SOME REARRANGEMENTS OF
TRIVALENT PHOSPHORUS COMPOUNDS

By

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STATEMENT

The work described in this thesis was carried out by the author in the Department of Chemistry of the University of Leicester under the supervision of Dr. S. Trippett. No part of it is concurrently being submitted for any other degree.

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Signed, M. P. Savage

(M. P. Savage)
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SUMMARY

The rearrangements of both three- and four-coordinated phosphorus compounds are reviewed.

The thermal rearrangements of alk-2-enyl diphenylphosphinites and alk-2-enyldiphenylphosphines have been studied. The rearrangements probably proceed via five-membered and four-membered cyclic transition states respectively. Also included are further examples of the rearrangement of the intermediates formed from the addition of trivalent phosphorus compounds, possessing a group capable of stabilising an anion, to aromatic aldehydes and ketones.

The neighbouring group effect of trivalent phosphorus compounds is reviewed followed by studies attempting to confirm the effect (if any) of trivalent phosphorus compounds undergoing participation via a three-membered cyclic phosphonium intermediate.

Following a brief review on the preparation and properties of vinylphosphorus compounds, the preparation and reactions of 1-phenylvinylidiphenylphosphine are discussed. These reactions are concerned with the ability of the α-phenyl group to stabilise an incipient phosphorane.
The phosphorus atom in its ground state has five electrons in its outer shell with a configuration of $s^2p^3$ as is common with other elements in group V of the periodic table. Most phosphorus compounds are 3- or 4- coordinated and have the following general structures:

\[
\begin{align*}
\text{R}_1 & \quad \text{P} \quad \text{R}_3 \\
\text{R}_2 & \quad \text{P} \quad \text{R}_3 \\
\text{R}_2 & \quad \text{P} \quad \text{X} \quad \text{R}_3
\end{align*}
\]

where X can be O (phosphine oxide), S (phosphine sulphide), NR (iminophosphorane) and CR$_2$ (alkyldenephosphorane). In the trivalent phosphorus compounds, $R_3P$, three of the outer shell electrons are employed to form $\sigma$ bonds with the groupings $R$. This leaves a remaining two electrons paired in a $sp^3$ orbital and these are available for nucleophilic reactions. Many of the following rearrangements of trivalent phosphorus compounds depend on the availability of this lone pair of electrons. The rearrangements of both 3- and 4- coordinated phosphorus compounds will be reviewed here.

**Rearrangements of Tertiary Phosphines**

Rearrangements involving tertiary phosphines are few in number. One of these types is reported by Horner and co-workers, who found that optically active allylmethylphenylphosphine racemises readily in refluxing toluene solution, whereas the saturated optically active methylphenylpropylphosphine requires a
temperature as high as 230° before complete optical inactivity is observed. Horner suggested that the smooth racemisation of the allyl compound was proceeding via an allylic rearrangement presumably by means of a symmetrical intermediate (1).

\[ \text{CH}_2\text{CH} \]

The above rearrangement envisages a migration of phosphorus from carbon to carbon. This is further exemplified in the isomerisation of 9-phenyl-9-phosphabicyclo[6.1.0]nonatriene (2) to (3).²

Addition of dipotassium cyclooctatetraenide to dichlorophenylphosphine and isolation below 50° yields the compound (2). This, above 70° in chloroform solution, isomerises to 9-phenyl-9-phosphabicyclo[4.2.1]nonatriene (3) by the following suggested pathway.

\[ \begin{array}{c}
\text{THF} \\
70°
\end{array} \]

(2)
The product (3) at higher temperatures (480°) or with acid catalysis at 100° further rearranges to the epimer (4).

As the above rearrangements are formally a migration of phosphorus from carbon to carbon, it is convenient to include here the 1,2 phosphorus migration in the skeletal rearrangement of α,β-epoxyvinylphosphonates. These phosphonate esters (5) are smoothly transformed by the action of heat or acid catalysis, using boron trifluoride, into α-formylalkylphosphonates (6).

\[
\begin{align*}
&\text{(5)} \\
&\text{(6)}
\end{align*}
\]

**Rearrangement of Phosphites, Phosphonites and Phosphinites.**

Alk-2-ynyl phosphites and diaryl-2-ynylphosphinites are found to be thermally unstable and at room temperature or above rearrange exothermically to the alk-1,2-dienylphosphonates or alk-1,2-dienyldiphenylphosphine oxides. The relative order of ease of rearrangement of the phosphites parallels the decreasing order of carbonium ion stabilities as shown.

\[
\begin{align*}
\text{Me} & \quad \text{Me} \\
\text{HC=O-CH-OP} & \quad \text{HC=O-CH-OP} & \quad \text{HC=O-CH2OP}
\end{align*}
\]

This lends itself to the following mechanism, which is not entirely synchronous and in which there is a build up of positive charge on
the phosphite-carrying carbon:

\[
\begin{align*}
R_2^1P^+ & + R_2^2P\equiv C\equiv C^− \\
& \xrightarrow{\text{δ−}} R_2^1P\equiv C\equiv C\text{δ+} \\
& \xrightarrow{\text{δ−}} R_2^1P−\text{CR}^\equiv C\equiv CR^3_− \\
\end{align*}
\]

(7) (8)

\(R^1 = \text{O-alkyl or Ar}\)

The ease of rearrangement is suggested as the result of a favourable planar transition state between the acetylenic and allenic structures through which the molecule passes, the driving force being the energy gain on the formation of the very strong P=O bond.

This reaction is found to proceed equally as well with propargyldichlorophosphites (7; \(R^1=\text{Cl}\)) which rearrange to alk-1,2-dienylphosphoric dichlorides (8; \(R^1=\text{Cl}\)).

This acetylenic - allenic rearrangement has been shown to be the first step in the isomerisation of dialkyl-\(\beta,\gamma\)-propynylphosphites (10; \(R=\text{alkyl}\)). The allene once formed (11; \(R=\text{alkyl}\))

\[
\begin{align*}
\text{RO}_2\text{POCH}_{2}\equiv\text{C} & \rightleftharpoons \text{Et}_2\text{O} \rightarrow \text{RO}_2\equiv\text{C}−\text{C}−\text{CH}_2 \\
& \rightarrow \text{RO}_2\equiv\text{C}−\text{C}−\text{CH}_2−\text{Me} \\
\end{align*}
\]

(10) (11) (12)

is unstable at 150° and in the presence of sodium methoxide at room temperature, when it undergoes a prototropic transformation
to give the acetylenic phosphonate (12; \( R = \text{alkyl} \)), when dialkyl-1,1-dimethyl-2-propynylphosphites (13) are subjected to the same reaction conditions or even more severely, the inductive effects of the two methyl groups hinder isomerisation and their hyper-conjugative effects stabilise the allenic system to the extent

\[
\begin{align*}
(R\text{O})_2\text{P} & \text{O}\text{C}\text{C}\text{CH} \quad \text{O} \\
\text{Me} & \text{He} \\
(13) & (14)
\end{align*}
\]

that the reaction ceases once the allene (14)\(^1\) is formed. When only one methyl group is attached to the allenic system the reaction path depends on the conditions employed.\(^1\) In ethereal solution the reaction stops after the first stage and the allene (15) is the exclusive product. In the absence of solvent an exothermic reaction takes place and the diethyl 1,2-butadienylphosphonate (15) rearranges to diethyl 3-methylpropynylphosphonate (16) and diethyl 3-methylprop-2-ynylphosphonate (17), the diethyl 1-methyl-2-propynylphosphimate acting as the base catalyst. An equilibrium mixture is formed but its composition has yet to be investigated by the authors.\(^1\)

\[
\begin{align*}
\text{(EtO)}_2\text{P}\text{C} & \text{C} \text{Et} \iff \text{(EtO)}_2\text{P} & \text{CH} \text{C} \text{CHMe} \\
\text{(EtO)}_2\text{P} & \text{CH}_2\text{C} \text{C} \text{Me} \\
(16) & (15) & (17)
\end{align*}
\]

Dialkynylphosphonites of the type (18) have two unsaturated groups with which the phosphorus can rearrange and reaction occurs
with the inversion of one of the unsaturated groups leaving the other unaltered as the phosphorus atom has reached pentacovalency and reacts no further. The product isolated is therefore 1-hexyne-3-yl(3-propylallenyl)-phenyl-phosphinate (19).

\[
\begin{align*}
(18) & \quad \rightarrow \quad (19)
\end{align*}
\]

When dialkyl phosphorochloridites are allowed to react with 2,5-dimethyl-3-hexyne-2,5-diol in the ratio of 2:1 molar equivalents, dialkyl 1-(1-hydroxy-1-methylethyl)-3-methyl-1,2-butadienylphosphonates (20) in yields of 20-38% and tetraalkyl [bis(1-methylethylidene)ethylene]diphosphonates (21) in yields of 13-30% are obtained after distillation. The reaction mechanism can best be illustrated by the following scheme:
The presence of the two methyl groups on the hydroxyl-carrying carbon facilitate the acetylenic rearrangement and the reaction proceeds via pathway (a) to give the hydroxy compound (20). This can then react with more dialkyl phosphorochloridite to give another phosphite (22) the phosphorus of which attacks the allenic system present via another five membered transition state to give the diphosphonate (21). In the absence of the methyl groups, i.e. in the case of 2-butyne-1,4-diol, the reaction with
the second molecule of phosphorochloridite is faster than the acetylenic rearrangement and the reaction path is that of (b) to and only the analogous compounds\(12\), namely \([2,3\text{-bis(dialkoxy-phosphinyl)}]1\text{-3-butadienes}\), have been isolated.

In contrast to alk-2-ynyl phosphites, alk-2-enyl phosphites are much more thermally stable but above temperatures of \(180^\circ\) give alk-2-enyl phosphonates with predominant inversion of the allyl group \(14,15\) presumably via a five-centre cyclic transition state similar to that in the alkynylphosphite rearrangement:

\[
\begin{align*}
R'_2\text{P} &\quad \text{O} &\quad R^2 &\quad \text{R'}_2\text{P} &\quad \text{O} \\
R^4\text{CH} &\quad \text{CH} &\quad R^3 &\quad \text{R'}^4\text{CH} &\quad \text{CR}^2\text{R}^3 \\
\end{align*}
\]

\(180^\circ\)

(23) \quad (24)

Lemper and Tieckelmann \(15\) found that whereas diethyl \(\alpha\)-methylallyl-phosphite (23; \(R^1=\text{OEt}, R^2=\text{Me}; R^3=R^4=\text{H}\)) gave exclusively diethyl crotylphosphonate (24; \(R^1=\text{OEt}; R^2=\text{Me}; R^3=R^4=\text{H}\), rearrangement of diethyl crotylphosphite gave diethyl crotlylphosphonate in addition to the previously reported diethyl \(\alpha\)-methylallyl-phosphonate. The reason for this anomaly is not yet understood.

Alk-2-enyl diphenylphosphinates undergo a similar rearrangement which will be discussed later (see discussion p. 30).

**Self Isomerisation of Phosphinites**

Very reactive phosphinites, e.g. methyl and benzyl diphenylphosphinites self isomerise very readily with a crystal
of iodine to the corresponding tertiary phosphine oxides. Their thio analogues behave similarly in this respect. The rearrangement probably proceeds by initial co-ordination of the iodine with the phosphorus to give a phosphonium intermediate, which is attacked by a further iodine atom to give the phosphine oxide and an alkyl halide. The alkyl iodide can then react with a further molecule of phosphinite in a normal Arbuzov reaction and propagate a chain reaction:

\[
\begin{align*}
\Phi_2\text{POR} + \text{I}_2 &\rightarrow \Phi_2\text{P}^+\text{OR} + \text{I}^- \\
\Phi_2\text{P}^-\text{R} &\rightarrow \Phi_2\text{P}^+\text{OR} + \text{RI} + \Phi_2\text{P}^-\text{I}
\end{align*}
\]

Reactions of Trivalent Phosphorus Compounds with Aldehydes and Ketones.

Many examples occur in the early literature of addition to carbonyl compounds, followed by rearrangement, of trivalent phosphorus reactants containing substituent(s) capable of forming a stable anion (e.g. -Cl, -NET₂).

Monochlorophosphines have been shown to react with aldehydes and ketones at room temperature. If the intermediate is treated with water, an α-hydroxyphosphine oxide is formed, e.g. benzaldehyde and chlorodiphenylphosphine under this treatment gives α-hydroxybenzyldiphenylphosphine oxide (25).
\[ \phi_2\text{PCl} + \phi\text{CHO} \xrightarrow{\text{R.T.}} [\text{H}_2\text{O}] \rightarrow \phi-	ext{CH-OH} \]

\[ \phi_2\text{P=O} \quad (25) \]

Similar products are obtained with \(\alpha\)-haloacetaldehydes and dialkyl- or diarylchlorophosphines.

\[ 1. \text{R.T.} \quad \phi_2\text{PCl} + \text{ClCH}_2\text{CHO} \xrightarrow{2. \text{H}_2\text{O}} \phi_2\text{P-CH(OH)-CH}_2\text{Cl} \]

If, instead of water, hydrogen sulphide is used in the isolation, sulphur is incorporated to give an \(\alpha\)-hydroxyphosphine sulphide (26). This prompted the authors to propose a mechanism which accounts for sulphur incorporation:

\[ \phi_2\text{P-CH(OH)-CH}_2\text{Cl} \quad (26) \]

\[ \text{H}_2\text{S} \]

Phosphorus trihalides give similar products to those cited above, but react more vigorously. When the reagents are added at room temperature an exothermic reaction takes place to give an intermediate which yields an \(\alpha\)-hydroxyphosphonic acid on treatment with water (27).

\[ 19-31 \]
With α-β unsaturated carbonyl compounds phosphorus trihalides undergo Michael addition followed by cyclisation (29), subsequent hydrolysis yields a 3-ketophosphonic acid (28).

Intermediates of the type (29) have been isolated from the action of phosphorus trichloride and acetic anhydride on mesityl oxide. The compound gave on hydrolysis a ketophosphonic acid analogous to (28).

Cyclic α-β unsaturated ketones behave in a similar manner e.g. 3-methyl-2-cyclohexene-1-one with phosphorus trichloride gives 1-methyl-3-oxocyclohexanephosphonic acid (30).
At elevated temperatures different products are obtained, in which apparent migration of chlorine from phosphorus to carbon takes place. When benzaldehyde and excess phosphorus trichloride are heated together at 195° α-chlorobenzylphosphoryl chloride (31) is the product.

\[
\PhiCHO + PCl_3 \xrightarrow{\Delta} \Phi(\text{Cl})-PCl_2
\]  

(31)

Similar results are obtained with other carbonyl compounds in sealed tube reactions at 200°. Recently it has been shown that such high temperatures are unnecessary as analogous products (32) are obtained when benzophenone and dichlorophenylphosphines are allowed to react at 100° with two molar equivalents of partly hydrated aluminium chloride catalyst. The following alternative mechanisms are suggested for the formation of (32).
Aminophosphonites and dialkyl phosphorochloridites have been shown to behave similarly under the same reaction conditions.

\[(\text{RO})_2\text{PR}^+ + \text{R}''\text{CHO} \xrightarrow{100^\circ} \text{RO}_2\text{P-CH-R}''\]

\((\text{R}' = \text{NET}_2, \text{Cl})\)

Replacement of the aldehyde or ketone with an \(\alpha-\beta\) unsaturated carboxylic acid gives rise to an acid chloride being formed. Shagidullin reports that ethylphosphonodichloride reacts exothermically with acrylic acid resulting in the formation of 3-((chlorophosphinyl)-propionylchloride (33). The reaction is seen as initial Michael addition to give the zwitterionic
structure (34) which rapidly cyclises and a subsequent internal Arbuzov rearrangement gives the alkanoyl chloride (33).

\[
\begin{align*}
\text{Et-P:} & \quad \text{CH}_2=\text{C} \quad \text{OH} \\
\text{Cl} & \quad \text{EtP}^+ \quad \text{CH}_2:\text{C} \quad \text{OH} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

(34)

\[
\begin{align*}
\text{EtP-CH}_2\text{CHCOCl} & \quad + \quad \text{EtP}^+ \quad \text{CH}_2:\text{C} \\
\text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

(33)

In a similar manner, chlorides of 1,2- and 1,3- glycol esters of phosphorus acid condense with methylvinylketone to give an intermediate of the type (38). Although this can theoretically undergo an internal Arbuzov reaction in two plausible ways to give (36) and (37), only (36) is isolated in practice.
Intramolecular Arbuzov Rearrangements

The Arbuzov reaction of phosphites \([(RO)_3P]\), phosphonites \([(RO)BR']\) or phosphinites \([ROPR']\) with alkyl halides RX can be summarised as nucleophilic displacement of halogen by phosphorus, followed by nucleophilic displacement on an alkoxy group by the displaced halogen anion viz: -

\[
\begin{align*}
  &X^- \\
  &R_2PR' + RX + R_2POR' + R_2R''P=O \\
  &R'' + R'X
\end{align*}
\]

Internal Arbuzov reactions are similar. The nucleophile \(X^-\) attacks the quasi phosphonium intermediate, \(X^-\) being already covalently bonded to the molecule as is shown in the following examples.

