SOME REACTIONS
of
PHOSPHORUS YLIDS

By

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Signed

(B. J. Walker)
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SUMMARY

Both the methods of preparation, and the reactions, of phosphorus ylids are reviewed.

The reactions of activated triple bonds with phosphorus ylids are studied and shown to give rearranged products, probably via a four-membered cyclic transition state.

A brief outline of the mechanism of the Wittig reaction is given, and reactions of intermediate betaines in the Wittig reaction, other than olefin formation, are studied. The reaction of phosphines with epoxides is used to demonstrate betaine dissociation and rearrangement.

Following a review of abnormal quaternisation reactions of activated alkyl halides, the reaction of triphenylphosphine with 1-bromo-nitroalkanes, to give α-hydroxyimino-alkyl phosphonium salts, is discussed.

A brief review of the reactions of aldehydes and ketones with trivalent phosphorus compounds is followed by a more detailed study of the reaction of aminophosphines with aldehydes and ketones to give rearranged products.
INTRODUCTION

Phosphoranes and Phosphorus Ylids.

Phosphorus, unlike nitrogen, is able to exist in the quinquevalent state because it has readily available d orbitals into which its outer shell can expand. The term phosphorane incorporates any compound containing five valent phosphorus.

Within the general group of compounds known as phosphoranes there are two distinct types. The first contain quinquevalent phosphorus bonded covalently to five separate groups, while the second have four covalent bonds and a fifth, charge separated, bond.

The parent compound of the first type can be considered to be phosphorus pentahydride (PH₅). Both the theoretical possibility,¹ ² and the actual existence of this compound have been studied. The evidence points to the fact that it has no finite existence even at temperatures as low as −100°C. It is suggested that in the free phosphorus atom the 3 d orbitals are too diffuse for good bonding with hydrogen.

The second type of phosphoranes are known as ylids
and have a structure best represented as a resonance hybrid of the covalent and ionic forms (1a) and (1b)

\[
\begin{align*}
R_3P &= X & R_3P &= X^+ - X^- \\
(1a) & & (1b)
\end{align*}
\]

X can be carbon - the alkylidene phosphoranes (2), or nitrogen - the iminophosphoranes (3).

\[
\begin{align*}
R_3P &= CR_2 & R_3P &= NR \\
(2) & & (3)
\end{align*}
\]

Both these groups of compounds owe their reactivity to the anionic character of their X atom and were originally prepared by Staudinger\(^\text{4,5}\) in 1919.

Some ylids do not exist as shown in (1a) and (1b). These are phosphorus ylids having a Ψ-carbonyl group (4), which gives a further possibility for resonance structures.

\[
R_3P = CR - O - R
\]

(4)

Although in many of their reactions ylids of this type behave as if they are in the form (4), there is considerable evidence to show that they are in fact best
represented by the resonance hybrid of forms (4) and (5).

\[ \begin{align*}
R_3P = CR - C - R & \quad \overset{\leftrightarrow}{\longrightarrow} \quad R_3^+P - CR = C - R \\
(4) & \quad (5)
\end{align*} \]

Asknes has shown that in compounds of this type the carbonyl stretching frequency falls to the 1,600 cm\(^{-1}\) region, which suggests a considerable contribution from the form (5). The original suggestion of the phosphobetaine form (5) was based on dipole moment measurements. The acetylene synthesis of Trippett is based on the assumption that (5) has a considerable contribution.
The Preparation of Phosphorus Ylids.

The first preparation of a phosphorus ylid involved treating triphenylphosphine with a diazo-alkane and heating the phosphineazine (6) formed.

\[
\text{Ph}_3\text{P} + \text{N}_2\text{CR}^2\text{R}^2 \rightarrow \text{Ph}_3\text{P} = \text{N} - \text{N} = \text{CR}^2\text{R}^2
\]

\[
\text{(6)}
\]

\[
\text{Ph}_3\text{P} = \text{CR}^2\text{R}^2 + \text{N}_2
\]

Bestmann has also prepared phosphineazines by the action of dibromotriphenylphosphorane (7) on hydrazones in the presence of a base such as triethylamine.

