimethyl t-butylphosphonate with sodium hydride, lithium aluminium hydride, phenylsilane, trichlorosilane, diphenylsilane and polymethylhydrogensiloxane were unsuccessful. Phosphine gas, generated by adding an excess of water to magnesium aluminium phosphide in dry petrol (100-120°C), was dried, by passing it through calcium chloride tubes, and passed into a dekalin (500 ml) solution of isobutylene (2 mol) cooled to -15°C to which was slowly added a 1:1 mixture (1.2 mol) of boron trifluoride gas dissolved in syrupy phosphoric acid (85%). After passing phosphine gas for 5 h the reaction mixture was allowed to warm to room temperature and was set aside overnight. After neutralizing the acidic reaction mixture with ammonia solution (8.8%) and separation of the organic layer, distillation yielded t-butylphosphine, 30%, bp 54-58°C (Literature 54°C), v max. 2282, 1480, 1380, 1075 and 798 cm⁻¹, δ 5.5 (0.5H, s) and 8.8 (9H, d, J p-H = 12 Hz), 31P + 80 p.p.m.

Reaction of t-Butylphosphine with Methyl Iodide

t-Butylphosphine (1.8 g; 0.02 mol) was added to an excess of methyl iodide. t-Butylmethylphosphonium iodide precipitated out of solution on standing overnight, yield 53%, m.p. 185-189°C, v max. 2340, 1290, 1060, 980, 950, 821 and 739 cm⁻¹, δ 8.2 (5H, m) and 8.8 (9H, d, J p-H = 20 Hz) (Found: C, 24.8; H, 6.5. C₆H₁₄P requires C, 25.1; H, 6.2%).

Reaction of t-Butylphosphine with Bromine

Bromine (13 g; 0.17 mol) in chloroform (13 ml) was added slowly to t-butylphosphine (3.9 g; 0.043 mol) in chloroform (20 ml) at 10-20°C.
A white solid formed which disappeared on warming to room temperature. Distillation yielded di-bromo-t-butylphosphine (29%), b.p. 85-88°/14mm., ν max, 1455, 1360, 1180, 1000 and 990 cm⁻¹, τ 8.7 (9H, d, J p-H 16Hz).

Reaction of t-Butylphosphine and Sulphur

T-Butylphosphine (0.9g; 0.01 mol) was added to sulphur (0.5 g; 0.015 mol in benzene (5 ml). The mixture was refluxed for 4 hr. On standing overnight, crystals appeared which on crystallization from petrol (40-60°) were found to be t-butylphosphine sulphide, 93-95°, ν max, 2350, 1483, 1462, 1190, 920, 910, 830, 690, 670, 580, 470 cm⁻¹, m/e 122 (1H, d, J p-H 51Hz) and 8.6 (9H, d, J p-H 21Hz) (Found C, 38.8; H, 8.9. C₆H₁₄PS requires C, 39.4 H, 9.0%)

T-Butylphosphine sulphide reacts with atmospheric oxygen to form t-butylpyrophosphinothioate, m/e 258, 216, 201, 122.

Reaction of t-Butylphosphine with Hydrogen Peroxide

Hydrogen peroxide (28%; 2.4g; 0.025 mol) was added slowly to t-butylphosphine (3 mls; 0.025 mol) in methanol (15 mls) cooled to 0° to form t-butylphosphine oxide, τ (in methanol) 7.3 (2H, d, J p-H 458Hz) and 9.0 (9H, d, J p-H 19Hz), 31P-p.p.m.