\(\beta\)-Lactones react readily with trialkyl phosphites \(69,70,71\) to give the corresponding phosphonates. Initial attack of the phosphorus atom opens the lactone to give the betaine (39). This either undergoes an internal Arbuzov reaction to give (40) or reacts with a second molecule of lactone to give a new betaine, which in its turn undergoes internal alkylation to give the phosphonate (41).
α-β unsaturated aldehydes and acids are known to behave in the same way with trialkyl phosphites to give the dialkyl phosphonates (42) (43) respectively. The reaction pathway is presumably similar to that above. After initial Michael addition internal alkylation takes place to give the observed products.
To confirm this scheme for the $\alpha$-$\beta$ unsaturated acid reaction, Kukhtin conducted the rearrangement in the presence of an alkyl bromide $R'Br$ and at elevated temperatures the mixed ester (45) was found, indicating that the alkyl halide had reacted

$$\text{(RO)}_2\text{P-CH}_2\text{CH}_2\text{COOR'} \quad \text{(45)}$$

with the proposed intermediate betaine (44). Further extensions to this reaction can be made using propionic acids. Here the product is $\alpha$-$\beta$ unsaturated carboxylic ester (46).

\[\text{e.g. (RO)}_3\text{P} \xrightarrow{H} \text{(RO)}_3\text{P}^+ \xrightarrow{H} (\text{RO})_2\text{P-CH} = \text{CH-COO} \] (46)

Intramolecular Arbuzov rearrangements have been postulated for the formation of $\alpha$-alkoxyphosphonates (47) and enol phosphonates (48) from the reaction of trialkyl phosphites and $\alpha$-diketones. The reaction is suggested as an initial attack on one of the carbonyl carbons to give the betaine (49) which either internally alkylates to give (47) or by oxygen insertion is converted to a new betaine (50) which collapses by an internal alkyl migration to give (48).
The oxygen insertion mechanism (49-50) has recently been employed to account for the reaction of trialkylphosphites with α-hydroxyketones.

Further confirmation of this reaction comes from Ramirez, who has isolated the intermediate cyclic oxy phosphorane (51) although its formation is postulated by a different mechanism. This phosphorane is distillable and very reactive towards moisture and carbonyl compounds (RCHO), to which it adds, to give a new phosphorane in meso (52) and racemic forms (53). Unfortunately, Ramirez does not report the isolation of any phosphonates of the types (47) and (48).
Cyclic 1:3-diketones also react with trialkyl phosphites with migration of an alkoxy group. Possible Arbuzov type displacement is precluded in favour of the pathway involving a cyclic oxyphosphorane, e.g.

Reactive aromatic aldehydes react readily with trialkyl phosphites and are claimed to undergo two independent internal
Arbuzov reactions to give α-alkoxyphosphonates (54) and acetalphosphonates (55). The mechanism suggested is comparable to the ring opening of lactones by trialkyl phosphites previously mentioned (p. 15).

Similarly, Borowitz and Anshel suggest an intramolecular Arbuzov rearrangement for the formation of the hydroxy ether (56), one of the products from the complex reaction of fluorenones with trialkyl phosphites.
Recently, Ramirez has cast some doubt on the authenticity of the nitrobenzaldehyde reactions with trialkyl phosphites. Ramirez states that only one type of product is formed which can have meso (57) and racemic (58) forms. Their mode of formation is directly analogous to that of the products (52) and (53) from biacetyl and trialkyl phosphites. No evidence whatsoever was found for the formation of (54) and (55) nor were the discrepancies rationalised.

Reactions of Primary and Secondary Phosphines with Aldehydes and Ketones

Primary phosphines, as does phosphine itself, react with aromatic aldehydes and ketones to give, with acid (HX) products (59) and (60) in which oxygen transfer has taken place.
Normal addition and multiple addition can also occur to give α-hydroxyphosphines or phosphonium salts. (61) (62) (63). Secondary phosphines react likewise to give the normal addition products (65) (66) (67) or an oxygen transfer product (64). The results obtained depend on reaction conditions,

\[
\begin{align*}
\text{RPPH}_2 & \rightarrow \text{RPP-CH}_2 \text{H} (59) \\
\text{RPPH}_2 + 2 \text{O} & \rightarrow \text{RPP-CH}_2 \text{OH} (60)
\end{align*}
\]

\[
\begin{align*}
\text{RP(-C-OH)}_2 (61) & \quad \text{RP(-C-OH)}_2 \text{HX} (62) & \quad \text{RP(-C-OH)}_3 \text{X}^- (63)
\end{align*}
\]

the nature of R groupings and the carbonyl compound used.

High temperatures and concentrated acid solutions favour the formation of (64). Under milder conditions (65) (66) (67) are formed. It is known that α-hydroxyphosphines (65) in the presence of strong acid are rapidly converted to the tertiary phosphine oxides (64). The mechanism is thought to take place via a carbonium ion (68) stabilised by π-π- conjugation with the phosphine.

\[
\begin{align*}
\text{R}_2\text{P}^+ + \text{R'}\text{CHO} & \rightarrow \text{R}_2\text{P}^+\text{CH-R'} \quad \text{H}^+ - \text{H}_2\text{O} \quad \text{R}_2\text{P}^+\text{CHR} (68)
\end{align*}
\]
Rearrangements Involving Four-Co-ordinated Phosphorus Compounds.

(a) Addition of phosphorus compounds to activated triple bonds.

Activated triple bonds are susceptible to nucleophilic attack and triphenylphosphine will add to 2 molar equivalents of acetylenedicarboxylate ester at low temperatures to give a stabilised zwitterion (69) which has been isolated as its hydriodide. The zwitterion can rearrange by a 1:5 phenyl migration to the more stable isomer (70).

Zbiral postulates a similar betaine (71) in the reaction of alkylidene phosphoranes with benzyne. This then undergoes a 1:4 phenyl migration to give the isolated α-substituted benzyl diphenylphosphine (72).
As expected, phosphoranes react readily with acetylene-dicarboxylic ester, the product being stabilised by proton transfer to give a new ylid (73).

When the α-hydrogen atom of the phosphorane is not labile, or is replaced by another grouping, a rearrangement occurs via a cyclobutene system giving a highly conjugated ylid (74).
Another interesting rearrangement in the formation of phosphoranes may be mentioned here. *N*-sulphenylsulphonamides with tertiary phosphines give stable imino-phosphoranes (75).

The mechanism proceeds by way of a three membered heterocyclic ring (74) or its dipolar form which loses sulphur monoxide to give the product.

\[
RSO_2-N=S=0 \xrightarrow{\Phi_3P:} \left[ \begin{array}{c} RSO_2-N=S=0 \\ P \\ \Phi_3 \end{array} \right] \xrightarrow{\Phi_3P=S} RSO_2-N=P\Phi_3 + [S=0] \quad (75)
\]

(74)

The same product is isolated by using the phosphine sulphide, the reaction proceeding this time via a four membered quasi-Wittig type intermediate.

\[
RSO_2-N=S=0 \xrightarrow{\Phi_3P=S} \left[ \begin{array}{c} RSO_2-N=S=0 \\ P \\ \Phi_3 \end{array} \right] \xrightarrow{\Phi_3P=S} RSO_2-N=P\Phi_3 + [S_2O] \quad (75) + [S_2O]
\]

Further rearrangement may take place in the imino compound (75) the phenyl groups are replaced by alkoxyls e.g., trialkyl (arylsulphonyl)phosphorimidates (76) isomerise at 200° to dialkyl alkyl-(arylsulphonyl)-phosphorimidates (77):

\[
ArSO_2N=P(OR)_3 \rightarrow \left[ \begin{array}{c} ArSO_2N=P(OR)_2 \\ R-O \end{array} \right] \xrightarrow{R-O} ArSO_2N-P(OR)_2 \quad (76) \quad (77)
\]
(b) **Rearrangement involved in base hydrolysis of phosphonium compounds.**

Quaternary phosphonium salts are hydrolysed by hydroxide ion to give a phosphine oxide and a hydrocarbon:

\[
\begin{align*}
R_3PR' + OH^- & \rightarrow R_3PO + R'H \\
R_3PR' & \leftarrow \begin{array}{c}
\text{R} \\
\text{R} \\
\text{R}
\end{array}
\end{align*}
\]

The displaced group \( R' \) being the one most stable, as the anion i.e. the least basic anion is expelled. Methoxymethyltriphenylphosphonium chloride (78) is reported to lose a phenyl group to give methoxymethyldiphenylphosphine oxide. If the methoxy group is replaced by chlorine (79) or thio-methyl then these leave preferentially to a phenyl grouping, as the hetero atom can stabilise the negative charge by \( d^-p^+ \) bonding. In the latter case a competing reaction is observed, whereby a phenyl group migrates to the \( \alpha \)-carbon with expulsion of a chloride ion to give benzyl-

\[
\begin{align*}
[\Phi_3P-\text{CH}_2\text{OMe}]OH^- & \rightarrow \Phi_2P-\text{CH}_2\text{OMe} + \Phi H \\
[\Phi_3P-\text{CH}_2\text{Cl}]OH^- & \rightarrow \Phi_3P=O + \text{CH}_3\text{Cl}
\end{align*}
\]

This reaction is paralleled when excess alkyl or aryl metallic bases are employed to prepare Wittig reagents from (79). The general scheme of both these reactions
can be illustrated as one  \( M = \text{alkali metal} \quad R = \text{alkyl or OH} \)

\[
\begin{align*}
(79) \quad & \text{MR} \quad \rightarrow \quad \Phi_3\text{P}=\text{CH}-\text{C}1 \quad \text{MR} \quad \rightarrow \quad \Phi_2\text{P}=\text{CH}^+\text{Cl}^-

\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
stabilizing the anion e.g. \((m-\text{Cl}) > \phi > p\text{Me}0\phi\).

Similar 1,2 shifts from phosphorus to carbon involving a hydride ion as opposed to an aryl group have also been postulated for the formation of methylphosphonic acid (82) from the hydrolysis of chloromethylphosphinic acid (83). The expected hydroxymethylphosphinic acid (84) is also produced but in small yield. As (84) is not a precursor of (82) it is suggested that the reaction proceeds by a synchronous 1,2-hydride shift accompanying the attack of hydroxide ion.

\[
\begin{align*}
\text{ClCH}_2\text{P(OH)} & \quad \text{(83)} \\
\text{OH}^- & \quad \text{OH}^- \\
\text{HO-CH}_2\text{P(OH)} & \quad \text{(84)} \\
\text{CH}_3\text{P(OH)}_2 & \quad \text{(82)}
\end{align*}
\]

In related work concerning the ethanolysis (in refluxing ethanol-ethoxide) and rearrangement of tris(chloromethyl)phosphine (85) to methyl bis(ethoxymethyl)phosphine oxide (86), Kabachnik suggests that the reaction proceeds via a 'pseudo-allylic shift' (\(\text{ClCH}_2\phi; \rightarrow \text{Cl}^{-}\text{CH}_2=\phi^+\)) as follows:-
(ClCH₂)₃P: \[ \text{EtO}^- \rightarrow \text{CH}_2=\text{P}-\text{OEt} + \text{Cl}^- \]

(85)

\[ \text{CH}_2\text{Cl} \]

\[ \text{CH}_2\text{Cl} \]

\[ \text{ROH} \]

\[ \text{OR} \]

\[ \text{P}^-+\text{CH}_3+\text{OR}^- \rightarrow (\text{EtOCH}_2)\text{P}-\text{Me} \] (86)

\[ + \text{ROR} \]

This concept is further applied to the conversion of (83)-(82) viz.

\[ \text{ClCH}_2\text{P}-\text{OH} \]

\[ \xrightarrow{\text{HO}^-} \]

\[ \text{CH}_2\text{P} \]

\[ \xrightarrow{\text{OH}} \text{H}_2\text{O} \]

\[ \text{CH}_3\text{P}-\text{OH} \]

(83)

\[ + \text{Cl}^- \] (82)

Methyl chloromethylyphosphinate (87) behaves in a similar manner with nucleophiles to give comparable products:

\[ \text{ClCH}_2\text{P}-\text{OMe} \] (87)

\[ \xrightarrow{\text{MeO}^-} \]

\[ \text{CH}_3\text{P(OMe)}_2 \]

\[ \xrightarrow{\text{MgBr}} \]

\[ \text{CH}_3\text{P}_2 \]

\[ \xrightarrow{\text{Me}_2\text{NH}} \]

\[ \text{CH}_3\text{P}-\text{OMe} \]

\[ \xrightarrow{\text{N(Me)}_2} \]

In careful studies on deuterated compounds to decide on the actual mechanism the authors found that whereas both were operating simultaneously, the hydride-shift pathway was the more favourable of the two.
The Rearrangement of Alk-2-enyl Diphenylphosphinites

The rearrangements of alk-2-ynyl phosphinites and alk-2-enyl phosphites have already been discussed (see p.3). The only observation of alk-2-enyl diphenylphosphinites undergoing a similar rearrangement is by Arbuzov and Nikonorov. They prepared allyl diphenylphosphinite and showed that it rearranged on attempted distillation to give allyldiphenylphosphine oxide. This was attributed to the self isomerisation of the phosphinite (see p.8) which was enhanced by the stability of the allylic carbonium ion (CH₂-CH=CH₂ → CH₂=CH-CH₂)

Several alk-2-enyl diphenylphosphinites were prepared and it was found that the conversion of phosphinite to phosphine oxide occurred as a general reaction of these systems. The phosphinites were readily rearranged at 140° or below with complete inversion of the allyl group, e.g., cinnamyl diphenylphosphinite gave 1-phenylallyldiphenylphosphine oxide and 1-phenylallyldiphenylphosphinite gave cinnamylidiphenylphosphine oxide. The mechanism probably proceeds via a five membered transition state as shown:

\[
\phi_2P-C\overset{O}{C}C\overset{R^2}{R^3} \xrightarrow{\Delta} \phi_2P-C\overset{O}{\text{C}\overset{\text{R}^1}{\text{R}^3}}\text{CR}^2\text{R}^3
\]

(88) (89)
Four methods were employed in preparing the phosphinites which were rearranged at \( \approx 140^\circ \) without isolation. The methods were:

(a) Addition of chlorodiphenylphosphine to a solution of the alcohol in ether in the presence of 1.2 equivalents of pyridine,

(b) Addition of chlorodiphenylphosphine to a solution of the alcohol in neat pyridine or 2,6-lutidine,

(c) The exchange reaction between the alcohol and a dialkylaminodiphenylphosphine at \( \approx 140^\circ \),

(d) The treatment of the alcohol at room temperature or at 70° with acetoxydiphenylphosphine in the presence of an equivalent of triethylamine.

The phosphine oxides were identified by independent synthesis and/or by their spectral properties. The results are summarised in Table 1.

The possibility of cis-trans isomerism exists round the double bond which has migrated, but in all cases only the trans-form was isolated. The life time of the cis-form, if produced, is probably very small under the conditions employed.

It is evident from the table that method (a) works very well only with primary alcohols. Where the reaction was unsuccessful the major product in all cases was a highly crystalline salt-like substance m.p. 251-2°. The structure of this compound is unknown but its analysis suggests the formula
Table 1

Preparation of phosphine oxides (89) from phosphinites (88)

<table>
<thead>
<tr>
<th>R^1</th>
<th>R^2</th>
<th>R^3</th>
<th>R^4</th>
<th>% (89) (Method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>60(a)</td>
</tr>
<tr>
<td>ϕ</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>65(a)</td>
</tr>
<tr>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>Me</td>
<td>52(a)</td>
</tr>
<tr>
<td>Me_{2}C:CH(CH_{2})_{2}</td>
<td>H</td>
<td>H</td>
<td>Me</td>
<td>38(a)</td>
</tr>
<tr>
<td>H</td>
<td>ϕ</td>
<td>H</td>
<td>H</td>
<td>4(a), 58(b), 60(c), 63(d)</td>
</tr>
<tr>
<td>H</td>
<td>Me</td>
<td>Me</td>
<td>H</td>
<td>4(a), 0(b), 10(c), 40(d)</td>
</tr>
<tr>
<td>H</td>
<td>C_{5}H_{10}</td>
<td>H</td>
<td>H</td>
<td>4(a), 45(b), 50(c)</td>
</tr>
<tr>
<td>H</td>
<td>ϕCH:CH</td>
<td>H</td>
<td>H</td>
<td>2(b), 22(c), 15(d)</td>
</tr>
<tr>
<td>H</td>
<td>Me_{2}C:CH(CH_{2})_{2}</td>
<td>Me</td>
<td>H</td>
<td>61(c)</td>
</tr>
</tbody>
</table>
Kabachnik has met with a somewhat related compound when preparing phosphinites from monoalkyl phosphoro-chloridites and Grignard reagents in the presence of pyridine. When R=Et and R1=isopropyl a compound C\textsubscript{15}H\textsubscript{28}PON is isolated

\[ \text{ROPCl}_2 + \text{R}^1\text{MgX pyridine} \rightarrow \text{R}_2^1\text{POR} \]

which is of unknown structure. Kabachnik suggests that the compound may be an N-phosphorylated-dihydropyridine derivative.

Acetoxydiphenylphosphine was prepared by the exothermic reaction of acetic anhydride with pyrrolidinyldiphenylphosphine. The N-acetylpyrrolidine could be separated by distillation but the phosphine was extensively decomposed by this procedure. The decomposition products were probably tetraphenyldiphosphine monoxide and acetic anhydride as this seems to be a general reaction of acyloxyphosphines at high temperature. The reaction mixture was used directly for the preparation of the phosphinites with no apparent loss of yields. With secondary alcohols acetoxydiphenylphosphine reacted readily at room temperature. The progress of the reaction was measured by the disappearance of the absorption in the infrared at 1750 cm\textsuperscript{-1} (\(\phi_2\text{POAc}\)).

To effect the phosphinite rearrangement a temperature of over 100\textdegree had to be employed before the absorption in the infrared at 1180 cm\textsuperscript{-1} (P=O) appeared. In the case of the
tertiary alcohol, 2-methylbut-3-en-2-ol, no reaction was observed with acetoxydiphenylphosphine at room temperature. On raising the temperature to 70° for 3 hrs., the formation of the phosphinite and its subsequent rearrangement had taken place.