\[
\text{Ph}_3\text{PBr}_2 + \text{N}H_2 - \text{N} = \text{CR}_2 \xrightarrow{\text{Et}_3\text{N}} \text{Ph}_3\text{P} = \text{N} - \text{N} = \text{CR}_2
\]

(7)

It is suggested that phosphoranes are formed from phosphineazines via triphenylphosphine and the carbene :CR^2R^2, which combine to give the phosphorane. Direct reaction between triphenylphosphine and carbenes has been reported. Chloromethylene with triphenylphosphine at -30°C gave a 65% yield of chloromethylenetriphenylphosphorane (8), which could be reacted with aldehydes and ketones in a Wittig reaction to give vinyl chlorides.
Dichloromethylene and methylene also react with triphenylphosphine to give the corresponding ylids.

Dichloromethylenetriphenylphosphorane (9) has also been prepared by the reaction of triphenylphosphine with carbontetrachloride. This reaction appears to proceed with attack of phosphine on halogen to give the phosphonium salt (10), elimination of chloride leads to dichlorotriphenylphosphorane and dichlorocarbene which can react with more phosphine to give dichloromethylenetriphenylphosphorane (9).

\[
\text{Ph}_3\text{P}: + \text{Cl}-\text{CCl}_3 \rightarrow \text{Ph}_3\text{P}^+\text{Cl}^- \quad \text{CCl}_3^- \\
(10)
\]

\[
\rightarrow \text{Ph}_3\text{PCl}_2 + :\text{CCl}_2^- \xrightarrow{\text{Ph}_3\text{P}} \text{Ph}_3\text{P} = \text{CCl}_2
\]

(9)

The reaction of carbontetra bromide with triphenylphosphine is similar. However if the product is treated with hydrogen bromide to give the phosphonium salt (11), this will undergo reaction with triphenylphosphine to give bromomethylenetriphenylphosphorane (12).
Phosphorus ylids can also be prepared from dihalophosphoranes of the type $R_3PCl_2$. Horner and Oediger have shown that in the presence of tertiary amines dihalophosphoranes will react with active methylene groups to give phosphoranes (13).

$$R_3PCl_2 + \text{CH}_2 \xrightarrow{2Et_3N} R_3P = C \text{X}_Y$$

(13)

Where X and Y are electron withdrawing groups.

A further indirect method of preparing phosphoranes has been developed by Bestmann. In a series of papers he has shown that alkylation and acylation of phosphoranes leads to $\alpha$-substituted products. Treatment of alkylidene phosphoranes (14) with alkyl halides leads to $\alpha$-substituted phosphonium salts (15).

$$\text{Ph}_3P = \text{CHR} + \text{R}^2\text{I} \rightarrow \text{Ph}_3P = \text{CHR}_2^+ \text{I}^-$$

(14)

This is also true for acylation. However, if the $\alpha$-hydrogen
in the phosphonium salt (15) is more acidic than that in the phosphonium salt, obtained on treating the phosphorane (14) with acid, the reaction does not stop at this point. The phosphonium salt (15) is dehydrohalogenated by the phosphorane (14) to give (16) and (17).

\[
\begin{align*}
\text{Ph}_3\text{P} - \text{CHR}^1\text{R}^- + \text{Ph}_3\text{P} = \text{CHR} & \rightarrow \text{Ph}_3\text{P} = \text{CRR}^1 + \text{Ph}_3\text{P} - \text{CH}_2\text{R}^- \\
(15) & \quad (14) \\
& \quad (16) \\
& \quad (17)
\end{align*}
\]

This reaction is known as transylidation and takes place when \(\text{R}^1\) is an electron withdrawing group. In cases of this type only a 50% equivalent of \(\text{R}^1\text{I}\) is added in order to avoid the complications of addition to (16).

Phosphoranes with a large range of \(\alpha\)-substituents can be produced by this method, e.g. \(-\text{COR}, \quad -\text{CHO}, \quad -\text{Br}, \quad -\text{T}, \quad -\text{COOR}\).