Reaction of t-Butylphosphine Oxide with Benzaldehyde

Concentrated hydrochloric acid (2 ml) and benzaldehyde (5.30g; 0.05 mol) were added to t-butylphosphine oxide (0.025 mol) in methanol. The mixture was set aside for two days. Filtering yielded 5-t-butyl-1,3-dioxo-2,4,6-triphenyl-5-phosphacyclohexane 5-oxide (0.15g), mp. 307.5-308° (from methanol) ν max. 1170, 1085, 1065, 1005, 987, 860, 820 and 800 cm⁻¹, τ in trifluoroacetic acid 7.1 (18H,m) and 9.3 (9H, d, J p-H 16Hz) (Found: C, 73.7; H, 6.8; P, 7.4. C₂₅H₂₇O₃P requires C, 78.0; H, 6.6; P, 7.6%).
The mother liquor was treated with water, and filtration yielded
\[ \text{t-butyl-(\(\alpha\)-hydroxybenzyl)-phosphine oxide} \quad (22\%) \text{ mp. 138-142°}, \]
\( \\text{\(\nu\) max, } 1130, 1040, 1010, 815, 780 \text{ and } 700 \text{ cm}^{-1}, \text{ m/e 212, 105, C} \)
(in D\(_{6}\)-DMSO) 8.7 (5H,m), 6.7 (1H,m), 6.8 (1H,s) and 9.2 (9H,d,\(\beta-H\) 13HZ)
(Found: C, 68.2; H,8.0; P,14.3. \(\text{C}_{11}\text{H}_{17}\text{O}_{2}\text{P}\) requires C, 68.0; H,7.3; P,14.6%)

**Reaction of t-Butylphosphine and Benzaldehyde**

Benzaldehyde (3.5g; 0.033 mol) and concentrated hydrochloric acid (2 mls)
were added to t-butyl phosphine (2 ml; 0.017 mol) in methanol (6 ml). The
mixture was heated under reflux for 4 h. Extraction with ether and
evaporation yielded benzyl-t-butyl-(\(\alpha\)-hydroxybenzyl)-phosphine oxide, (47%)
m.p. 126-127°(from acetone),\( \text{\(\nu\) max, } 3200, 1140, 1115, 1055, 825, 770 \text{ and}
700 \text{ cm}^{-1}, \text{ m/e 302,196, 106,91, C1.5 (10H,m), 5.0 (2H,m,2 p=7HZ), 6.9}
(2H,m) and 8.9 (9H,d,\(\beta-H\) 14HZ) (Found: C,70.6; H,7.8; P,11.0. \(\text{C}_{18}\text{H}_{25}\text{O}_{2}\text{P}\)
requires C, 71.5; H, 7.6; P,10.2%).

**Reaction of t-Butylphosphine Oxide with Acrylonitrile**

Sodium methoxide (0.008 mol) and acrylonitrile (3.18g; 0.06 mol) were
added to a methanolic solution of t-butylphosphine oxide (2.65g; 0.025 mol)
colled to 0°. The solution was stirred for three days. Following extraction
with methylene chloride and evaporation, chromatography on silica yielded
\(\beta\)-cyanoethyl methyl ether (ether) (0.1g),\( \text{\(\nu\) max, } 2250, 1455, 1380, 1223, 1183,
1110, 995 and 815 cm\(^{-1}\), m/e 85, 54,45, C 6.4 (2H,t,\(\lambda-6HZ\), 6.6 (3H,s) and
7.4 (2H,t,\(\lambda-6HZ\) and \(t\)-butyl-bis(2-cyanoethyl)-phosphine oxide
(50% methanol-ether) (0.2g)\( \text{\(\nu\) max, } 2260, 1475, 1420, 1150, 815, 750 \text{ cm}^{-1},
m/e 212, 158,104, C 7.3 (2H,m), 7.8 (2H,m) and 8.8 (9H,d,\(\beta-H\) 16HZ)
Reaction of t-Butylphosphine Oxide with Sodium Hydroxide

Sodium hydroxide (1g; 0.025 mol) dissolved in water (4 ml) was added slowly to t-butylphosphine oxide (2 ml; 0.016 mol) in methanol (3 ml). The mixture was set aside overnight. After acidification, extraction with chloroform yielded t-butylphosphinic acid, which was taken up in benzene and an excess of aniline was added. Crystals of anilinium t-butylphosphinate were formed after 0.5 h shaking, identified by m.p. and mixed m.p.