These observations show that the relative rates of reaction of alcohols with acetoxydiphenylphosphine to give phosphinites proceeds in the order

Prim. > Sec. > Tert. as expected on steric grounds.

The relative rates of rearrangement is the reverse of this i.e. tert. > sec. > prim., the reasons for this being similar to those put forward by Mark to explain the relative ease of the alkynyl phosphite rearrangements.

It would be expected that the phosphinite from 1-phenylpenta-1,4-dien-3-ol would give two isomeric phosphine oxides (90) (91) as there are two allylic systems the phosphorus

\[
\phi\text{-CH:CH:CH:CH}_2\text{-P}_2\phi (90) \quad \phi\text{-CH:CH:CH:CH}_2 \quad (91)
\]

can attack. In practice, only 5-phenylpenta-2,4-dienyldiphenylphosphine oxide (90) was isolated, showing the rearrangement had proceeded to give the product with the maximum conjugation.

If the enhanced stability of the allylic cation over that of an ordinary unconjugated species promotes self isomerism of the phosphinite at elevated temperatures, it would be reasonable to expect a mixture of phosphine oxides (92)(93).
The only case in which two isomeric phosphine oxides were isolated was in the rearrangement of geranyl diphenylphosphinite. This gave a comparatively low yield (38%) of the allylic rearranged product, linalyldiphenylphosphine oxide, and 7% of isomerised phosphinite, geranyldiphenylphosphine oxide.

None of the methods employed for rearrangement gave a good yield with allylic alcohol (94) with which the maximum yield obtained was 8%. This was probably because the conditions employed preferentially dehydrated the compound to give the tetraene.

The phosphine oxides once prepared were subjected to a Horner phosphine oxide olefin synthesis. The only successful application was using (90) with the sodio derivative of dimethylsulphoxide as base and benzaldehyde. This gave a 42% yield of 1,6-diphenylhexa-1,3,5-triene.
Optically active allylmethylphenylphosphine racemises more readily than methylphenylpropylphosphine. Horner suggests that the faster racemisation of the allyl compound proceeds by way of a cyclic transition state (1). The preparation of the allylic phosphine oxides above allowed this rearrangement to be studied more closely.

Once prepared, it was found that alk-2-enyldiphenylphosphines (91) rearranged smoothly at 200° with inversion of the allyl grouping to give the isomeric product (92) which has the more substituted and hence more stabilised double bond, e.g.

\[
\phi-\text{CH:CH:CH:CH:CH:PH_2} \xrightarrow{1. \text{CH}_3\text{SOCH}_2^-} \phi-\text{CH:CH:CH:CH:CH:PH}\xrightarrow{2. \phi\text{CHO}}
\]

Rearrangement of Alk-2-enyldiphenylphosphines.

1-phenylallyldiphenylphosphine gave cinnamyldiphenylphosphine. The reaction probably proceeds via a four-membered cyclic transition state as shown. The phosphines studied are illustrated in Table (2).
Table 2

Preparation of phosphines (92) by rearrangement of isomeric phosphines (91)

<table>
<thead>
<tr>
<th>$R^1$</th>
<th>$R^2$</th>
<th>$R^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi$</td>
<td>$H$</td>
<td>$H$</td>
</tr>
<tr>
<td>Me</td>
<td>$H$</td>
<td>$H$</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>$H$</td>
</tr>
<tr>
<td>Me</td>
<td>$\text{Me}_2\text{C:CHCH}_2\text{CH}_2$</td>
<td>$H$</td>
</tr>
</tbody>
</table>

The phosphines were characterised by their conversion to the corresponding phosphine oxides by shaking with 100 volume hydrogen peroxide in benzene. These were then compared with authentic samples.

Preparation of phosphines (91) and (92)

The initial phosphines were prepared by reduction of the corresponding phosphine oxides. Several reagents have been used for the reduction of phosphine oxides to phosphines. These include lithium aluminium hydride, sodium hydride, metallic sodium, Raney Nickel and silanes.

Lithium aluminium hydride was employed with 1-phenylallyldiphenylphosphine oxide but apart from giving the desired phosphine,
also cleaved the compound to give diphenylphosphine and presumably 3-phenylprop-2-ene. Of the silanes used by Fritzshe et al., trichlorosilane and phenyl-silane were employed.

Trichlorosilane reduces triphenylphosphine oxide and benzyldiphenylphosphine oxide in refluxing benzene solution, the mechanism of which proceeds via a four-membered cyclic transition state:

\[
\begin{align*}
\text{a} - & \text{P}=\text{O} + \text{HSiCH}_3 & \rightarrow & \text{b} - \text{P}=\text{O} & \rightarrow & \left[ \begin{array}{c}
\text{a} \rightarrow \text{P}-\text{H} \quad \text{cSiCl}_3 \\
\text{c} \quad \text{H-SiCl}_3
\end{array} \right] \\
\text{b} - & \text{P}=\text{H} & \rightarrow & \text{c}
\end{align*}
\]

Trichlorosilane was found to be completely inactive toward the allylic phosphine oxides under the above conditions. However, phenylsilane was quite successful for the reduction of these phosphine oxides when used in the absence of solvent at 130°.

After the initial reduction, the reaction mixtures were rapidly distilled and the phosphines heated at 200° until the absorptions in the infrared at 1640, 985 and 920 cm\(^{-1}\) (-CH=CH\(_2\)) disappeared and the absorption at 970 cm\(^{-1}\) (trans -CH=CH-) appeared. The period for this was about 4 hrs. Temperatures of about 200° seem to be necessary as heating at
lower temperatures for longer periods, e.g. 130°C, overnight, gave no rearrangement. In all the cases observed, the possibility of cis-trans isomerism exists around the double bond which has migrated, but only the trans form was isolated. Here again the conditions, to which the cis isomer is subjected, are not favourable for its isolation.

Several attempts were made to isolate one of the starting phosphines (91) in a pure state, namely 1-phenylallyldiphenylphosphine, which proved difficult owing to the extreme ease with which it was oxidised. The phosphine when obtained in a pure state was a crystalline solid m.p. 74-75°C. Its infrared spectrum showed the absence of an absorption at 1180 cm⁻¹ (P=O) and the presence of absorptions at 985 and 920 cm⁻¹ (-CH=CH₂). On oxidation, the phosphine yielded the expected 1-phenylallyldiphenylphosphine oxide. However, the preparation of the quaternaryphosphonium salt with methyl iodide gave a salt the analysis of which suggested the formula C₂₂H₂₂IP required for the expected methyl(1-phenylallyl)-diphenylphosphonium iodide (93). The p.m.r. spectrum showed a doublet integrating for three protons at τ7.2 (JₚH = 13 c.p.s.) (P-Me) and a quartet integrating for three protons at τ8.07 (JₚH = 7, Jₚₚ = 4 c.p.s.). From this it appeared that the compound was not the expected methiodide but methyl(1-phenylprop-1-enyl)diphenylphosphonium iodide (94). This was presumably formed by a rearrangement of the expected methiodide.
The pure phosphine when subjected to the normal conditions for rearrangement underwent no change whatsoever. All attempts to catalyse the reaction failed, mainly because side reactions at 200° were more favourable than rearrangement, e.g. toluene-$p$-sulphonic acid was deoxygenated to give the phosphine oxide, hydrobromic acid cleaved the compound to give diphenylphosphine, stannous chloride gave apparently an organo-tin complex as suggested by the infrared spectrum and resublimed aluminium trichloride again cleaved the compound to give tetraphenyldiphosphine monoxide after isolation in air. When the pure 1-phenylallyldiphenylphosphine was heated at 200° with a few drops of phenylsilane, the rearrangement proceeded smoothly to give cinnamylidiphenylphosphine. This infers that the original heating reactions contained some organo-silicon compound which catalyses the rearrangement. The probable catalyst is a silanol which would distil over with the phosphine and act as an acid catalyst for the rearrangement.

This suggests that Horner's original postulation that
pure optically active allylmethylphenylphosphine racemises by means of an allylic rearrangement, is incorrect, and that the racemisation in being catalysed in some way.

The allylic phosphines (92) were further utilised in an activated olefin synthesis to prepare conjugated unsaturated systems.

Trippett has shown that phosphines which possess a proton on the α-carbon and a group to stabilise the incipient phosphorane, on heating under reflux with acrylonitrile and an aldehyde, give high yields of olefins. The mechanism is suggested to proceed by way of a proton transfer mechanism as follows:

\[
\begin{align*}
\text{R}_2\text{PCH}_2\text{R'} + \text{CH}_2\text{CHR'}' & \quad \text{R}_2\text{PCH}_2\text{R'}' \quad \text{R}_2\text{PCH}_2\text{CHR'}' \\
\text{CH}_2\text{CHR'}' & \quad \text{CH}_2\text{CH}_2\text{R'}' \\
\text{R}_2\text{PCH}_2\text{CH}_2\text{CHR'}' & \quad \text{R}_2\text{PCH}_2\text{CH}_2\text{CHR'}' \\
0 & \quad 0 \text{=} < \\
\text{R}_2\text{PCH}_2\text{CH}_2\text{CHR'}' & \quad \text{R}_2\text{PCH}_2\text{CH}_2\text{CHR'}' \\
+ \text{R'}\text{CH} = \text{C} < 
\end{align*}
\]

Cinnamylidiphenylphosphine, when subjected to the same reaction using benzoaldehyde and acrylonitrile in refluxing ethanol, gave a 53% yield of 1,4-diphenyl-buta-1,3-diene.

Addition of trivalent phosphorus compounds to Aldehydes and Ketones.

Trivalent phosphorus compounds which possess a group capable of stabilising an anion, react with aromatic aldehydes
to give α-substituted phosphine oxides as already mentioned (p. 9).

Dimethylaminodiphenylphosphine is capable of forming such a stable anion. When this phosphine was allowed to react with benzaldehyde at 120° an exothermic reaction was observed giving a highly crystalline phosphine oxide which analysed for C_{21}H_{22}NOP. The p.m.r. spectrum showed a singlet integrating for six protons at t7.65 (−NMe₂) and a doublet integrating for one proton at t5.7 (J_pH = 10 c.p.s.) (P−CH−). This coupled with the mass spectral information, m/e = 335 (mass peak), 201 (P₂PO), 134 (P.CH(NMe)), indicated that the compound was α-dimethylamino-benzylidiphenylphosphine oxide (95). The mechanism of its formation may be as follows:-

\[
\begin{align*}
\text{NMe}_2 & \xrightarrow{\Delta} \text{NMe}_2 \\
\phi_2\text{P} & \quad \text{C=O} \quad \phi_2\text{P−CH} & \quad \phi_2\text{P−CH} \\
\text{H} & \quad \text{O} & \quad \text{O} \\
\end{align*}
\]

Similarly, acetoxydiphenylphosphine on heating with benzaldehyde afforded α- acetoxybenzylidiphenylphosphine oxide. Its structure was ascertained by comparison with an authentic specimen.

Attempts to extend this reaction to other carbonyl compounds met with varying results. With acraldehyde, dimethylaminodiphenylphosphine gave only polymeric substances, but with
acetophenone, tetraphenyldiphosphine monoxide was obtained as the major product (60%) and 1-(methyl)-1-(phenyl)-2-(benzoyl)-ethyl-diphenylphosphine oxide (97) in 15% yield.

The formation of (97) is probably by an initial base catalysed condensation of two molecules of acetophenone to give dipynone (96) and diphenylphosphine oxide. The diphenylphosphine oxide then undergoes a normal Michael addition to the unsaturated ketone and it was by this method the oxide was independently synthesised.

\[
\begin{align*}
2\text{CMe}_2O &\xrightarrow{\text{O}_2\text{PNMe}_2} \phi\text{-C-CH=CH-C-}\phi \quad (96) + \phi\text{2PH} + \text{Me}_2\text{NH} \\
&\downarrow \phi\text{2PH} \quad \downarrow \phi\text{2PNMe}_2 \\
\phi\text{-C-CH}_2\text{-CH}_2\text{-C-}\phi &\quad \phi\text{2P-P\phi}_2 + \text{HNMe}_2 \\
\text{Me} &\quad (60\%) \\
\text{O} &\quad \text{O} \\
\phi &\quad \phi \\
\text{Me} &\quad \text{Me} \\
\text{O} &\quad \text{O} \\
\text{P\phi}_2 &\quad \text{P\phi}_2
\end{align*}
\]

(97) (15%)

The p.m.r. spectrum of (97) showed a doublet at r8.1 equivalent to three protons and two doublets equivalent to one proton each centred at r6.1. Two doublets appear for the -CH\text{2}-protons as opposed to one as the -CH\text{2}- group is adjacent to an assymetric carbon thus making the two protons magnetically non-equivalent.
Experimental

All reactions involving tervalent organophosphorus compounds were carried out under oxygen-free nitrogen. Light petroleum had b.p. 69-80°. P.m.r. spectra were recorded in deuteriochloroform with tetramethylsilane as internal standard on a Varian Associates A60 spectrometer. Mass spectra were recorded on an A.E.I. MS-9 spectrometer. All melting points were corrected.

1-Phenylallyldiphenylphosphine Oxide. Method (a).

A solution of chlorodiphenylphosphine (11 g.) in ether (25 ml.) was added slowly to a stirred solution of cinnamyl alcohol (6.6 g.) and pyridine (9 ml.) in ether (50 ml.) cooled in ice. After 1 hr., the resulting suspension was filtered and the filtrate evaporated under reduced pressure. The residue was heated at 130° for 1 hr. and then recrystallised from benzene-ether to give 1-phenyl-allyldiphenylphosphine oxide (10 g.), m.p. (from ethylacetate) 193-193.5°, \( \nu_{\text{max}} \) 1175 (P=O), 990, 920 cm.\(^{-1}\) (CH=CH\(_2\)) (Found: C, 79.1; H, 5.8; P, 9.6. \( \text{C}_{19}\text{H}_{14}\text{OP} \) requires C, 79.4; H, 6.0; P, 9.75%).

In a similar way, crotol alcohol (3.6 g.) gave 1-methyl-allyldiphenylphosphine oxide (7.5 g.), m.p. (from ether) 90-91°, \( \nu_{\text{max}} \) 1180 (P=O), 995, 920 cm.\(^{-1}\) (CH=CH\(_2\)), quartet at 18.64 (\( J_{\text{HH}} = 7 \), \( J_{\text{PH}} = 16 \) c.p.s.) (Found: C, 74.7; H, 6.6; P, 12.0.
C\textsubscript{14}H\textsubscript{17}PO requires C, 75.0; H, 6.65; P, 12.1%; geraniol (7.7 g.) gave, after chromatography of the reaction mixture on alumina (60 g.), geranyldiphenylphosphine oxide (1.25 g.), m.p. (from benzene-light petroleum) and mixed m.p. 113-4°; and linalyldiphenylphosphine oxide (6.4 g.), m.p. (from light-petroleum) 68-9°, \(v_{\text{max}}\) 1170 (P:O), 995, 910 cm\(^{-1}\) (CH:CH\(_2\)) (Found: C, 78.07; H, 7.89; P, 9.34. C\textsubscript{22}H\textsubscript{27}PO requires C, 78.2; H, 8.0; P, 9.16%); 3-methylbut-3-en-1-ol (4.2 g.) gave, after chromatography on alumina (60 g.), 1,1-dimethylallyldiphenylphosphine oxide (7 g.), m.p. (from benzene-light petroleum) 105-6°, \(v_{\text{max}}\) 1180 (P:O), 990, 915 cm\(^{-1}\) (CH:CH\(_2\)), doublet at 8.7\(\tau\) equivalent to 6 protons (\(J_{PH} = 14\) c.p.s.) (Found: C, 75.71; H, 7.20; P, 11.67. C\textsubscript{17}H\textsubscript{19}PO requires C, 75.6; H, 7.04; P, 11.5%); 1-vinylcyclohexanol (2.8 g.) gave, after chromatography of the reaction mixture on alumina (60 g.), 2-cyclohexylidene-ethyldiphenylphosphine oxide (0.26 g.), m.p. (from benzene-light petroleum) and mixed m.p. 166-167°; 1-phenylallyl alcohol (2 g.) gave cinnamylidiphenylphosphine oxide (0.2 g.), m.p. (from benzene-light petroleum) and mixed m.p. 181-182°, and 2-methylbut-3-en-2-ol (4.2 g.) gave, after chromatography on alumina, 3-methylbut-2-enylidiphenylphosphine oxide (0.5 g.), m.p. (from benzene-light petroleum) and mixed m.p. 124-125°. The major product from these last three experiments was a substance, m.p. (from chloroform-ethyl acetate) 251-252° (Found: C, 64.3; H, 5.0; N, 1.9; P, 13.85%).
Cinnamyldiphenylphosphine Oxide. Method (b).

Chlorodiphenylphosphine (3.4 g.) was added slowly to a solution of 1-phenylallyl alcohol (2 g.) in pyridine (35 ml.) at room temperature and the solution set aside for 2 hr. and then heated under reflux for 1 hr.

Pyridine was removed under reduced pressure and the residue, in chloroform, washed with dilute hydrochloric acid (3×), sodium hydrogen carbonate solution, and water. The solution was then dried and evaporated. The residue crystallised from benzene-light petroleum to give cinnamyldiphenylphosphine oxide (2.8 g.), m.p. and mixed m.p. 181-182°.

In a similar way, 1-vinylcyclohexanol (2.8 g.) gave 2-cyclohexylidene-ethyldiphenylphosphine oxide (3 g.), m.p. and mixed m.p. 166-167°.