Phosphoranes may also be prepared from unsaturated compounds. Oda \(^{27}\) and Hoffmann \(^{28}\) have shown that phosphines will add to activated double bonds, in ethanol, presumably initially forming the betaine (18) which then takes up, and loses, a proton from, and to, the solvent to give the more stable phosphorane (19).
\[
R_g P + CH_2 = CHX \rightarrow R_g^+ CH_2 CH^- X
\]
(18) \[\downarrow\text{EtOH}\]
\[
R_g P = CH - CH_2 X + \text{EtOH} \leftarrow R_g^+ CH_2 CH_2 - X \text{EtO}^-
\]
(19)

Where \(X\) can be \(-\text{CN}, -\text{COOEt}, -\text{CONH}_2\).

Hoffmann carried out these reactions in the presence of acid and isolated the corresponding phosphonium salts, while Oda added aldehydes and isolated the olefins produced from a Wittig elimination (see p. 83).

Osuch, and other workers, have added triphenylphosphine to maleic anhydride to give the phosphobetaine (21). This reaction presumably takes place by a mechanism similar to that described above, initial formation of the betaine (20) and proton transfer to give the phosphobetaine.

The reaction of methylenetriphenylphosphorane with tetramethylocyclobutadione leads to the phosphobetaine (22),
perhaps by initial attack at a carbonyl group followed by ring opening and a proton transfer.

\[
\text{Ph}_3\text{P} = \text{CH}_2 + \xrightarrow{\text{Me}} \text{Ph}_3\text{P} \begin{array}{c}
\text{CH} \\
\text{Me}
\end{array} \begin{array}{c}
\text{C} \\
\text{Me}
\end{array} \begin{array}{c}
\text{CH} \\
\text{Me}
\end{array} \begin{array}{c}
\text{C} \\
\text{Me}
\end{array} \begin{array}{c}
\text{Me}
\end{array} \xrightarrow{\text{Me}} \text{Ph}_3\text{P} \begin{array}{c}
\text{CH} \\
\text{Me}
\end{array} \begin{array}{c}
\text{C} \\
\text{Me}
\end{array} \begin{array}{c}
\text{C} \\
\text{Me}
\end{array} \begin{array}{c}
\text{Me}
\end{array} \begin{array}{c}
\text{Me}
\end{array} \begin{array}{c}
\text{Me}
\end{array} 
\]

\[\text{(22)}\]

Seyferth\(^{32}\) has added diphenylmethyolphosphine to benzyne to produce methylenetriphenylphosphorane (23), which was trapped with cyclohexanone in a conventional Wittig reaction.

\[
\text{Ph}_3\text{P} - \text{CH}_3 + \xrightarrow{\text{Me}} \text{Ph}_3\text{P} \begin{array}{c}
\text{CH} \\
\text{Me}
\end{array} \begin{array}{c}
\text{C} \\
\text{Me}
\end{array} \begin{array}{c}
\text{CH} \\
\text{Me}
\end{array} \begin{array}{c}
\text{C} \\
\text{Me}
\end{array} \begin{array}{c}
\text{Me}
\end{array} \xrightarrow{\text{Me}} \text{Ph}_3\text{P} \begin{array}{c}
\text{CH} \\
\text{Me}
\end{array} \begin{array}{c}
\text{C} \\
\text{Me}
\end{array} \begin{array}{c}
\text{C} \\
\text{Me}
\end{array} \begin{array}{c}
\text{Me}
\end{array} \begin{array}{c}
\text{Me}
\end{array} \begin{array}{c}
\text{Me}
\end{array} \begin{array}{c}
\text{Me}
\end{array} 
\]

\[\text{(23)}\]
All these methods may be used to produce phosphoranes, however the most general method of preparation is the treatment of the corresponding phosphonium salt with a suitable base.

$$R_d^+ - CHR^2 + B \rightarrow R_d P = CR^2 + BH$$

A wide range of bases are available and the choice depends on the type of phosphorane to be prepared, its stability to further reaction with the media and the ease of removal of the α-proton in the phosphonium salt.