Reaction of t-Butylphosphine with an Excess of Oxygen

t-Butylphosphine (0.9 g; 0.01 mol) was left exposed to the atmosphere for 10 h. An excess of aniline was added to the resulting syrupy liquid dissolved in benzene (5 ml). The mixture was set aside for 0.5 h and crystals of anilinium t-butylphosphinate appeared, \( \lambda_{\text{max}} 2285, 1600, 1500, 1360, 1150, 1030, 990, 960, 818, 750 \) and 690 cm\(^{-1}\), \( \tau 1.9 \) (3H, s), 3.0 (5H, m), 7.6 (1H, s) and 9.0 (9H, d, \( \lambda_{H}^{10\text{HZ}} \)). (Found: C, 56.1; H, 8.3; P, 14.0 \( \text{C}_{10}^{18} \text{H}_{18}^{17} \text{O}_{10} \text{NP} \) requires C, 55.8; H, 8.4; P, 14.4%).

Reaction of t-Butylphosphine with Sodamide in Liquid Ammonia and Methyl Iodide

Liquid ammonia (50 ml) was dried over sodium wire and distilled into the reaction flask containing sodamide (1.75 g; 0.044 mol). To this was added t-butylphosphine (4 g; 0.044 mol). The mixture was stirred for 0.5 h keeping the temperature at \( -45^0 \). Then methyl iodide (6.3 g; 0.044 mol) in ether (20 ml) was slowly added. Evaporation and distillation yielded t-butylmethyphosphine (22%) b.p. 78-82\(^0\), \( \tau 7.2 \) (0.5H, s), 8.8 (3H, d, \( \lambda_{H}^{10\text{HZ}} \)), and 8.8 (9H, d, \( \lambda_{H}^{12\text{HZ}} \)).
t-Butylmethyolphosphine (1.04 g; 0.01 mol) was added to an excess of methyl iodide, filtration and crystallization from chloroform-ethyl acetate yielded \textit{t}-butyldimethylphosphonium iodide (89%) m.p. 300°d, ν max. 1300, 1220, 980, 960, 873, and 724 cm⁻¹, \(\text{C}(\text{trifluoroacetic acid}) 8.3 (6\text{H}, d, 2 \text{ p.p.} 36 \text{HZ}), 8.5 (1\text{H}, s) \text{ and } 8.9 (9\text{H}, d, 2 \text{ p.p.} 18 \text{HZ}) \)

(Found: C, 29.5; H, 6.3; P, 12.1. Requires C, 29.2; H, 6.5; P, 12.6%).

\textbf{Attempted Reaction of t-Butylphosphine, Sodamide in Liquid Ammonia and 1,2-Dichloroethane}

t-Butylphosphine (3.3 g; 0.033 mol) was added to dry liquid ammonia (50 ml) containing sodamide (1.3 g; 0.033 mol). Keeping the temperature between -45° and -35°, 1,2-dichloroethane (1.63 g; 0.065 mol) in ether (5 ml) was slowly added. Evaporation of the solvent and careful distillation yielded t-butylphosphine and an unidentifiable material containing a P-H bond (from i.r. spectrum).

\textbf{Reaction of t-Butylphosphine with Cyclohexanone}

t-Butylphosphine (3 ml; 0.025 mol) was added to cyclohexanone (4.4 g; 0.05 mol) in concentrated hydrochloric acid (12 ml). The mixture was heated under reflux for 3 days. Extraction with chloroform and chromatography on silica yielded \textit{t}-butylcyclohexylphosphine oxide (50% methanol-ether) (3.7 g) m.p. 36-38°, b.p. 103-106°/1.25 mm, ν max. 2280, 1475, 1395, 1160, 948, 885, 820, 745 and 660 cm⁻¹, \(\text{m/e} 188, 131, 105, \text{C 3.6}

(1\text{H}, d, 2 \text{ p.p.} 436 \text{HZ}), 8.3 (11\text{H}, m) \text{ and } 8.6 (9\text{H}, d, 2 \text{ p.p.} 16 \text{HZ}) \)

(Found: C, 65.0; H, 11.2; P, 15.7. \(\text{C}_{10}\text{H}_{12}\text{OP} \text{ requires C, 63.9; H, 11.2; P, 16.5%).}