2-Cyclohexylidene-ethyldiphenylphosphine Oxide.

A solution of 2-cyclohexylidene-ethyl bromide (0.88 g.) and methyl diphenylphosphinite (1 g.) in benzene (10 ml.) was heated under reflux for ½ hr., evaporated, and the residue crystallised from benzene-light petroleum to give 2-cyclohexylidene-ethyldiphenylphosphine oxide (0.85 g.), m.p. 166-167°, v_max, 1180 cm⁻¹ (P=O) (Found: C, 77.45; H, 7.4. C_{29}H_{23}OP requires C, 77.4; H, 7.4%).

Similarly, cinnamyl bromide gave cinnamyldiphenylphosphine oxide (55%), m.p. (from benzene-light petroleum)
181-182°, \( \nu_{\text{max}} \) 1180 (P=O), 970 cm\(^{-1}\) (trans -CH\(_2\)CH) (Found: C, 79.25; H, 5.8; P, 9.6; \( \text{C}_{21}\text{H}_{12}\text{OP} \) requires C, 79.4; H, 6.0; P, 9.75%), and 3-methylbut-2-enyl bromide gave 3-methylbut-2-enyldiphenylphosphine oxide (72%), m.p. (from benzene-light petroleum) 124-125°, \( \nu_{\text{max}} \) 1180 cm\(^{-1}\) (P=O) (Found: C, 75.45; H, 7.1; P, 11.4. \( \text{C}_{17}\text{H}_{19}\text{OP} \) requires C, 75.5; H, 7.0; P, 11.5%).

Geranyldiphenylphosphine Oxide. Method (c).

Linalool (2.25 g.) and dimethylaminodiphenylphosphine (3 g.) were heated at 130° for 24 hr. and the residue crystallised from benzene-light petroleum to give geranyldiphenylphosphine oxide (2.7 g.), m.p. 113-114°, \( \nu_{\text{max}} \) 1180 cm\(^{-1}\) (P=O), quartet at \( \delta \) 6.93 equivalent to two protons (\( J_{\text{HH}} = 7, J_{\text{PH}} = 15 \) c.p.s.) (Found: C, 78.0; H, 8.0; P, 9.35. \( \text{C}_{22}\text{H}_{27}\text{OP} \) requires C, 78.2; H, 8.0; P, 9.2%).

Similarly, 1-phenylallyl alcohol (3.0 g.) and dimethylaminodiphenylphosphine (5.1 g.) gave cinnamyldiphenylphosphine oxide (4.5 g.), m.p. and mixed m.p. 181-182°; the same alcohol (2.6 g.) and pyrrolidinyldiphenylphosphine (5 g.) gave the same phosphine oxide (3.6 g.); 2-methylbut-3-en-2-ol (2 g.) and dimethylaminodiphenylphosphine (7 g.) gave 3-methylbut-2-enyldiphenylphosphine oxide (0.5 g.), m.p. and mixed m.p. 124-125°; 1-vinylcyclohexanol (1.65 g.) and the same phosphine (3.0 g.) gave 2-cyclohexylidene-ethylidiphenylphosphine oxide (2.0 g.), m.p. and mixed m.p. 167-168°; and 1-phenylpenta-1,4-dien-3-ol (3.2 g.) and the same phosphine (4.6 g.) gave 5-phenylpenta-2,4-
diényldiphenylphosphine oxide (1.6 g.), m.p. (from benzene) 221-222°, ν max. 1180 (P=O), 990 cm.⁻¹ (trans CH=CH), quartet at τ 6.82 equivalent to two protons (JHH = 7, JPH = 15 c.p.s.), λ max. 292, 311 μ (ε 48,500, 27,800 in ethanol) (Found: C, 80.2; H, 6.0. C23H21OP requires C, 80.4; H, 6.1%).

1,6-Diphenylhexa-1,3,5-triene.

A suspension of sodium hydride (30 mg.) in dimethyl sulphoxide (50 ml.) was stirred at 60° for ½ hr.; 5-phenylpenta-2,4-diényldiphenylphosphine oxide (0.4 g.) was added and the solution set aside at room temperature for ½ hr. Benzaldehyde (1.26 g.) was then added and the solution set aside at room temperature overnight, then poured into saturated brine (150 ml.). The mixture was extracted with ether (3 x 50 ml.) and the combined extracts washed with water, dried, and evaporated. Crystallisation of the residue from ethanol gave 1,6-diphenylhexa-1,3,5-triene (120 mg.), m.p. 200-202° (lit., m.p. 203°), having the recorded ultraviolet spectrum.

Vinyl-β-ionol (94).

To an ice cooled, stirred solution of magnesium turnings (9 g.) and one crystal of iodine in tetrahydrofuran (150 ml.) was added slowly a solution of vinyl bromide (40 g.) in tetrahydrofuran (80 ml.). To this solution, β ionone (40 g.) in tetrahydrofuran (40 ml.) was added slowly at room temperature. The solution was set aside for ½ hr. then poured into saturated
ammonium chloride solution (1 l.). The organic phase was separated and the aqueous phase extracted with ether (2 x 350 ml.), dried, and evaporated. Distillation under reduced pressure gave vinyl-β-ionol (80%), b.p. 1.0 mm. 103-6° (lit., b.p. 2.0 mm. 113-5°).

3-Methyl-5-(2',6',6'-trimethylcyclohex-1'-enyl)penta-2,4-dienyl-diphenylphosphine Oxide. (A).

Dimethylaminodiphenylphosphine (10 g.) and vinyl-β-ionol (10 g.) were heated at 140° for 36 hr. The residue, in benzene, was chromatographed on neutral alumina (300 g.). Ether 0.5% methanol eluted the phosphine oxide (A; 1.4 g.), m.p. (from benzene-light petroleum) 126-127°, which gave only one spot on thin-layer chromatography; λ max. 260, 266.5, 273 μ (ε 12,700, 13,000, 12,300 in ethanol), mass peak m/e 404, base peak m/e 201 (P:O), other significant peaks at m/e 389, 215, 202, quartet at τ6.78 equivalent to two protons (J H,H = 8, J H,P = 15 c.p.s.) (Found: C, 80.1; H, 8.05. C27H33OP requires C, 80.1; H, 8.2%).

Experiments with Acetoxydiphenylphosphine. Method (d).

Pyrrolidinylidiphenylphosphine (13.2 g.) and acetic anhydride (5.2 g.) were mixed and set aside until the temperature of the mixture, which rose to 70°, fell to 25°. The mixture then had ν max. 1660 (MeCO.NC4H8), 1750 cm.⁻¹ (P:OAc).

The above product (2.8 g.), triethylamine (1.4 g.), and 1-phenylallyl alcohol (1.4 g.) were mixed and set aside at room
temperature for 1/2 hr. The mixture, which then showed no absorption at 3300 or 1750 cm.\(^{-1}\) was heated to 130° for 1 hr., cooled, and recrystallised from benzene-light petroleum to give cinnamyl diphenylphosphine oxide (2 g.), m.p. and mixed m.p. 183-184°. Similarly, 1-phenyl-penta-1,4-dien-3-ol (1.6 g.) gave 5-phenylpenta-2,4-dienyldiphenylphosphine oxide (0.5 g.), m.p. and mixed m.p. 221-222°.

The above mixture of N-acetylpyrrolidine and acetoxydiphenylphosphine (2.8 g.), triethylamine (1.2 g.), and 2-methylbut-3-en-2-ol (0.86 g.) were mixed and kept at room temperature for 3 hr. The absorption at 3300 and 1750 cm.\(^{-1}\) showed no diminution and the mixture was therefore kept at 70° for 3 hr. whereupon these absorptions had disappeared. Recrystallisation of the product from benzene-light petroleum gave 3-methylbut-2-enyldiphenylphosphine oxide (1.2 g.), m.p. and mixed m.p. 123-124°.

Phenylsilane.

To an ice cooled suspension of lithium aluminium hydride (10 g.) in ether (150 ml.), phenyltrichlorosilane (60 g.) was added slowly. After the addition was complete, the reaction mixture was heated under reflux for 1 hr. The solution was recooled in ice and excess water was added slowly. The mixture was heated under reflux for a further 1 hr. and then poured onto ice-water (500 ml.). The ether layer was separated and the aqueous
layer extracted with ether (2 x 100 ml.). The combined ether layers were dried and evaporated. Distillation gave phenylsilane (90%), b.p. 760 mm. 120° (lit., b.p. 760 mm. 120°).

Rearrangement of 1-Phenylallyldiphenylphosphine.

1-Phenylallyldiphenylphosphine oxide (4.25 g.) was heated with phenylsilane (3 g.) at 140° for 2 hr. Rapid distillation under reduced pressure gave 1-phenylallyldiphenylphosphine (3.3 g.), b.p. 0.6 mm. 190-5°, characterised by oxidising an aliquot with 100 vol. hydrogen peroxide in benzene to give 1-phenylallyldiphenylphosphine oxide, m.p. (from ethyl acetate) and mixed m.p. 193-194°.

The phosphine was heated at 120° overnight after which a small portion, when oxidised in the same manner, gave 1-phenylallyldiphenylphosphine oxide. Heating at 210° for five hours gave cinnamyl- diphenylphosphine, characterised by oxidation of an aliquot to cinnamylidiphenylphosphine oxide, m.p. (from benzene-light petroleum) and mixed m.p. 184-185°.

Similarly, 1-methylallyldiphenylphosphine oxide (4.2 g.) and phenylsilane (3 g.) were heated together at 120° for 2 hr. Distillation under reduced pressure gave 1-methylallyldiphenylphosphine (3.6 g.), b.p. 0.7 mm. 138-144°, $v_{\text{max}}$. 990, 910 cm$^{-1}$] (CH:CH$_2$). An aliquot was oxidised to give 1-methylallyldiphenylphosphine oxide, m.p. (from ether) and mixed m.p. 90-91°. Heating at 210° for 4 hr. gave crotyldiphenylphosphine, $v_{\text{max}}$. 960 cm$^{-1}$ trans (CH:CH). An aliquot was oxidised with 100 vol. hydrogen peroxide in benzene to give crotyldiphenylphosphine oxide, m.p.
(from benzene-light petroleum) and mixed m.p. 115-116°; linalyl-
diphenylphosphine oxide (3.5 g.) on heating with phenylsilane gave,
after distillation under reduced pressure, linalyldiphenylphosphine
(2.6 g.), b.p. 0.4 mm. 180-200°. Heating at 200° for 3 hr. gave
geranyldiphenylphosphine characterised by the formation of its
oxide, m.p. (from benzene-light petroleum) and mixed m.p. 113-114°;
1,1-dimethylallyldiphenylphosphine oxide (4 g.) on heating with
phenylsilane (3 g.) at 140° for 4 hr. gave, after distillation
under reduced pressure, 1,1-dimethylallyldiphenyl phosphine (3.2 g.),
b.p. 1.0 mm. 160-165°, an aliquot was quaternised with methyl
iodide in benzene to give 1,1-dimethyl allylmethylidiphenyl-
phosphonium iodide, m.p. (from chloroform-ethyl acetate) 119-120°,
υ max. 990, 920 cm.−1 (CH₃CH₂) (Found: C, 54.84; H, 5.43; P, 8.05.
C₁₁H₂₂P requires C, 54.6; H, 5.55; P, 7.84%). The remainder of
phosphine was heated at 200° for 3 hr. to give 3-methylbut-2-enyl-
diphenylphosphine, characterised by oxidation to 3-methylbut-2-
enyldiphenylphosphine oxide, m.p. (from benzene-light petroleum)
and mixed m.p. 123-124°.

1-Phenylallyldiphenylphosphine

1-Phenylallyldiphenylphosphine oxide (6 g.) and phenyl-
silane (4 g.) were heated at 150° for 4 hr. The excess phenyl-
silane was then evaporated under reduced pressure. 20% sodium
hydroxide solution (40 ml.) was added and the solution heated
under reflux for ½ hr. The solution was extracted with benzene
(50 ml.), the extract was washed with water (20 ml.), dried and evaporated. Recrystallisation from aqueous methanol gave 1-phenylallyldiphenylphosphine (2.3 g.), m.p. 74-76\(^\circ\)C, \(v_{\text{max}}\) 985, 920 cm\(^{-1}\) (CH:CH\(_2\)). Quaternisation with methyl iodide gave methyl(1-phenylprop-1-enyl)diphenylphosphonium iodide, m.p. (from chloroform-ethyl acetate) 172-3\(^\circ\) (Found: C, 59.36; H, 4.85; P, 7.1%. C\(_{22}\)H\(_{22}\)IP requires C, 59.6; H, 4.96; P, 7%).

**Rearrangement of 1-Phenylallyldiphenylphosphine without a Catalyst.**

Pure 1-phenylallyldiphenylphosphine (0.4 g.) was heated at 200\(^\circ\) overnight with no change. An aliquot was oxidised to give 1-phenylallyldiphenylphosphine oxide, m.p. and mixed m.p. 193-194\(^\circ\). A further aliquot on quaternisation with methyl iodide gave methyl(1-phenylprop-1-enyl)diphenyl phosphonium iodide m.p. and mixed m.p. 172-3\(^\circ\).

**Attempted Rearrangement of 1-Phenylallyldiphenylphosphine with Catalysts.**

Pure 1-phenylallyldiphenylphosphine (0.4 g.) was heated together with phenylsilane (0.06 g.) at 200\(^\circ\) for 4 hr. The reaction mixture was then heated under reflux for \(\frac{1}{2}\) hr. with 20% sodium hydroxide solution (30 ml.). The solution was extracted with benzene (20 ml.). The extract was washed, dried and evaporated to give cinnamylidiphenylphosphine (0.25 g.). Quaternisation with
methyl iodide gave cinnamylmethylidiphenylphosphonium iodide, m.p. (from chloroform-ethyl acetate) 156-157°, ν max. 970cm.⁻¹ (trans CH:CH), doublet at 7.2 equivalent to three protons (J PH = 14 c.p.s.), quartet at 5.53 equivalent to two protons (J HH = 7, J PH = 16 c.p.s.) (Found: C, 59.39; H, 4.94; P, 7.16. C 22H 22IP requires C, 59.6; H, 4.96; P, 7.0%).

In a similar manner, the same phosphine (0.2 g.) was heated with toluene-p-sulphonic acid (0.05 g.) at 200° to give 1-phenylallylidiphenylphosphine oxide, m.p. and mixed m.p. 193-194°; the same phosphine (0.2 g.) with concentrated hydrobromic acid (0.02 g.) gave, after isolation in air, diphenylphosphonic acid (0.1 g.), m.p. (from benzene) and mixed m.p. 191-192°, and the same phosphine (0.4 g.) with resublimed aluminium trichloride (0.1 g.) gave, after trituration with ether, tetraphenyldiphosphine monoxide (0.2 g.), m.p. and mixed m.p. 156-159°.

1,4-Diphenylbuta-1,3-diene.

A solution of cinnamylidiphenylphosphine (1.4 g.), benzaldehyde (0.5 g.), and acrylonitrile (0.6 g.) in absolute ethanol (30 ml.) was heated under reflux overnight. The solution was evaporated under reduced pressure and chromatography of the residue on basic alumina (60 g.) gave 1,4 diphenylbuta-1,3-diene (0.4 g.), m.p. (from aqueous ethanol) and mixed m.p. 154-5° (lit., m.p. 152.5°).
Reaction of Acetoxydiphenylphosphine with Benzaldehyde.

The reaction mixture of N-acetylpyrrolidine and acetoxy-diphenylphosphine (2.8 g.) (from p. 49) was heated to 180° for 1/2 hr. with benzaldehyde (1.06 g.) and the product recrystallised from benzene-light petroleum to give α-acetoxybenzyldiphenylphosphine oxide (1.4 g.), m.p. and mixed m.p. 176-177°.

α-Acetoxybenzyldiphenylphosphine.

To a solution of α-hydroxybenzyldiphenylphosphine oxide (1 g.) in pyridine (25 ml.), acetic anhydride (3 ml.) was added and the solution set aside overnight.

Ethanol (2 ml.) was added and the solution set aside for a further 1 hr., then poured into water (70 ml.). The mixture was extracted with chloroform (3 x 25 ml.), and the combined extracts were washed with water (2 x 50 ml.) and dried. Evaporation under reduced pressure gave a residue which was recrystallised from benzene-light petroleum to give α-acetoxybenzyldiphenylphosphine oxide (0.7 g.), m.p. 176-7° (lit., m.p. 175°).

α-Dimethylaminobenzyldiphenylphosphine Oxide.

Dimethylaminodiphenylphosphine (5 g.) was heated to 165° for 1/2 hr. with benzaldehyde (2.3 g.) and the product recrystallised from chloroform-ethyl acetate to give α-dimethylaminobenzyldiphenylphosphine oxide (4.5 g.), m.p. 195-196°.
(Found: C, 75.35; H, 6.55; P, 4.04. \( \text{C}_{21}\text{H}_{22}\text{NOP} \) requires C, 75.4; H, 6.57; P, 4.18%).

**Reaction of Dimethylaminodiphenylphosphine with Acetophenone.**

Dimethylaminodiphenylphosphine (5 g.) was heated to 200° for 4 hr. with acetophenone (3 g.). The solution on cooling deposited crystals of tetraphenyldiphosphine monoxide (2.5 g.), m.p. and mixed m.p. 156-159°. The mother-liquors were chromatographed on basic alumina (46 g.). Elution with ether gave 1-(methyl)-1-(phenyl)-2-(benzoyl)-ethyldiphenylphosphine oxide (97; 0.8 g.), m.p. (from benzene) and mixed m.p. 148-149°.