Generally phosphoranes can be divided into two groups, "stable" and "unstable". The "stable" phosphoranes are those in which the negative charge residing on the α-carbon atom is delocalised to some extent by substituents. When this delocalisation is not present we have the "unstable" phosphoranes. The electron withdrawal by substituents which stabilises the phosphorane will also aid removal of a proton from the phosphonium salt, thus the production of "unstable" phosphoranes requires a more powerful base than that of "stable" phosphoranes.

Bases used to produce "unstable" phosphoranes are usually metal alkyls, commonly lithium alkyls. The mechanism of phosphorane formation using these bases has yet to be fully
explained, and a number of side reactions have been shown to take place. In the reaction of methyltriphenylphosphonium bromide with n-butyl-lithium, Seyferth has shown that, as well as butane, a 20% yield of benzene is produced and treatment of tetraphenylphosphonium bromide with methyl-lithium gives at least 58% of methylenetriphenylphosphorane. However, if the base is changed to vinyl-lithium the products from this reaction are styrene and triphenylphosphine. Seyferth has proposed the quinquevalent phosphorus derivative (24) as the intermediate in these reactions.

\[ \text{Ph}_4P\text{Br}^- + \text{CH}_3\text{Li} \rightarrow \begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array} \rightarrow \text{Ph}_3P = \text{CH}_2 \]

(24)

The reaction of lithium-alkyls with halomethyltriphenylphosphonium salts is also complex. Although chloromethyltriphenylphosphonium bromide gave only chloromethylenetriphenylphosphorane and benzene on treatment with lithium-phenyl, bromomethyltriphenylphosphonium bromide gave benzene (59%) and
bromobenzene (40%) under the same conditions, presumably by attack at both carbon-hydrogen and carbon-bromine bonds.

\[ \text{Ph}_3\text{P} - \text{CH}_2 - \text{Cl} \quad \text{Br}^- \quad \text{PhLi} \quad \rightarrow \quad \text{Ph}_3\text{P} = \text{CHCl} + \text{PhH} + \text{LiBr} \]

\[ \text{Ph}_3\text{P} - \text{CH}_2 - \text{Br} \quad \text{Br}^- \quad \rightarrow \quad \text{Ph}_3\text{P} = \text{CHBr} + \text{PhH} + \text{LiBr} \]

When the reaction is extended to iodomethyltriphenylphosphonium iodide the proportion of attack on the halogen-carbon bond is increased still further, the products being benzene (28%) and iodobenzene (70%). This trend is in agreement with the observed reactivity of carbon halogen bonds towards lithium hydrocarbons. Kobrich has found that carbon-halogen cleavage is minimised by the use of piperidyl-lithium as the base. He obtained a 70% yield of olefin from the reactions of β-ionone with bromomethylenetriphenylphosphorane produced in this way.

\[ \text{Ph}_3\text{P} - \text{CH}_2 - \text{Br} \quad \text{Br}^- \quad \text{LiC}_6\text{H}_5\text{N} \quad \rightarrow \quad \text{Ph}_3\text{P} = \text{CHBr} \]

\[ \begin{align*}
\text{Ph}_3\text{P} - \text{CH}_2 & \quad \text{Br}^- \quad \text{LiC}_6\text{H}_5\text{N} \\
\text{Ph}_3\text{P} & = \text{CHBr} \\
\end{align*} \]
In all these reactions an excess of lithium hydrocarbon must be avoided because the anion (25) may be produced, which can undergo rearrangement to give the benzylidene phosphorane (26).

\[
\text{Ph}_3\text{P} = \text{CHCl} \xrightarrow{RL1} \text{Ph}_3\text{P} \begin{array}{c} \text{Ph} \\ \text{N} \\ \text{Cl} \end{array} \text{CH} \rightarrow \text{Ph}_2\text{RP} = \text{CHPh}
\]

(25) \hspace{2cm} (26)