The oxide was unchanged after being heated under reflux with 0.1 N sodium hydroxide overnight.
Reaction of t-Butylphosphine with Acetophenone

T-Butylphosphine (5 ml; 0.041 mol) was added to acetophenone (4.9 g; 0.041 mol) in concentrated hydrochloric acid (25 ml). The mixture was heated under reflux for 20 h. After extraction with chloroform, chromatography on silica yielded t-butyl-(α-methylbenzyl)-phosphine oxide (10% ethyl acetate-ether) (15%), mp. 95-98°C, fractional crystallization from petrol (40-60°C) separated the two diastereoisomers, $\nu_{max}$ 2295, 1595, 1215, 950, 815, 760 and 700 cm$^{-1}$, $\delta$ 2.6 (5H, m), 6.8 (1H, m), 8.2 (3H, d, $\delta$ p-H, 8Hz) and 9.0 (9H, d, $\delta$ p-H, 16Hz) and 2.6 (5H, m) 6.6 (1H, m), 8.1 (3H, d, $\delta$ p-H, 8Hz) and 8.8 (9H, d, $\delta$ p-H, 16Hz) (Found: C, 69.2; H, 9.3; P, 14.3. C$_{12}$H$_{19}$OP requires C, 68.6; H, 9.5; P, 14.75%).

One pure isomer of the oxide (0.1g; 0.0005 mol) was treated with sodium in ethanol (1 equiv) and stirred at room temperature for 1 h. Removal of the solvents and extraction yielded a mixture of isomers in the ratio of 98:2.

Attempted Reaction of t-Butyl-(α-methylbenzyl)-phosphine Oxide with Benzaldehyde

Benzaldehyde (0.05g; 0.0005mol) was added to t-butyl-(α-methylbenzyl)-phosphine oxide (0.1g; 0.0005 mol) in dry methanol (2 ml). Then two drops of sodium methoxide in methanol were added. The reaction was heated under reflux for 1.5 h. Evaporation of solvents followed by chromatography on silica (30% methanol-ether) yielded starting material (90%).

Attempted Reaction of t-Butyl-(α-methylbenzyl)-phosphine Oxide with Di-t-butyl Disulphide:

Di-t-butyl disulphide (0.42 g; 0.0024 mol) was added to one pure isomer of t-butyl-(α-methylbenzyl)-phosphine oxide (0.5g; 0.0024 mol) in
o-dichlorobenzene. The reaction was heated to 175° for one day. Chromatography yielded o-dichlorobenzene and unidentifiable brown tar.

**Attempted Reaction of t-Butyl-(α-methylbenzyl)-phosphine Oxide with Dibenzyl Disulphide.**

One pure isomer of t-butyl-(α-methylbenzyl)-phosphine oxide (0.53g; 0.0025 mol) and dibenzyl disulphide (0.62g; 0.0025 mol) in benzene (10 ml) were irradiated in a pyrex tube at > 300nm, for 48 h. Analysis of reaction mixture by n.m.r. spectroscopy showed no reaction had taken place. Chromatography on silica yielded t-butyl-(α-methylbenzyl)-phosphine oxide (96%)

**Reaction of t-Butylphosphine with Chloroacetone**

t-Butylphosphine (3 ml; 0.025 mol), chloroacetone (2.3g; 0.025 mol) and concentrated hydrochloric acid (30 ml) were heated under reflux for 16 h. Extraction with chloroform and chromatography on alumina (1% methanol-ether) gave t-butyl-(α-methylvinyl)-phosphine oxide, b.p. 159-164°/2.5mm \( \nu \) max. 2290, 1460, 1363, 1230, 1163,920,815 and 650 cm\(^{-1}\), m/e 146, 145,131, 105, 89, 3.3 (1H, d, \( J_{PH} 453\) Hz), 6.4.2 (2H, m), 7.8 (3H, d, \( J_{PH} 12\) Hz) and 8.9 (9H, d, \( J_{PH} 17\) Hz) (Found: C, 58.0; H, 10.5; P, 21.8. \( C_{7}H_{15}OP \) requires C, 57.5; H, 10.3; P, 21.2%).