1-(Methyl)-1-(Phenyl)-2-(Benzoyl)ethyldiphenylphosphine Oxide (97)

To a solution of dypnone (3 g.) and diphenylphosphine oxide (3 g.) in absolute ethanol (50 ml.), sodium ethoxide solution was added until the solution was alkaline to litmus. The solution was allowed to stand overnight. Evaporation under reduced pressure and recrystallisation of the residue from benzene gave the phosphine oxide (97; 3.4 g.), m.p. 148-149°, mass peak \( m/e \ 424 \), base peak \( m/e \ 201 (\text{Ph}_2\text{PO}) \), other significant peaks at \( m/e \ 319, 305 \), doublet at \( \tau 8.09 \) equivalent to three protons \((J_{PH} = 16 \text{ c.p.s.})\), doublet at \( \tau 6.0 \) equivalent to one proton \((J_{PH} = 11 \text{ c.p.s.})\), doublet at \( \tau 6.1 \) equivalent to one proton \((J_{PH} = 8 \text{ c.p.s.})\) (Found: C, 79.7; H, 5.89; P, 7.02. \( \text{C}_{28}\text{H}_{35}\text{O}_2\text{P} \) requires C, 79.5; H, 5.81; P, 7.32%).
The Effect of Trivalent Phosphorus as a Neighbouring Group.

Neighbouring group participation by the nitrogen, oxygen and sulphur atoms in promoting certain nucleophilic displacements is well established. Little evidence has emerged supporting a similar anchimeric effect occurring in the case of a trivalent phosphorus atom.

Mann and Hitchcock have reported the self quaternisation of (2-bromoethyl)ethylphenylphosphine at room temperature to form 1,4-diethyl-1,4-diphenyl-1,4-diphosphonicyclohexane dibromide. Similarly 1,3-diiodopropane, on refluxing with diphenylphosphine in acetonitrile, gives 1,1,5,5-tetraphenyl-1,5-diphosphonio-cyclooctane diiodide.

The leaving group in the quaternisation is not restricted to a halogen atom as dialkyl-2-acetoxyethylphosphines exothermically self quaternises with the formation of 1,1,4,4-tetraalkyl-diphosphonicyclohexanes. However, unlike the dihalides mentioned, the analogous 3-acetoxypropylphosphines do not undergo a similar reaction even at elevated temperatures.

Further work on these systems by Soloway et. al. confirm these observations. The authors report that 2-hydroxyethylidiphenylphosphine (98a) undergoes thermal decomposition to give both diphenylvinylphosphine (12%) (99) and 1,2-bis(diphenylphosphinyl)ethane (100) (55%). The acetate (98b) and benzoate (98c) of this alcohol behave in a similar manner with the formation
of the vinylphosphine and 1,2-bis(diphenylphosphino)ethane (101).

To explain this, the authors assume the initial formation of a highly labile 1,1-diphenylphosphonio-cyclopropane salt (102). Their supporting evidence for this intermediate was the observation that the rate of decomposition increased as the ability of the group (OR) to leave increased. The cyclic phosphonium salt is envisaged as being capable of undergoing

\[
\begin{align*}
\phi_2PCHCHOR & \rightarrow \phi_2PCH:CH_2 + \phi_2POR + ROH \\
(98) & \quad (102)
\end{align*}
\]

\[
\begin{align*}
\phi_2PCHCHP(\phi)CHCHOR & \rightarrow \phi_2PCHCH\phi \rightarrow \phi_2PCH\phi + \phi_2POR \\
(103) & \quad (102)
\end{align*}
\]

\[
\begin{align*}
\phi_2PCHCHP(\phi)CH:CH_2 & \rightarrow \phi_2PCH:CH_2 + \phi_2POR \\
(104) & \quad (102)
\end{align*}
\]

\[
\begin{align*}
\phi_2PCH_2CH_2P & \rightarrow \phi_2PCH_2CH_2P \rightarrow \phi_2PCH_2CH_2P \rightarrow \phi_2PCH_2CH_2P + \phi_2POR \\
(100) & \quad (101) & \quad (102)
\end{align*}
\]

a, \( R = H \)  
b, \( R = C_{OME} \)  
c, \( R = CO\phi \)
two reactions: ring opening to give diphenylvinylphosphine and reaction with another molecule of phosphonium salt to give (103).

This dimer can then form a vinylphosphonium salt via an ylid, the base for this step being the starting phosphine. Cyclisation of this intermediate gives the observed 1,1,4,4-tetraphenyl-1,4-diphenoniocyclohexane salts (104). These salts at elevated temperatures would be expected to give the 1,2-bis(diphenylphosphinyl)ethane when \( R = \text{OAc}, \text{OBz.} \) and 1,2-bis(diphenylphosphine)ethane when \( R = \text{H} \).

Confirmation of this suggested neighbouring group effect, was sought by studying the acetolysis of trans-\( \alpha \)-(diphenylphosphino)cyclohexyl tosylate (105; \( R = \text{Tosyl} \)).

\[
\text{OR} \\
\text{P} \phi_2
\]

\( \text{(105)} \)

It has long been known that the solvolysis of trans-2-acetoxy-cyclohexyl \( p \)-toluenesulphonate and other related compounds in glacial acetic acid containing potassium acetate proceeds with retention of configuration to give trans-2-acetoxy-cyclohexyl acetate. The suggested mechanism is as follows, the acetoxy group undergoing \((\text{AcO})_5\) participation:-
From the above it could be assumed that the acetolysis of (105; R=Tsyl) could proceed via a similar route involving a cyclic phosphonium compound resulting in the formation of trans-2-(diphenyl-phosphino)cyclohexyl acetate.

The parent alcohol (105; R=H) was prepared by the ring' opening of 1,2-epoxycyclohexane with sodium diphenylphosphide in 90% yield by the method of Issleib. All methods used for the preparation of the tosylate resulted in the formation of the 3-hydroxyphosphine oxide. This seems to be a general reaction of trivalent phosphorus compounds with sulphonyl halides and sulphonic acids.

\[
R_3P + \phiSO_2Cl \xrightarrow{\text{CHCl}_3} R_3P=O + \phiSH + (\phiS)_2 \\
R_3P + \phiSO_2H \xrightarrow{\text{benzene}} \phiSH + R_3P=O
\]

However, it was found to be equally impossible to tosylate either the corresponding phosphine oxide or the methylphosphonium iodide. Independent tosylations of 2-hydroxyethyltriphenylphosphonium bromide gave a product which appeared to be 2-hydroxyethyltriphenylphosphonium toluene-p-sulphonate. The starting material could be regenerated from this salt by shaking with excess saturated potassium bromide solution.

As the benzoyloxy- residue is a better leaving group than the acetoxy, it was thought that a similar acetolysis would
be observed, using the benzoate (105; R=CO$), as hoped for with the tosylate, i.e.

The benzoate was duly prepared by the standard method employing benzoyl chloride in pyridine solution. However, in all the solvolytic reactions carried out, no conditions could induce the benzoyloxy group to be replaced by acetoxy.

Further work by Weinheim et al.,$^{115,116}$ regarding the solvolysis of trans-2-methoxy-cyclohexylbromide and related compounds with silver salts suggested the use of a bromide ion as a leaving group. Bromination of (105; R=H) by the standard reaction$^{117}$ of hydrogen bromide in glacial acetic acid on the alcohol gave the corresponding acetate (105; R=COMe). From this it was assumed that the large diphenylphosphino-group held the molecule predominantly in the diequatorial configuration; thus esterification occurred rather than bromination which needs a trans-diaxial configuration.

To eliminate this conformational effect, a fused ring
system was used, the compound employed being 3α-diphenylphosphino-
cholestan-2β-ol (106; R=H) which was prepared by the following route.

![Chemical structure diagram]

Similar experiments to those cited above were carried out but with the same observed results i.e. the benzoyloxy-group in the compound (106; R=COΦ) did not solvolyse in glacial acetic acid containing potassium acetate and treatment of (106; R=H) with hydrogen bromide in acetic acid gave the acetate (106; R=COMe). A minor product of this latter reaction was found to be cholest-2-ene, identified by its mass spectrum. This can be explained by assuming that a proton transfer occurs to give an intermediate betaine which undergoes a Wittig reaction to give the
olefin and diphenylphosphine oxide.

\[
\begin{align*}
\text{HO} & \quad \leftrightarrow \quad \text{O} \\
\phi_2P & \quad \phi_2P \\
\end{align*}
\]

Even in the steroid system it is not completely possible
to rule out conformational effects i.e. the bulky diphenylphosphino-
group even here may be forcing ring A of the steroid system into
the boat form which would favour esterification once more.
Hence, attention was drawn to acyclic systems, the first of which
was the compound (107), 2-hydroxypropyl-diphenylphosphine. This
behaved in a similar manner to its predecessors in the reactions
\[
\text{OH} \\
\phi_2P-\text{CH}_2-\text{CH-CH}_3 \\
\]
mentioned above. In addition to these experiments the \(p\)-nitro-
benzoate ester was prepared as \(p\)-nitrobenzoic acid is a reasonably
proficient leaving group and has been known to promote participation
reactions. However, after heating under reflux in
aqueous acetone or aqueous dioxan for several days no reaction
was observed.

The preparation, by Mann, \(121,122,123,124\) of cyclised
products from the action of hydrogen bromide in acetic acid on
\(o\)-(methoxymethyl)benzyldiphenylphosphine, presumably by way of
the intermediate \(o\)-(bromomethyl)benzyldiphenylphosphine, led to
the preparation of the two isomeric ethers (108, 109; R=Me).

\[
\begin{align*}
&\text{CH}_3 \\
&\phi_2\text{P-CH}_2\text{-CH-OR} \\
&\text{(108)} \\
&\text{CH}_3 \\
&\phi_2\text{P-CH-CH}_2\text{OR} \\
&\text{(109)}
\end{align*}
\]

On treating these ethers with hydrogen bromide refluxing acetic acid, protonation of the oxygen function and subsequent cleavage of the ether group could be envisaged to give a carbonium ion. If trivalent phosphorus provides anchimeric assistance the reaction of the two ethers should pass through a common intermediate (110). Attack on this intermediate by any anion \(X^-\) be it bromide, acetate or hydroxide should give a predominance of one product viz.

\[
\begin{align*}
&\text{CH}_3 \\
&\phi_2\text{P-CH}_2\text{-CH-OR} \\
&\text{(108)} \\
\text{or} \quad \text{HBr/HX} \\
&\text{CH--CH}_2 \\
&\downarrow X^- \\
&\text{X-CH-CH}_2\text{-P}\phi_2 \\
&\text{Me} \\
&\text{(109)} \\
&\text{(110)}
\end{align*}
\]

However, treatment of the ethers (108,109; R=Me) with either hydrogen bromide in refluxing acetic acid or refluxing constant boiling hydrobromic acid gave the corresponding acetates (108, 109; R=COMe) or alcohols (108, 109; R=H) respectively with no mixed products.

Similar experiments were carried out on 3-methoxypropyl-diphenylphosphine in which the methoxy-group is one carbon atom
further away from the diphenylphosphino-group.

It was found that treatment of the phosphine with hydrogen bromide in glacial acetic acid gave a non-crystallisable phosphine oxide the infrared spectrum of which inferred an acetate group being present. However, on heating the phosphine with constant boiling hydrobromic acid under reflux, 3-bromopropyl-diphenylphosphine was the product.

**Conclusions.**

From the experiments detailed above there is no evidence for trivalent phosphorus compounds undergoing neighbouring group participation at least via a three-membered ring, i.e. \((R_2P:)_3\) participation. The limiting factor must be the stability of the three-membered phosphonium ring in the transition state if anchimeric assistance is to be observed. Three-membered cyclic phosphines have been isolated\(^2,138,139,140\) even the parent, \(140\) phosphirane, has a lifetime of c.a. 24 hr. at room temperature. However, no quaternary phosphonium salts of these phosphines are known. When phosphirane is treated with hydrogen chloride below room temperature it rapidly decomposes to mainly ethylene and phosphine. 2-Chloroethylidiphenylphosphine, \(^{141}\) which has
recently been prepared, is said to have been distilled at
temperatures above $100^\circ$ but this seems very dubious. It is
therefore probable that the energy of the transition state for
participation to be observed is too great and the reaction takes
a more energetically favoured course. Thus the observations of
Turner and Soloway cannot be accounted for by their mechanism
involving a cyclic phosphonium salt. However, it is known that
a trivalent phosphorus atom can stabilise an $\alpha$-carbanion
and that vinylphosphines and their phosphonium salts are
susceptible to Michael addition, and it may be that the
$1,2$-bis(diphenylphosphino)ethane is formed via a vinylphosphine
shown in the following scheme:

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{OR} & \xrightarrow{\Delta} \text{CH}_2\text{CH}_2\text{P} \text{ROH} \\
\text{CH} & \equiv \text{CH} \quad \text{CH} & \equiv \text{CH} \\
\text{CH} & \equiv \text{CH} \quad \text{CH} & \equiv \text{CH} \\
\text{P} & \equiv \text{P} \quad \text{P} & \equiv \text{P} \\
\text{OR} & \equiv \text{OR} \quad \text{OR} & \equiv \text{OR} \\
\text{OR} & \equiv \text{OR} \quad \text{OR} & \equiv \text{OR} \\
\text{OR} & \equiv \text{OR} \quad \text{OR} & \equiv \text{OR} \\
\text{OR} & \equiv \text{OR} \quad \text{OR} & \equiv \text{OR} \\
\end{align*}
\]
Experimental

All reactions involving tervalent phosphorus compounds were carried out under oxygen-free nitrogen. Light petroleum had b.p. 60-80°. P.m.r. spectra were recorded in deuteriochloroform with tetramethylsilane as internal standard on a Varian Associates A 60 spectrometer. Mass spectra were recorded on an A.E.I. MS-9 spectrometer. All m.p.s were corrected.

2-Diphenylphosphinocyclohexanol.

Sodium wire (6 g.) was added to a solution of diphenylphosphine (6 g.) in tetrahydrofuran (100 ml.) and the solution heated under reflux for 2 hr. The excess of sodium was then removed and a solution of 1,2-epoxycyclohexane (5 g.) in tetrahydrofuran (50 ml.) was added slowly. Dilute acetic acid (1:1) was then added until the solution was acid to litmus. The solution was evaporated under reduced pressure and the residue dissolved in chloroform (250 ml.). The solution was washed with water (4 x 100 ml.), dried and evaporated under reduced pressure to give 2-diphenylphosphino-cyclohexanol (8.5 g.), m.p. (from ethanol-water) 138-139°, \( \nu_{\text{max}} \) 3400 cm\(^{-1}\) (OH); the methiodide had m.p. (from chloroform-ethyl acetate) 227.5-228°, \( \nu_{\text{max}} \) 3350 (OH), 1420 cm\(^{-1}\) (P\(\phi\)) (Found: C, 53.33; H, 5.64; P, 7.23. \( \text{C}_{19}\text{H}_{24}\text{IOP requires } \text{C}, 53.5; \text{H}, 5.64; \text{P}, 7.3\% \)). The phosphine oxide had m.p. (from benzene-light petroleum) 156-157°, \( \nu_{\text{max}} \) 3300 (OH), 1180 (P\(\phi\)) (Found: C, 71.67; H, 6.75. \( \text{C}_{18}\text{H}_{21}\text{O}_{2}\text{P} \))
requires C, 72.0; H, 7.0%.

2-Diphenylphosphinocyclohexyl Acetate.

A solution of 2-diphenylphosphinocyclohexanol (1 g.) and acetic anhydride (3 ml.) in pyridine (25 ml.) was set aside for 24 hr. Ethanol (2 ml.) was then added and the solution set aside for a further 1 hr. Evaporation under reduced pressure gave a residue which crystallised from ethanol-water to give 2-diphenylphosphinocyclohexyl acetate (0.9 g.), m.p. 73-74°, \( \nu_{\text{max}} \) 1730 cm.\(^{-1}\) (C:O); the methiodide had m.p. (from chloroform-ethyl acetate) 221-222°, \( \nu_{\text{max}} \) 1725 (C:O), 1230 cm.\(^{-1}\) (OCO.Me) (Found: C, 54.0; H, 5.56. \( C_{21}H_{26}IO_{2}P \) requires C, 53.84; H, 5.55%).

2-Diphenylphosphinocyclohexyl Benzoate.

A solution of 2-diphenylphosphinocyclohexanol (2.5 g.) and benzoyl chloride (3 ml.) in pyridine (30 ml.) was set aside for 24 hr. Water (100 ml.) was then added slowly and the mixture extracted with chloroform (3 x 40 ml.). The combined extracts were washed with dilute acid, sodium hydrogen carbonate solution, water and dried. Evaporation under reduced pressure gave a residue which was recrystallised from ethanol-water to give 2-diphenylphosphinocyclohexyl benzoate (2.7 g.), m.p. 98-101°, \( \nu_{\text{max}} \) 1720 (C:O), 1275 cm.\(^{-1}\) (OCO.\( \phi \)); the methiodide had a m.p. (from acetone-ethyl acetate) 187-188°, \( \nu_{\text{max}} \) 1720 (C:O), 1270 cm.\(^{-1}\) (OCO.\( \phi \)) (Found: C, 58.89; H, 5.52. \( C_{26}H_{28}IO_{2}P \) requires C, 58.89; H, 5.52%); the phosphine oxide had a m.p. (from benzene-light petroleum)
192-193°, $v_{\text{max}}$, 1720 (C=O), 1280 (OCO$\cdot$), 1180 cm$^{-1}$ (P=O)

(Found: C, 73.84; H, 6.24. C$_{25}$H$_{25}$O$_3$P requires C, 74.2; H, 6.20%).