To produce "unstable" phosphoranes, very reactive bases such as the lithium hydrocarbons must be used, and it is just this reactivity that hinders their use in the production of many phosphoranes. If the phosphonium salt contains a group which will react with the lithium hydrocarbon (e.g. carbonyl) then alkali-metal alkoxides can be used. These may be employed in a variety of solvents (e.g. the parent alcohol, \(\text{N}_2\text{N}\)-dimethylformamide, hexamethylphosphoric triamide) and on addition of the phosphonium salt an equilibrium is established:

\[
\text{Ph}_3\text{P}^+ \text{CHR}^1\text{R}^2 + \text{OR} \rightleftharpoons \text{Ph}_3\text{P} = \text{CR}^1\text{R}^2 + \text{ROH}
\]

Some phosphonium alkoxides can decompose to phosphine oxides (see p. 94) and so the phosphorane is best used quickly.
Another base which is becoming widely used has been developed by Corey. Sodium hydride dissolves in dimethylsulphoxide (27) to give the sulphoxide anion (28) and hydrogen.

\[
\begin{align*}
\text{CH}_3\text{S}=0 & \xrightarrow{\text{NaH}} \text{CH}_3\text{S}^{-0} + \text{H}_2 \\
(27) & \quad (28)
\end{align*}
\]

This anion is an extremely powerful base and the system has the advantage that dimethylsulphoxide is completely miscible with water. However, the anion will react with ketones and this can cause complications.

Sodium hydroxide and even, in exceptional cases, sodium bicarbonate, can be used as a base, but only to produce the more stable phosphoranes. Ethoxycarbonylmethylenetri-phenylphosphorane (29) can be produced in this way, at 0°C in aqueous solution.

\[
\begin{align*}
\text{Ph}_3\text{P}^- \cdot \text{Br} & \xrightarrow{\text{NaOH}, 0^\circ\text{C}} \text{Ph}_3\text{P} = \text{CH} \cdot \text{COOEt} \\
(29)
\end{align*}
\]

Not all phosphorus ylids may be prepared by the
treatment of a phosphonium salt with the appropriate base.

If alkyltriphenylphosphonium salts, having in the β-position, in the alkyl group a group, which is capable of stable existence as an anion or uncharged molecule, are treated with base they may eliminate this group to give a vinyltriphenylphosphonium salt.

\[
\begin{align*}
\text{Ph}_3^+\text{P} &\text{CH}_2\text{CH}_2\text{CH}_2\text{X} & \xrightarrow{\text{B}^-} & \text{Ph}_3^+\text{P} &\text{CH}^\equiv\text{CH}_2\text{CH}_2\text{X} \\
& & & \text{Ph}_3^+\text{P} &\text{CH} = \text{CH}_2\text{X}^- \\
\end{align*}
\]

This occurs where \( X \) is: \( \text{Ph}_3^+ \), \( ^\text{44} \) - \( \text{OEt} \), \( ^\text{45} \) halogen, \( ^\text{45} \) and hydroxyl, and is reversible under the correct conditions. \( ^\text{46} \)

It is even possible for this effect to be transmitted through a conjugated system. \( ^\text{45} \)

\[
\begin{align*}
\text{Ph}_3\text{P} &\text{CH}^\equiv\text{CH} = \text{CH}_2\text{CH}_2\text{PPh}_3 & \rightarrow & \text{Ph}_3\text{P} &\text{CH} = \text{CH} = \text{CH} = \text{CH}_2 + \text{Ph}_3\text{P} \\
& & & \text{X}^- & \text{X}^- \\
\end{align*}
\]

Mondon, \( ^\text{47} \) and other workers, \( ^\text{21}, ^\text{48} \) have shown that a similar reaction takes place with \( \text{O}^\text{O} - \text{bromobutyltriphenylphosphonium bromide on treatment with phenyl-or butyl-lithium. The expected phosphorane (30) being produced initially and then undergoing self alkylation to give cyclobutyltriphenylphosphonium bromide.} \)
Various workers \(^{46,49}\) have shown that vinylphosphonium salts themselves behave abnormally in the presence of base. Keough and Grayson treated the vinylphosphonium salt (31) with a series of anions and showed that addition occurred across the double bond in preference to the removal of an α-proton.