**Reaction of t-Butylphosphine with Hexafluoroacetone**

Hexafluoroacetone (8.3g; 0.05 mol) was weighed into a flask at -70°. This was allowed to warm to room temperature and the gas was bubbled into t-butylphosphine (3 ml; 0.025 mol) in hexane (30ml). The reaction was set aside at -70° for 0.25 h. After warming to room temperature removal of the solvents and exposure to the air, the residue yielded hexafluoroisopropyl-t-butylphosphinate, mp. 93-94°, \( \nu \) max. 2370, 1401, 1260, 1220, 1135,
982, 900, 810, 752 and 710 cm$^{-1}$, m/e 272, 166, 147, δ(D$_2$-DMSO), 
3.8 (1H, s), 6.4 (0.5H, s) and 9.0 (9H, d, δ $p$-H$^2$OHz)(Found: C, 30.7; 
H, 5.1; P, 10.9. C$_7$H$_{11}$O$_2$F$_6$P requires C, 30.9; H, 4.45; P, 11.4%).

**Reaction of t-Butylphosphine with Acetone**

T-Butylphosphine (3 ml; 0.025 mol) was added to acetone 
(2.9 g; 0.05 mol) in concentrated hydrochloric acid (15 ml). The mixture 
was heated under reflux for 72 h. After extraction with chloroform and 
evaporation of the solvent, the residue yielded t-butylisopropylphosphine 
oxide, b.p. 75-77°/0.8 mm. ν max. 2280, 1465, 1360, 1160, 1135, 935, 910 and 
810 cm$^{-1}$, δ 3.8 (1H, d, δ $p$-H$^4$OHz), 7.8 (1H, m), 8.6 (6H, dd, δ $p$-H$^4$OHz) 
(Found: C, 56.5; H, 11.8; P, 19.1. C$_7$H$_{17}$OP requires C, 56.8 
H, 11.5; P, 20.09%).

This oxide readily reacts with atmospheric oxygen to give 
t-butylisopropylphosphinic acid, m/e: 164, 121, 108.

**Reaction of t-Butylphosphine with Succinaldehyde**

2,5 - Diethoxytetrahydrofuran (6.88 g; 0.043 mol) in tetrahydrofuran (10 ml) 
was added over the period of an hour to t-butylphosphine (3.69 g, 0.041 mol) 
in tetrahydrofuran (20 ml) and concentrated hydrochloric acid (20 ml). 
The reaction was heated to reflux for 0.5 h. Filtration of the solid and 
washing with isopropanol and ether yielded l-t-butyl-2,5-dihydroxy-
phospholanium chloride (53%) m.p. 165-166°, ν max. 3200, 1318, 1200, 1076, 
960, 884, 811 cm$^{-1}$ (Found: C, 46.2; H, 8.3; P, 13.2; Cl, 16.3. C$_8$H$_{18}$O$_2$PCI 
requires C, 45.7; H, 8.7; P, 14.6; Cl, 16.7%).
Attempted Reaction of t-Butylphosphine with Diacetyl

Diacetyl (0.73g; 0.008 mol) was added to t-butylphosphine (0.74g;0.008 mol) in dry methylene chloride at -80° N.m.r. spectrum shows complex structure in which absorptions of starting materials can only be observed. The reaction was set aside for 3 days at room temperature but there was no change in the spectrum. No identifiable products were obtained from the acidified reaction of t-butylphosphine and diacetyl.

Attempted Reaction of t-Butylphosphine and Acetonylacetone

t-Butylphosphine (2.05g; 0.023 mol) was added to acetonylacetone (2.5g; 0.023 mol) in tetrahydrofuran and concentrated hydrochloric acid (10 mls). The reaction was heated to reflux for 18 h. Extraction with chloroform gave a brown tar whose n.m.r. spectrum was too complex for analysis, chromatography on alumina yielded nothing.

The experiment was repeated in a sealed tube, and heating to 80° for 12h gave an unidentifiable tar.
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