**Action of Tosyl Chloride on 2-Diphenylphosphinocyclohexanol.**

Tosyl chloride (0.7 g.) was added slowly to a cooled solution of the phosphine (1 g.) in pyridine (10 ml.) over a period of 2 hr. Water (1 ml.) was then slowly added over a further ½ hr. A further quantity of water (10 ml.) was then added and the solution extracted with chloroform (3 x 10 ml.). The combined extracts were washed with cold dilute sulphuric acid (3 x 10 ml.), sodium hydrogen carbonate solution, water and dried. Evaporation gave 2-diphenylphosphinocyclohexanol (0.8 g.), m.p. (from benzene-light petroleum) and mixed m.p. 156-157°.

Similarly, the phosphine oxide (0.5 g.) gave 2-diphenylphosphinocyclohexanol (0.4 g.), m.p. and mixed m.p. 156-157°; and 2-hydroxyethyltriphenylphosphonium bromide (3.8 g.) gave 2-hydroxyethyltriphenylphosphonium toluene-$p$-sulphonate (1.0 g.), m.p. (from chloroform-ethyl acetate) and mixed m.p. 184-185°.

**2-Hydroxyethyltriphenylphosphonium Toluene-$p$-sulphonate**

A solution of 2-hydroxyethyltriphenylphosphonium bromide (0.5 g.) in chloroform (5 ml.) was added to a solution of toluene-$p$-sulphonic acid (1 g.) which had been made alkaline with sodium hydrogen carbonate solution. The mixture was then shaken for 2 hr. The organic layer was removed and ethyl acetate added to precipitate 2-hydroxyethyltriphenylphosphonium toluene-$p$-sulphonate.
(0.6 g.), m.p. (from chloroform-ethyl acetate) 184-185°, ν_max.
3270 (OH), 1110 cm.⁻¹ (S=O) (Found C, 67.92; H, 5.64. C_{27}H_{27}O_{4}PS
requires C, 67.80; H, 5.65%).

Attempted Acetolysis of 2-Diphenylphosphinocyclohexyl Benzoate.

A solution of the phosphine (0.8 g.) and fused
potassium acetate (0.3 g.) in anhydrous glacial acetic acid
(5 ml.) was heated under reflux for 24 hr. The mixture was
quenched with water (20 ml.) and extracted with chloroform
(3 x 20 ml.). The combined extracts were washed with sodium
hydrogen carbonate solution and dried. Evaporation of the solvent
gave 2-diphenylphosphinocyclohexyl benzoate (0.6 g.), m.p.
(from ethanol-water) and mixed m.p. 98-100°.

Similarly, 2-diphenylphosphinylcyclohexyl benzoate
(0.3 g.) returned the starting material (0.3 g.), m.p. (from
benzene-light petroleum) and mixed m.p. 192-193°.

The Reaction of 2-Diphenylphosphinocyclohexanol with Hydrogen
Bromide in Glacial Acetic Acid.

A solution of the phosphine (2.5 g.) in glacial acetic
acid (50 ml.) was saturated with hydrogen bromide (prepared by
the action of bromine on tetraline). The solution was heated
under reflux for 6 hr. with a slow stream of hydrogen bromide
passing through it. The mixture was poured into water (250 ml.)
and extracted with chloroform (3 x 150 ml.). The combined
extracts were washed with sodium hydrogen carbonate solution and
dried. Evaporation of the solvent gave 2-diphenylphosphino-
cyclohexyl acetate (25 g.), which was characterised by its
methiodide, m.p. (from chloroform-ethyl acetate) and mixed m.p.
223-224°.

In a similar way, the methiodide of the phosphine
(1.5 g.) gave, after shaking the chloroform extracts with
saturated potassium iodide solution (4 x 20 ml.), drying and
evaporating, 2-acetoxycyclohexylmethylidiphenylphosphonium iodide
(1.0 g.), m.p. (from chloroform-ethyl acetate) and mixed m.p.
223-224°.

Cholestan-2,3-8-oxide

Cholestan-2,3-8-oxide was prepared from cholesterol
by standard methods via cholestanol, cholestanone,
2α-bromocholestanone and 2α-bromocholestan-3β-ol.

3α-Diphenylphosphinocholestan-2β-ol.

Sodium wire was added to a solution of diphenylphosphine
(1.8 g.) in tetrahydrofuran (60 ml.) and the solution heated under
reflux for 2 hr. The excess of sodium was then removed and a
solution of cholestan-2β,3β-oxide (3.7 g.) in tetrahydrofuran
(60 ml.) was added slowly. The solution was then heated under
reflux for 15 mins. Acetic acid (2 ml.) was then added and the
solution evaporated under reduced pressure. The residue, in
chloroform (40 ml.), was washed with water (4 x 10 ml.) and dried.
Evaporation of the solvent gave a residue which was recrystallised
from ethanol-water to give 3a-diphenylphosphinocholestan-2β-ol
(3.8 g.), m.p. 142-143°, \( \nu_{\text{max.}} \) 3300 cm\(^{-1}\) (OH); the phosphine oxide had a m.p. (from benzene-light petroleum) 232-233°,
[α]D + 92.5 (in ethanol), \( \nu_{\text{max.}} \) 3400 (OH), 1180 cm\(^{-1}\) (P:O)
(Found: C, 79.39; H, 9.92; P, 5.16. \( \text{C}_{39}\text{H}_{57}\text{O}_{2}\text{P} \) requires C, 79.6; H, 9.75; P, 5.26%).

3a-Diphenylphosphino-cholestan-2β-benzoate.

A solution of 3a-diphenylphosphinocholestan-2β-ol (1.0 g.) and benzoyl chloride (1 ml.) in pyridine (20 ml.) was set aside overnight. Water (1 ml.) was then added and the solution set aside for a further 2 hr. The solution was evaporated under reduced pressure and the residue dissolved in chloroform (30 ml.). The solution was washed with dilute hydrochloric acid, sodium hydrogen carbonate solution, water and dried. Evaporation of the solvent gave a residue which was recrystallised from ethanol to give 3a-diphenylphosphino-cholestan-2β-benzoate (0.4 g.), m.p. 174-175°, \( \nu_{\text{max.}} \) 1730 (C:O), 1270 cm\(^{-1}\) (OCO.),
the phosphine oxide had a m.p. (from light-petroleum 40-60°)
193.5-194.5°, \( \nu_{\text{max.}} \) 1730 (C:O), 1260 (OCO.), 1190 cm\(^{-1}\) (P:O)
(Found: C, 79.65; H, 8.61; P, 4.3. \( \text{C}_{46}\text{H}_{61}\text{O}_{3}\text{P} \) requires C, 79.8; H, 8.8; P, 4.48%).

3a-Diphenylphosphinyl-cholestan-2β-acetate.

A solution of 3a-diphenylphosphinyl-cholestan-2β-ol (0.3 g.) and acetic anhydride (1.5 ml.) in pyridine (20 ml.)
was set aside overnight. Ethanol (1 ml.) was added and the solution set aside for a further 1 hr. Evaporation under reduced pressure gave a residue which was chromatographed on basic alumina (25 g.). Elution with benzene-ether (70:30) gave 3α-diphenylphosphiny1-cholestan-28-acetate (60%), m.p. (from light petroleum) 204–205°, νₘₐₓ. 1750 (C=O), 1240 (OCO.Me), 1180 cm⁻¹ (P=O) (Found: C, 78.07; H, 9.44; P, 4.87. C₄₁H₉₃O₃P requires C, 78.7; H, 9.36; P, 4.92%).

Acetolysis of 3α-Diphenylphosphino-cholestan-28-benzoate.

A solution of the phosphine (0.4 g.) and potassium acetate (0.3 g.) in acetic acid (8 ml.) was heated under reflux for 6 hr. Water (50 ml.) was added to precipitate the product which was filtered and taken up in chloroform (30 ml.). The chloroform solution was washed with water, sodium hydrogen carbonate solution, water and dried. Evaporation of solvent gave the starting phosphine (0.4 g.) [characterised as the phosphine oxide, m.p. (from light petroleum) and mixed m.p. 195–196°].

In a similar way, the phosphine oxide (0.1 g.) gave 3α-diphenylphosphiny1-cholestan-28-benzoate (80 mg.), m.p. (from light petroleum) and mixed m.p. 196–197°.

Bromination of 3α-Diphenylphosphino-cholestan-28-ol.

A solution of the phosphine (1 gm.) in acetic acid (20 ml.) was saturated with hydrogen bromide and then heated under reflux for 2 hr. with a slow stream of hydrogen bromide passing
through the solution. Water was added to precipitate all the solid matter which was filtered off and taken up in chloroform (30 ml.). The chloroform solution was washed with water, sodium hydrogen carbonate solution, water and dried. Evaporation of solvent gave an oil which on recrystallisation from methanol-ether-water gave cholest-2,3-ene (0.1 g.), m.p. 70-72° (lit.: m.p. 75-76), mass peak m/z 370. The mother-liquors were evaporated and chromatographed on alumina (20 g.). Elution with benzene-ether (80:20) gave 3α-diphenylphosphinyl-cholestan-2β-acetate (60%), m.p. (from light petroleum) and mixed m.p. 204-205°.

2-Hydroxypropyldiphenyl-Phosphine

To a solution of sodium diphenylphosphide prepared as above from diphenylphosphine (7 g.) in tetrahydrofuran (70 ml.), propylene oxide (3 g.) was slowly added in tetrahydrofuran (50 ml.). When the vigorous reaction had subsided, glacial acetic acid (6 ml.) was added and the solution evaporated under reduced pressure. The residue, in chloroform (50 ml.), was washed with water (3 x 20 ml.), and the solution dried and evaporated. Distillation of the residue gave 2-hydroxypropyldiphenylphosphine (6.5 g.), b.p. 2.0 m.m. 152-153°, doublet at 7.8 equivalent to 3 protons (\(J_{HH} = 6\) c.p.s.), quartet at 7.76 equivalent to two protons (\(J_{HH} = 3, J_{PH} = 9\) c.p.s.). The methiodide had a m.p. (from chloroform-ethyl acetate) 166.5-167.5°, \(v_{max} 3400\) cm\(^{-1}\) (OH), quartet at 7.54 equivalent to 3 protons (\(J_{HH} = 7, J_{PH} = 2\) c.p.s.), doublet at 7.25 equivalent to 3 protons.
(J\textsubscript{PH} = 16 c.p.s.). (Found: C, 49.48; H, 5.34; P, 7.94.)

\[ \text{C}_{16}\text{H}_{20}\text{OP} \text{ requires } \text{C}, \text{ 49.5; } \text{H}, \text{ 5.18; } \text{P}, \text{ 8.04\%}; \text{ the phosphine} \]

oxide had m.p. (from benzene-light petroleum) 84-84.5°, (lit.,

b.p. 2.5 m.m. 160-165°), \( \nu \text{ max.} \; 3380 \; (\text{OH}), \; 1165 \; \text{cm.}^{-1} \; (\text{P} : \text{O}), \)

quartet at \( \tau 8.75 \) equivalent to 3 protons (\( J_{HH} = 7, \; J_{PH} = 2 \; \text{c.p.s.} \))

(Found: C, 69.1; H, 6.42. \( \text{C}_{11}\text{H}_{17}\text{O}_{2}\text{P} \text{ requires } \text{C}, \text{ 69.25; } \text{H}, \text{ 6.54\%}. \)

2-Acetoxypropyldiphenylphosphine.

A solution of 2-hydroxypropyldiphenylphosphine (1.3 g.)

and acetic anhydride (4 ml.) in pyridine (10 ml.) was set aside

overnight. Ethanol (1 ml.) was added and the solution set aside

for a further 1 hr. Evaporation under reduced pressure gave

2-acetoxypropyldiphenylphosphine (1.4 g.); the phosphine oxide

had a m.p. (from benzene-light petroleum) 94.5-95.5°, \( \nu \text{ max.} \)

1750 \( (\text{C=O}), \; 1240 \; (\text{OCO.Me}), \; 1185 \; \text{cm.}^{-1} \; (\text{P} : \text{O}), \text{ doublet at } \tau 8.62 \)

equivalent to 3 protons (\( J_{HH} = 7 \; \text{c.p.s.} \)), singlet at \( \tau 8.31 \)
equivalent to 3 protons (Found: C, 67.51; H, 6.20. \( \text{C}_{17}\text{H}_{19}\text{O}_{3}\text{P} \text{ requires } \text{C}, \text{ 67.6; } \text{H}, \text{ 6.3\%}. \)

In a similar manner \( p \)-nitrobenzoyl chloride (1.85 g.)
gave 2-\( p \)-nitrobenzoyloxypropyldiphenylphosphine (2.3 g.), m.p.

(from benzene-light petroleum) 112-113°; the methiodide had a

m.p. (from chloroform-ethyl acetate) 166-167°, \( \nu \text{ max.} \; 1720 \; (\text{C=O}), \)

1525 \( \text{cm.}^{-1} \; (\text{NO}_2) \) (Found: C, 51.76; H, 4.42; N, 2.70. \( \text{C}_{23}\text{H}_{23}\text{INO}_4\text{P} \text{ requires } \text{C}, \text{ 51.6; } \text{H},\text{4.3; } \text{N}, \text{ 2.62\%}. \)
1-Methoxy-2-bromopropane.

A mixture of triphenylphosphite (101.5 g.) and benzyl bromide (53 g.) were heated together at 120° for 48 hr. The mixture was cooled and washed with ether (3 x 50 ml.). The solvent was removed under reduced pressure and the mixture heated to 120° for 45 mins. with 1-methoxy-propan-2-ol (22.5 g.). Distillation gave 1-methoxy-2-bromopropane (15 g.), b.p. 40-41° (lit., b.p. 60 m.m. 49-49.5°).

2-Methoxypropyldiphenylphosphine.

To a solution of sodium diphenylphosphide, prepared as above from diphenylphosphine (9.5 g.) in tetrahydrofuran (80 ml.), 2-methoxypropylbromide (7.8 g.) in tetrahydrofuran (10 ml.) was added slowly. When the vigorous reaction had subsided the solvent was removed under reduced pressure. The residue, in chloroform (100 ml.), was washed with water (3 x 25 ml.) and the solution dried and distilled to give 2-methoxypropyldiphenylphosphine (9.5 g.), b.p. 0.1 m.m. 126-127°; the methiodide had a m.p. (from chloroform-ethyl acetate) 172-173°, quartet at $\delta 8.68$ equivalent to 3 protons ($J_{HH} = 6, J_{PH} = 3$ c.p.s.), singlet at $\delta 7.1$ equivalent to 3 protons (Found: C, 50.96; H, 5.52; P, 7.60. $C_{17}H_{22}IOP$ requires C, 51.1; H, 5.5; P, 7.75%).

In a similar manner, sodium diphenylphosphide, prepared from diphenylphosphine (7.5 g.) in tetrahydrofuran (80 ml.), and 2-bromo-1-methoxypropane (6.5 g.) gave 1-(methoxymethyl)ethy-
diphenylphosphine (6.5 g.), b.p. 0.1 m.m. 132-134°; the methiodide had a m.p. (from chloroform-ethyl acetate) 189-190°, quartet at \( \tau 8.6 \) equivalent to three protons \( (J_{HH} = 7, J_{PH} = 18 \text{ c.p.s.}) \), singlet at \( \tau 6.8 \) equivalent to 3 protons (Found: C, 51.14; H, 5.66; P, 7.60. \( \text{C}_{17}\text{H}_{22}\text{IOP} \) requires C, 51.1; H, 5.5; P, 7.7%), and sodium diphenylphosphide, prepared from diphenylphosphine (7 g.) with \( \gamma \)-methoxypropylchloride (4.5 g.) gave 3-methoxypropyl-diphenylphosphine (7.5 g.), b.p. 0.1 m.m. 125-126° (lit., b.p. 0.75 m.m., 140-140.5°); the methiodide had a m.p. (from chloroform-ethyl acetate) 154-155° (lit., 155-156°).

The Action of Hydrogen Bromide in Acetic Acid, on 2-Hethoxypropyl-diphenylphosphine.

A solution of the phosphine (2 g.) in glacial acetic acid (20 ml.) which had been saturated with hydrogen bromide was heated under reflux for 7 hr. with a slow stream of hydrogen bromide passing through the solution. The mixture was poured into water (80 ml.) and extracted with chloroform (2 × 40 ml.). The combined extracts were washed with water, sodium hydrogen carbonate solution, water and dried. Oxidation with hydrogen peroxide and evaporation of the solvent gave 2-acetoxypropyl-diphenylphosphine oxide (1.5 g.), m.p. (from benzene-light petroleum) and mixed m.p. 90-91°.

In a similar manner, 1-(methoxymethyl)ethylidiphenylphosphine (1.5 g.) gave 2-acetoxy-1-methyl-ethylidiphenylphosphine.
oxide (1.1 g.), m.p. (from benzene-light petroleum) 132-133°,

\[ v_{\text{max}} \] 1750 (C=O), 1240 (OCO.Me), 1180 (P=O), quartet at 7.82 equivalent to three protons \( J_{\text{HH}} = 7, J_{\text{PH}} = 15 \) c.p.s.

(Found: C, 67.69; H, 6.31. \( \text{C}_{17}\text{H}_{19}\text{O}_{3}\text{P} \) requires C, 67.6; H, 6.6%);

and 2-hydroxypropyldiphenylphosphine (0.7 g.) gave \( \alpha \)-acetoxypropyldiphenylphosphine oxide (0.4 g.), m.p. (from benzene-light petroleum) and mixed m.p. 92-93°.

**Action of Constant Boiling Hydrobromic Acid on 2-Methoxypropylphenylphosphine.**

A solution of the phosphine (2 g.) in constant boiling hydrobromic acid (20 ml.) was heated under reflux for 2 hr. The solution was evaporated to c.a. 3 ml. in volume and chloroform and sodium hydrogen carbonate solution (25 ml.) added. The organic layer was separated, dried and evaporated to give 2-hydroxypropyldiphenylphosphine (1.2 g.); the methiodide had a m.p. (from chloroform-ethyl acetate) and mixed m.p. 166-167°.

Similarly, 1-(methoxymethyl)ethyldiphenylphosphine (2 g.) gave 1-(hydroxymethyl)ethylidiphenylphosphine (1.3 g.); the methiodide had a m.p. (from chloroform-ethyl acetate) 142-143°, quartet at 7.8.7 equivalent to three protons \( J_{\text{HH}} = 6, J_{\text{PH}} = 17 \) c.p.s. (Found: C, 47.93; H, 5.07. \( \text{C}_{16}\text{H}_{20}\text{IOP} \) requires C, 49.5; H, 5.18%); and 3-methoxypropyldiphenylphosphine (1.4 g.) gave 3-bromo-propyldiphenylphosphine (1.2 g.); the phosphine oxide had a m.p. (from benzene-light petroleum) 92.5-93.5°.
mass peaks m/e 323, 321 (Found: C, 55.73; H, 4.93; Br, 27.71.
C₁₅H₁₅BrOF requires C, 55.8; H, 4.95; Br, 24.8%).

Attempted Decomposition of 2-p-Nitrobenzoyloxypropyldiphenyl-
phosphine.

A solution of the phosphine (0.4 g.) in 90% acetone-
water (60 ml.) was heated under reflux for 6 hr. Evaporation of
the solvent gave the starting material (0.4 g.) m.p. and mixed
m.p. 112-113°.

Similarly, the phosphine in 90% dioxan-water solution
with hydrochloric acid (0.05 g.) gave the starting material,
m.p. and mixed m.p. 112-113°.
Vinylphosphorus Compounds.

Vinylphosphines, the phosphorus analogues of enamines, possess an unsaturated system α,β to the phosphorus atom. A brief review of the preparation and properties of such phosphines, their quaternary salts and oxides will be given here.

Preparation of Vinylphosphorus Compounds.

1. By the use of organometallic reagents

Organophosphorus halides will react with various vinyl metals to give vinyldichlorophosphines, e.g. divinylmercury reacts with phosphorus trichloride to give vinyldichlorophosphine itself. These phosphines may then be substituted further by the use of Grignard reagents. Similarly chlorodiphenylphosphine

\[
\begin{align*}
\text{PCl}_3 & \quad \text{+ (CH}_2\text{=CH}_2\text{Hg + CH}_2\text{=CHPCl}_2 + CH}_2\text{=CHHgCl} \\
& \quad \downarrow \text{RMgX} \\
& \quad \text{CH}_2\text{=CHPR}_2
\end{align*}
\]

with vinylmagnesium halides in tetrahydrofuran gives diphenyl-vinylphosphine. Vinylphosphorus dichlorides have also been prepared by the direct action of phosphorus pentachloride on olefins in 1,2-dichloroethane after decomposing the intermediate formed with antimony.

\[
\begin{align*}
\text{Me}_2\text{C=CH}_2 & \quad 1. \text{PCl}_5 \quad \text{Me}_2\text{C=CHPCl}_2 \\
& \quad 2. \text{Sb}
\end{align*}
\]
Good yields of vinylphosphines may also be obtained by using the opposites of the above reagents i.e. metallic phosphides and vinylhalides.

\[
\begin{array}{c}
\text{R} \quad \text{C}=\text{C} \quad \text{R} \\
\text{H} \quad \text{P} \quad \Phi_2
\end{array} \quad \text{H} \quad \text{P} \quad \Phi_2
\]

These metallic derivatives will also add to acetylenes to give vinylphosphines.

\[
\Phi_2\text{P} \text{Li} + \text{HC} \equiv \text{CR} \quad \text{T.H.F.} \\
\Phi \quad \text{C}=\text{C} \quad \text{H} \\
\text{H} \quad \text{P} \quad \Phi_2
\]

If the acetylenic triple bond is activated with an electron withdrawing group, tertiary phosphines, in strong acid solution, will add to them to give vinylphosphonium compounds.

\[
\begin{array}{c}
\text{R}_3\text{P} + \text{RC} \equiv \text{CCOO} \end{array} \quad \text{H}^+ \\
\Phi \quad \text{C}=\text{C} \quad \text{R} \\
\text{H} \quad \text{OOC} \quad \Phi_3
\]

2. **Involving elimination reactions.**

Phosphorus ylids possessing a hydrogen atom on the \(\alpha\)-carbon are known to react with chlorodiarylphosphines to give a new ylid (III). This ylid on treatment with benzaldehyde
undergoes a normal Wittig olefin synthesis by eliminating a phosphine oxide to give the vinylphosphine (112).

\[
2RCH=\text{P} \quad \text{PCl} \quad \text{PCl} \quad \rightarrow \quad \begin{array}{c}
\text{C=\text{P}} \\
\text{\text{PCl}}
\end{array} + R\text{CH}_2\text{P} \quad \text{PCl} \\
\text{\text{PCl}}
\]

Similarly, unsymmetrical methylenidiphosphorus compounds on treatment with a strong base and aldehydes give the vinyl phosphorus compounds as shown.

Ethylphosphonium salts which possess a grouping R, capable of stabilising an anion on the \( \beta \)-carbon (113) in general, undergo \( \beta \)-elimination with bases to give vinylphosphonium salts, 152 153 154 (where R can be \( \text{PR}_3 \), \( \text{O}^+ \), \( \text{Br}^- \)).
Vinylphosphonium salts have also been prepared by the addition of hydrogen halides to vinylidene-phosphoranes. A recent example of this is the addition of hydrogen chloride to (114) which was prepared by heating the stable phosphorane from hexafluoroacetone and hexaphenylcarbodiphosphorane.

\[ \Phi_3P=C=CP\Phi_3 (CF_3)_2CO \xrightarrow{\Delta} \Phi_3P-C=P\Phi_3 + O-C-CF_3 \xrightarrow{\Delta} \Phi_3P=O \]

The preparation and properties of vinylphosphorus acids has been extensively reviewed by Gefter, the general method of preparation being the addition of phosphorus pentachloride to olefins and subsequent hydrolysis of the addition product with water.

\[ RCH=CH_2 + 2PCl_5 \rightarrow R.CHCl.CH_2PCl_4 + PCl_5 \xrightarrow{7H_2O} \]
\[ RCH=CHPO.(OH)_2 + H_3PO_4 + 10HCl \]

A further elimination reaction to give a vinylphosphine oxide is reported by Kabachnik who prepared a-methylvinylidiphosphine oxide by heating chlorodiphosphine with propylene
oxide at 60° and treating the intermediate formed with triethylamine. No mechanism was put forward for the process but it could be illustrated as follows.

Reactions of Vinylphosphorus Compounds.

Vinylphosphorus compounds are highly susceptible to nucleophilic attack as is shown by the addition of various nucleophiles to vinylphosphonium salts to produce saturated phosphonium compounds.

\[
\[
\]_{9}^{+}PCH=CH_{2}Br^{-} + Z-H + [\text{9}_{9}^{+}PCH_{2}CH_{2}Z]Br^{-}
\]

Organolithium reagents add similarly to phosphoranes which can react further with carbonyl compounds to give olefins.

\[
\]

This reaction has been extended further by Schweizer in elegant ring syntheses which proceed
via internal Wittig reactions.

\[
\begin{align*}
\text{base} & & \begin{array}{c}
\text{XH} \\
\end{array} & \xrightarrow{\text{X}^-} & \begin{array}{c}
\text{X}^+ \text{PCH=CH}_2 \\
\end{array} & \xrightarrow{\text{X}^-} & \begin{array}{c}
\text{X-CH}_2\text{CH-P}=\text{O}_3 \\
\end{array} \\
\text{X} & = & 0, \text{H} \\
\end{align*}
\]

If the vinylphosphonium salts possess groups capable of stabilising unsaturated systems, then with phenyl-lithium unsaturated phosphoranes are obtained which produce allenes on treatment with aldehydes or ketones.

\[
\begin{align*}
[\phi_2\text{C}=\text{CH}._\text{P}=\text{O}_3] & \xrightarrow{\text{Li}^+} [\phi_2\text{C}=\text{C}=\text{P}=\text{O}_3] \\
\phi_2\text{C}=\text{C}=\text{C}=\phi_2 + \phi_3\text{P}=\text{O} \\
\end{align*}
\]

\(\alpha,\beta\)-Unsaturated phosphorus compounds can also behave as dienophiles and with dienes give Diels-Alder adducts.
To study the addition reactions of vinylphosphines mentioned above, it was hoped to prepare a vinylphosphine possessing a phenyl group on the α-carbon. As all the addition reactions mentioned pass through an intermediate phosphorane (115) the presence of a phenyl group on the α-carbon would facilitate the formation of the phosphorane.

Initial attempts at preparing such a system were directed at the formation of the phosphine oxide and reducing this with silanes to the parent phosphine.

The first of these attempts was a reaction analogous to that of Kabachnik in which chlorodiphenylphosphine on treatment with propylene oxide gave 1-methylvinylidiphenylphosphine oxide after treating the intermediate formed with triethylamine.

Replacing the propylene oxide by styrene oxide under the same conditions 1-phenylvinylidiphenylphosphine oxide would be the expected product. However, styrene oxide under similar treatment gave the isomeric styryldiphenylphosphine oxide as shown by its catalytic hydrogenation to the known 2-phenylethylidiphenylphosphine oxide.

\[
\Phi_2PCl + CH_2\rightleftharpoons CH\Phi \xrightarrow{60^\circ} [ \quad ] \xrightarrow{\text{Bu}_3N} \Phi_2P-CH=CH-\Phi
\]

The second method used was the direct isomerisation of the readily available allyldiphenylphosphine oxides under
strongly basic conditions - e.g. KOBu⁺ in tBuOH. The most favourable case was chosen, i.e. 2-cyclohexylidene-ethyldiphenylphosphine oxide which has an exocyclic double bond, for a trial experiment but proved to be unaffected by the base used.

A more direct approach was the partial hydrogenation of alk-1,2-dienyldiphenylphosphine oxides (116) produced by the reaction of chlorodiphenylphosphine with acetylenic alcohols.

\[
\begin{align*}
&\text{O} \text{R} \\
&\phi_2\text{P}-\text{C} : \text{C} : \text{CR}_2 \overset{\text{H}_2}{\longrightarrow} \text{Lindlar} \\
&\phi_2\text{P}-\text{CH} \text{CH}: \text{CR}_2 \\
\end{align*}
\]

(116)

The catalytic reduction of 3-methylbuta-1,2-dienyldiphenylphosphine oxide (116; R¹=Me, R=H) gave, after chromatography, a 45% yield of the vinylphosphine oxide (117; R¹=Me; R=H) and a 16% yield of the allylic-phosphine oxide. The analogous 1-phenylprop-1,2-dienyldiphenylphosphine oxide (116; R¹=H, R=Ph) was duly prepared from chloro-diphenylphosphine and phenylpropargyl alcohol but was found to be unstable to basic alumina and under the hydrogenation conditions used. The product formed by its decomposition was that of addition of diphenylphosphine oxide to the allene. The structure of this compound was deduced from an accurate mass determination and by

\[
\begin{align*}
&\text{O} \text{P} \text{H} \text{O} \\
&\phi_2\text{P}-\text{C} : \text{C} : \text{CH}_2 \overset{\phi_2\text{P} \text{H} \text{O}}{\longrightarrow} \phi_2\text{P}-\text{CHC} : \text{CH}_2 \\
\end{align*}
\]
analogy to the type of products observed by Pudovik from the addition of dialkyl hydrogen phosphites to alka-1,2-dienylphosphonates.

The preparation of the desired 1-phenylvinylidiphenylphosphine was finally achieved by the method of Aguilar using sodium diphenylphosphide and α-bromostyrene.

\[
\phi\text{-CBr:CH}_2 \xrightarrow{\phi_2\text{PNa}} \phi_2\text{P-C:CH}_2
\]

The 1-phenylvinylidiphenylphosphine, on heating under reflux with acrylonitrile in the presence of benzaldehyde, gave 4-cyano-1,2-diphenyl-5-diphenylphosphinyl-pent-1-ene, (119). The mode of its formation is no doubt by initial attack of the phosphorous on the acrylonitrile to give an intermediate betaine (120). This then internally attacks the newly formed vinylphosphonium residue to give a cyclic ylid (121) which is stabilised by the α-phenyl group. With benzaldehyde the ylid (121) undergoes a normal Wittig olefin formation to give the observed product viz:-

\[
\begin{align*}
\phi_2\text{P} & \quad \Leftrightarrow \quad \phi_2\text{P} \\
\text{CH}_2=\text{CH-CN} & \quad \Leftrightarrow \quad \phi_2\text{P} \quad \text{CH}_2=\text{CH-CN} \\
\phi & \quad \phi_2\text{P} \quad \phi_2\text{P} \quad \phi_2\text{P} \\
\text{CN} & \quad \phi_2\text{P} \quad \phi_2\text{P} \quad \phi_2\text{P} \\
\phi & \quad \phi_2\text{P} \quad \phi_2\text{P} \quad \phi_2\text{P} \\
\text{CN} & \quad \phi_2\text{P} \quad \phi_2\text{P} \quad \phi_2\text{P} \\
\phi_2\text{P} \quad \phi_2\text{P} \quad \phi_2\text{P} \quad \phi_2\text{P} \\
\phi_2\text{P} \quad \phi_2\text{P} \quad \phi_2\text{P} \quad \phi_2\text{P}
\end{align*}
\]
A homologous compound was obtained when the benzaldehyde was replaced by p-tolualdehyde. The structure of these compounds was confirmed by their elemental analysis and spectral properties. In both the above cases the possibility exists of cis-trans isomerism around the newly formed double bond. From comparison of their ultraviolet spectra with the recorded spectra for substituted stilbenes it would appear that the isolated compounds are the trans- configurations. In both of the above reaction mixtures thin layer chromatography showed the presence of further compounds of similar retention time to the isolated phosphine oxides; these were probably the cis isomers present in small yields.

A similar reaction was envisaged between the vinylphosphine and styrene oxide in the presence of benzaldehyde to give the ether (122).

\[ \phi_2P-C:CH_2 \xrightarrow{\text{O}} \phi_2P-C\Phi-CH-O-\text{CH}_2\Phi = \text{CH}_2\Phi \]

(122)

However, it is known that tertiary phosphines react with styrene oxide to give predominantly rearranged products. Hence for a control experiment the vinylphosphine was treated with styrene oxide alone in ethanolic solution. Styrene (40%) and 1-phenylvinylphosphine oxide were isolated, the products expected from a normal Wittig reaction, but no rearranged
product similar to that expected was obtained. The major product was styryldiphenylphosphine oxide (123); the mechanism of its formation could be as shown with the displaced anion abstracting a proton from the α-carbon.

\[
\begin{align*}
\phi_2P & \quad \phi_2P - CH_2 \\
\phi_2P - CH_2 & \quad \phi_2P - CH_2 \\
\phi - CH_2 & \quad \phi - CH:CH_2 \\
\end{align*}
\]

When carried out in the absence of solvent and in the presence of an equivalent of p-tolualdehyde, the reaction took a completely different course. After dilution with methanol, vapour phase chromatography showed the presence of styrene (28%), p-methystyrene (24%), benzaldehyde (25%) and the unreacted starting materials styrene oxide (35%) and p-tolualdehyde (67%). The presence of these volatile products can be explained on the grounds that betaine formation in a Wittig olefin synthesis is reversible. Thus the betaine (124) initially formed can either decompose to styrene and the phosphine oxide or to benzaldehyde.
and the methyldenediphosphorane.

This newly formed phosphorane can now either recombine with benzaldehyde or combine with the p-tolualdehyde present to give a new betaine which can undergo a Wittig reaction to give p-methylstyrene:

\[
\begin{align*}
\phi C&:CH_2 \\
\phi \text{P}&:CH_2CH\phi \\
\overset{O}{O} \\
\overset{O}{\phi C}&:CH_2 \\
\phi \text{P}&:CH_2CH\phi \\
\overset{O}{O} \overset{\text{Wittig}}{\text{\phi P:O + CH}_2\phi} \\
\text{(124)} \\
\end{align*}
\]

(28%)

\[
\begin{align*}
\phi C&=CH_2 \\
\phi \text{P}=CH_2 + \phi CHO (25\%) \\
\overset{\text{Me}}{\text{Me}} &\text{CHO} \\
\end{align*}
\]

\[
\begin{align*}
\overset{\text{P}}{\phi C}&:CH_2 \\
\overset{\text{O}}{\phi C}&:CH\phi \text{Me} \\
\overset{\text{Wittig}}{\phi \text{P}:O} \\
\text{(24%)} \\
\end{align*}
\]
A minor product formed in the reaction was 1,2-bis-(diphenylphosphinyl)-1-phenylethane (125). This could have been formed at the end of the reaction in the methanolic solution by a Michael addition of phosphine to the phosphine oxide present to give a phosphonium salt. This salt, when subjected to chromatography on basic alumina, would hydrolyse to give the product (125).

\[
\begin{align*}
\phi_2P-C=CH_2 &\overset{\text{MeOH}}{\longrightarrow} \phi_2P-CH-CH_2+\phi_2CH_2-P-P-C=CH_2 \\
&\text{alumina} \\
&\phi_2P-CH-CH_2-P\phi_2 + \phi-CH=CH_2
\end{align*}
\]

The 1-phenylvinyl anion is known to be preferentially expelled in these hydrolyses as independent reactions of methyl-(1-phenylvinyl)diphenylphosphonium iodide (126) and benzyl-(1-phenylvinyl)diphenylphosphonium bromide (127) with ethanolic sodium hydroxide gave methyldiphenylphosphine oxide and benzyl-diphenylphosphine oxide respectively.

\[
\begin{align*}
\phi_2P-C=CH_2 &\overset{\text{CH}^-}{\longrightarrow} \phi_2PMe \\
(126) \\
\phi_2P-C=CH_2 &\overset{\text{OH}^-}{\longrightarrow} \phi_2PCH_2\phi \\
(127)
\end{align*}
\]
Hence the 1-phenylvinyl anion is more stable than the phenyl or even the benzyl anion.

In all of the above reactions a positive charge is being developed on the phosphorus atom in situ. A similar system is present in the readily isolable phosphonium salts and these are susceptible to Michael addition by nucleophiles to give phosphoranes. These phosphoranes decompose with aldehydes to give products similar to those above.

When methyl(1-phenylvinyl)diphenylphosphonium iodide was added to a solution of sodium diphenylphosphide in tetrahydrofuran the red colour of the solution deepened indicating the presence of a phosphorus ylid. The colour disappeared on the addition of p-tolualdehyde and 2-phenyl-1-p-tolyl-3-diphenylphosphinyl-propene (128) was isolated in cis and trans forms after oxidation of the reaction mixture. Methyldiphenylphosphine oxide was also isolated indicating the formation of the products proceeds via a Wittig reaction after the initial Michael addition.
Experimental

All reactions involving tervalent organophosphorus compounds were carried out under oxygen-free nitrogen. Light petroleum had b.p. 60-80°. P.m.r. spectra were recorded in deuteriochloroform with tetramethyldisilane as internal standard on a Varian Associates A 60 spectrometer. Mass spectra were recorded on an A.E.I. MS-9 spectrometer. All m.p.s were corrected.

Styryldiphenylphosphine Oxide.

To a solution of chlorodiphenylphosphine (11 g.) in benzene (30 ml.) heated to 60°, styrene oxide (6.7 g.) was added slowly. The solution was heated under reflux for 1 hr. and the solvent evaporated under reduced pressure. Tributylamine (13 g.) was added and the reaction mixture heated to 130° for 3 hr. The residue, in chloroform (100 ml.), was washed with dilute hydrochloric acid (3 x 30 ml.), sodium hydrogen carbonate solution (2 x 30 ml.), dried and evaporated. The residue, after chromatography on basic alumina (100 g.), gave styryldiphenylphosphine oxide, m.p. (from benzene-light petroleum) 167-168°, (lit., m.p. 168-169), ν\textsubscript{max} 1610 (C=C), 1180 cm\textsuperscript{-1} (P=0) (Found: C, 78.86; H, 5.45; P, 10.29. C\textsubscript{20}H\textsubscript{17}OP requires C, 79.0; H, 5.6; P, 10.2%).

2-Phenylethylidiphenylphosphine Oxide

A solution of styryldiphenylphosphine oxide (0.5 g.)
in absolute ethanol (100 ml.) was hydrogenated over 10% palladium on charcoal catalyst (50 mg.). The solution was filtered and the solvent evaporated to give 2-phenylethyl-
diphenylphosphine oxide (0.5 g.), m.p. (from light petroleum) and mixed m.p. 101-102°.

**Attempted Isomerisation of 2-Cyclohexylidene-ethyldiphenyl-
phosphine Oxide.**

A solution of the phosphine oxide (1.0 g.) in tert. butanol (50 ml.), containing potassium (0.4 g.), was heated under reflux for 48 hrs. The solution was evaporated and water (100 ml.) was added depositing crystals of 2-cyclohexylidene-ethyldiphenyl-
phosphine oxide (1.0 g.), m.p. (from benzene-light petroleum) and mixed m.p. 166-167°.

**3-Methylbuta-1,2-dienyldiphenylphosphine Oxide.**

To an ice-cooled solution of 3-methyl-but-1-yne-3-ol (2.1 g.) and pyridine (2.0 g.) in benzene (20 ml.), a solution of chlorodiphenylphosphine (5.5 g.) in benzene (20 ml.) was slowly added. After the addition was complete the reaction mixture was set aside for 1 hr. at 0° then set aside for a further 6 hr. at 20°. The solution was filtered and the filtrate evaporated under reduced pressure. The residus, after chromatography on basic alumina (50 g.), gave 3-methyl-buta-1,2-
dienyldiphenylphosphine oxide (2.65 g.), m.p. (from light petroleum) 74-75° (lit., m.p. 70-73°).
Catalytic Hydrogenation of 3-Methylbut-1,2-dienyl-diphenylphosphine Oxide.

A solution of the phosphine oxide (1.5 g.) in absolute ethanol (100 ml.) was hydrogenated over a Lindlar catalyst (0.10 g.) at room temperature and pressure. The theoretical amount of hydrogen equivalent for the reduction of one double bond was taken up. The solution was filtered and evaporated. The residue, after chromatography on basic alumina (40 g.), gave 3-methylbut-1-enyl-diphenylphosphine oxide (0.6 g.), m.p. (from light petroleum) 82-83°, ν_{max} 1620 (C=C), 1180 cm⁻¹ (P=0), doublet at τ9.1 equivalent to six protons (J_{HH} = 7 c.p.s.), mass peak m/e 270, base peak m/e 201 (P₂PO), other significant peaks at m/e 255 (Found: C, 75.72; H, 7.24; P, 13.43. C₁₇H₁₉PO requires C, 75.6; H, 7.05; P, 11.5%); and 3-methylbut-2-enyl-diphenylphosphine oxide (230 mg.), m.p. (from benzene-light petroleum) and mixed m.p. 124-125°.

Phenylpropargyl alcohol.

To a solution of potassium hydroxide (110 g.) in absolute ethanol (200 ml.) kept at 140°, 2,3-dibromo-3-phenylpropyl acetate (102 g.) was added, over a period of 1 hr. The mixture was heated under reflux for a further ½ hr. after the addition was complete. The reaction mixture was then poured into water (1 litre) and extracted with ether (4 x 250 ml.). The combined extracts were washed with dilute hydrochloric acid
(1 x 250 ml.), sodium hydrogen carbonate solution (1 x 250 ml.),
dried and evaporated. Distillation of the residue gave phenyl-
propargyl alcohol (18.4 g.), b.p. 13 m.m. 136-140° (Lit.,
b.p. 15 m.m. 138-139°).

1-Phenylprop-1,2-dienyldiphenylphosphine Oxide.

To an ice-cooled solution of phenylpropargyl alcohol
(5.0 g.) and pyridine (3.6 g.) in ether (50 ml.), a solution of
chlorodiphenylphosphine (8.4 g.) in ether (10 ml.) was added
slowly. After the addition had been completed the solution was
set aside at room temperature overnight. Water (30 ml.) was
added and the solution extracted with chloroform (3 x 50 ml.).
The combined extracts were washed with dilute hydrochloric acid
(3 x 30 ml.), and sodium hydrogen carbonate solution (1 x 30 ml.),
and dried. Evaporation of the solvent gave a residue which,
after chromatography on basic alumina (160 g.), gave 1-phenylprop-
1,2-dienyldiphenylphosphine oxide (5.7 g.), m.p. (from benzene-
light petroleum) 125-126°. The infrared spectrum showed the
an
presence of an allene group (doublet at 1930 cm.⁻¹) and the presence
of a phosphine oxide grouping (absorption at 1180 cm.⁻¹), doublet
at τ5.12 equivalent to two protons (JPH = 11 c.p.s.)

In a similar experiment, the alcohol (6.6 g.) with
chlorodiphenylphosphine (11 g.) gave, after chromatography on
basic alumina (60 g.), 2,3-bis(diphenylphosphinyl)-3-phenyl-
propene, (3.0 g.), m.p. (from benzene-light petroleum) 195-196°,
$v_{\text{max.}}$ 1180 cm$^{-1}$ (doublet).

An accurate molecular weight determination established the formula as $C_{33}H_{28}O_2P_2$ (Found: C, 77.14; H, 5.45; P, 12.24. $C_{38}H_{28}O_2P_2$ requires C, 76.5; H, 5.4; P, 12.0%).

Catalytic Hydrogenation of 1-Phenylprop-1,2-diencyldiphenylphosphine Oxide.

A solution of the phosphine oxide (1.6 g.) in absolute ethanol (70 ml.) was hydrogenated over a Lindlar catalyst (0.2 g.) at room temperature and pressure. The uptake of hydrogen ceased after 0.75 equivalents of hydrogen had been absorbed. The solution was filtered and evaporated to give a residue which crystallised from benzene-light petroleum to give 2,3-bis(diphenylphosphinyl)-3-phenyl-propene (0.8 g.), m.p. and mixed m.p. 195-196$^\circ$.

1-Phenylvinylidiphosphine Oxide.

Sodium wire (8.0 g.) was added to a solution of diphenylphosphine (15 g.) in tetrahydrofuran (300 ml.) and the solution heated under reflux for 2 hr. The excess of sodium was then removed and a solution of $a$-bromostyrene (15 g.) in tetrahydrofuran (20 ml.) added slowly. The solution was evaporated under reduced pressure and the residue taken up in chloroform (300 ml.). The solution was washed with water (50 ml.), dried and evaporated under reduced pressure to give a residue which was recrystallised from methanol to give 1-phenylvinylidiphosphine.
(15 g.), m.p. 91.5-92.5°, \(v_{\text{max.}}\) 908 cm.\(^{-1}\) (C=CH\(_2\)), the methiodide had a m.p. (from chloroform-ethyl acetate) 211-212°, doublet at \(\tau\) 7.22 equivalent to three protons (J\(\text{PH} = 14\) c.p.s.), singlet at \(\tau\) 2.9 equivalent to five protons, (Found: C, 59.00; H, 4.64; P, 7.43. C\(_{21}\)H\(_{20}\)IP requires C, 59.1; H, 4.76; P, 7.22%). The benzylphosphonium bromide had a m.p. (from chloroform-ethyl acetate) 203-204°, doublet at \(\tau\) 6.93 equivalent to two protons (J\(\text{PH} = 14\) c.p.s.) (Found: C, 70.62; H, 5.47; P, 6.93. C\(_{27}\)H\(_{24}\)BrP requires C, 70.8; H, 5.25; P, 6.76%). The phosphine oxide had a m.p. (from benzene-light petroleum) 114-115°, \(v_{\text{max.}}\) 1180 (P=O), 930, 945 cm.\(^{-1}\) (C=CH\(_2\)) (Found: C, 78.71; H, 5.74; P, 10.33. C\(_{20}\)H\(_{17}\)OP requires C, 78.9; H, 5.6; P, 10.2%).

**Hydrolysis of Benzyl(1-phenylvinyl)diphenylphosphonium Bromide.**

A solution of the phosphonium bromide (0.1 g.) and sodium hydroxide (0.5 g.) in aqueous ethanol (40 ml.) was heated under reflux for 4 hr. The solution was evaporated to dryness under reduced pressure. The residue, in benzene (60 ml.), was washed with water (3 x 30 ml.), dried, and evaporated to give benzylidiphenylphosphine oxide (50 mg.), m.p. (from benzene-light petroleum) and mixed m.p. 192-193°.

Similarly, methyl(1-phenylvinyl)diphenylphosphonium iodide (0.2 g.) gave methyldiphenylphosphine oxide (50 mg.), m.p. (from benzene-light petroleum) 110-111° (lit., 108-109°).
4-Cyano-1,2-diphenyl-5-diphenylphosphinyl-pent-1-ene.

A mixture of 1-phenylvinylidiphenylphosphine (1.4 g.), benzaldehyde (0.6 g.) and acrylonitrile (2 ml.) was heated under reflux for 12 hr. The solution was evaporated and the residue chromatographed on silica gel (60 g.). Elution with ether gave 4-cyano-1,2-diphenyl-5-diphenylphosphinyl-pent-1-ene (0.5 g.), m.p. (from benzene-light petroleum) 118-119°, ν max. 2260 (CN), 1180 cm. -1 (P=O), λ max. 260, 265, 272 μ (ε 14,000, 14,500, 12,800 in ethanol), mass peak m/e 447, base peak m/e 201, other important peaks at m/e 330, 245, 215 (Found: C, 80.09; H, 5.87; N, 3.23; P, 6.94%).

Similarly, the same phosphine (2.0 g.) and p-tolualdehyde (0.85 g.) in acrylonitrile (5 ml.) gave, after chromatography on silica gel (60 g.), 4-cyano-2-phenyl-1-p-tolyl-5-diphenylphosphinyl-pent-1-ene (0.5 g.), m.p. (from benzene-light petroleum) 127-128°, ν max. 2290 (C=O), 1185 cm. -1 (P=O), λ max. 261, 265, 267 μ (ε 14,700, 15250, 14,400 in ethanol), mass peak m/e 461, base peak m/e 201, other important peaks at m/e 260, 215, (Found: C, 80.50; H, 6.04; N, 3.03; P, 6.91. C31H28NOP requires C, 80.6; H, 6.07; N, 3.04; P, 6.72%).

Reaction of 1-Phenylvinylidiphenylphosphine with Styrene Oxide.

A solution of the phosphine (2.0 g.) and styrene oxide (0.85 g.) in ethanol (25 ml.) was heated under reflux for 24 hr.
Styrene (44%) was estimated by g.l.c. using an 2m x \( \frac{1}{8} \) in. Apiezon L column at 120°. Evaporation of the solution and chromatograph of the residue on basic alumina (60 g.) gave styryldiphenylphosphine oxide (0.85 g.), m.p. (from benzene-light petroleum) and mixed m.p. 168-169°, and 1-phenylvinylidiphenylphosphine oxide (0.4 g.), m.p. (from benzene-light petroleum) and mixed m.p. 114-115°.

**Reaction of 1-Phenylvinylidiphenylphosphine and Styrene Oxide in the Presence of \( p \)-Tolualdehyde.**

A mixture of the phosphine (2.0 g.), styrene oxide (0.85 g.) and \( p \)-tolualdehyde (0.85 g.) was heated to 130° for 26 hr. Methanol (20 ml.) was added and g.l.c. of the solution on 2m x \( \frac{1}{8} \) in. Carbowax 1500 column at 100° showed the presence of styrene (28%), \( p \)-methylstyrene (24%), benzaldehyde (25%), \( p \)-tolualdehyde (67%) and styrene oxide (35%). The solution was evaporated to dryness and the residue quaternised with methyl iodide in benzene to give methyl(1-phenylvinyl)diphenylphosphonium iodide (0.6 g.), m.p. (from chloroform-ethyl acetate) and mixed m.p. 211-212°. The mother-liquors were evaporated and the residue chromatographed on basic alumina (60 g.). Elution with ether gave 1-phenylvinylidiphenylphosphine oxide (52%), m.p. (from benzene-light petroleum) and mixed m.p. 114-115°. Elution with ethanol gave 1,2-bis(diphenylphosphinyl)-1-phenylethane (28%), m.p. (from ethanol) and mixed m.p. 284-285°.
Reaction of Methyl(1-phenylvinyl)diphenylphosphonium.Iodide with Sodium Diphenylphosphide and p-Tolualdehyde.

Sodium wire (4 g.) was added to a solution of diphenylphosphine (1.7 g.) in tetrahydrofuran (100 ml.), and the solution heated under reflux for 2 hr. The excess of sodium was then removed and a suspension of the phosphonium iodide (4.0 g.) in tetrahydrofuran (30 ml.) was added and the solution set aside for 1/2 hr. p-Tolualdehyde (1.1 g.) was added and the solution set aside for a further 1/2 hr. The solution was then evaporated under reduced pressure. The residue, in chloroform (200 ml.), was washed with water (3 x 50 ml.), dried and evaporated. The residue was chromatographed on basic alumina (60 g.). Elution with ether gave trans-2-phenyl-1-p-tolyl-3-diphenylphosphinyl-propane (1.2 g.), m.p. (from benzene-light petroleum) 186-187°, \( \nu_{\text{max}} \) 1180 cm\(^{-1}\) (P=O), \( \lambda_{\text{max}} \) 260, 266 \( \mu \) (\( \epsilon \) 15,500, 15,500 in ethanol), singlet at \( \tau \) 7.7 integrating for three protons, doublet at \( \tau \) 6.18 integrating for two protons (\( J_{\text{PH}} = 15 \) c.p.s.) (Found: C, 82.14; H, 6.11; P, 7.81. \( C_{28}H_{25}P \) requires C, 82.5; H, 6.14; P, 7.6%). Further elution with ether gave cis 2-phenyl-1-p-tolyl-3-diphenylphosphinyl-propene (0.2 g.), m.p. (from benzene-light petroleum) 160-161°, \( \nu_{\text{max}} \) 1180 cm\(^{-1}\)(P=O), \( \lambda_{\text{max}} \) 260, 267 \( \mu \) (\( \epsilon \) 13,700, 13,400 in ethanol), singlet at \( \tau \) 7.72 equivalent to three protons, doublet at \( \tau \) 6.5 equivalent to two protons (\( J_{\text{PH}} = 15 \) c.p.s.) (Found: C, 82.29; H, 6.02; P, 7.88. \( C_{28}H_{25}P \) requires C, 82.5;
H, 6.14; P, 7.6%). Elution with ethyl acetate gave methyl-
diphenylphosphine oxide (0.5 g.), m.p. (from benzene-light
petroleum) and mixed m.p. 111-112°.


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