\[
\begin{align*}
\text{Ph}_3\text{P} - (\text{CH}_2)_2 - \text{Br} & \quad \text{Br}^- \xrightarrow{\text{RLi}} \quad \text{Ph}_3\text{P} = \text{CH} \xrightarrow{\text{CH}_2} \text{CH}_2 \xrightarrow{\text{Br}} \\
& \quad \Downarrow \\
& \quad \text{Ph}_3\text{P}^+ - \text{CH} - \text{CH}_2 \quad \text{Br}^- \\
& \quad \Downarrow \\
& \quad \text{Ph}_3\text{P}^+ - \text{CH}_2 - \text{CH}_2 \quad \text{Br}^-
\end{align*}
\]

\(^{(30)}\)

X could be carbon, \(^{46,49}\) nitrogen, \(^{46,49}\) oxygen, sulphur \(^{46,49}\) or phosphorus. \(^{48}\)

Schweizer and Light \(^{49}\) have also shown that when XH is the substituted pyrrole (32), the initial Michael addition product undergoes an internal Wittig reaction to give compound (33) in high yield.
This type of reaction has been developed into a general ring synthesis. When phosphonium salts with a keto group in the $\varepsilon$ position are treated with sodium alkoxides the phosphorane is initially formed, but then undergoes an internal Wittig reaction to produce a cyclic olefin.

\[ \text{Ph}_3\text{P} = \text{CH} - (\text{CH}_2)_3 - \text{CO} - \text{Ph} \rightarrow \text{Ph}_3\text{PO} + \text{Ph} - \text{CH} - (\text{CH}_2)_3 \]

A series of these reactions have been carried out...
on phosphonium salts of the type (34)

\[
\text{Ph}_3P - \text{CH}_2 - (\text{CH}_2)_n - \text{COPh Br}^- \\
(34)
\]

When \( n = 1 \), and sodium ethoxide is used as a base, a \( \beta \)-elimination takes place to give triphenylphosphine. 52

\[
\text{Ph}_3P - \text{CH}_2 \overset{\text{CH} - \text{CO} - \text{Ph}}{\longrightarrow} \text{Ph}_3P + \text{CH}_2 = \text{CH} - \text{COPh} \\
\overset{\text{H}}{\overset{\text{OEt}}{\longrightarrow}}
\]

However, if lithium phenyl is used as the base, 1,4 diphenyl-1,4-cyclohexadiene is formed, 52 presumably by an intermolecular reaction.

When \( n = 2 \), no olefin is formed under any conditions, and only in small yield when \( n = 4 \). 53

Phosphonium salts with ester groups in the \( \gamma \), \( \delta \), and \( \epsilon \) positions in the side chain give acylated phosphoranes when treated with sodium alkoxides. 54

\[
\text{Ph}_3P = \text{CH} - (\text{CH}_2)_n - \overset{\text{OEt}}{\text{C}} \quad \rightarrow \quad \text{Ph}_3P = \overset{\text{OEt}}{\text{C}} - (\text{CH}_2)_n \\
\text{n} = 2, 3, 4.
\]

Bestmann 55 has also shown that pyrolysis of the lactone (35) leads to decarboxylation and the formation of
the cyclopropylphosphonium salt (36).

\[
\begin{align*}
\text{CH}_2\text{CH}-\text{C}^\text{\text{=}}\text{PPh}_3^+ & \quad \xrightarrow{180\text{--}190^\circ\text{C}} \quad \text{CO}_2 \\
\text{CH}_2 & \quad \text{CH} & \quad \text{Br} \\
\text{CH}_2 & \quad \text{C} & \quad \text{O} \\
\text{CH}_2 & \quad \text{CH} & \quad \text{C}^\text{=}\text{PPh}_3^+ & \quad \text{Br}^- \\
\end{align*}
\]

(35) (36)
Reactions of Phosphorus Ylids.

(a) Phosphorus Ylids in the Wittig Reaction

The enormous interest in the reactions of phosphorus ylids, over the past decade, stems mainly from the development, by Wittig, of a general olefin synthesis involving these compounds.

A large number of reviews on the Wittig reaction have appeared, together with more than one hundred and fifty papers. A discussion of the mechanism of the Wittig reaction will be found below (p. 83) and here its general applications will be discussed.

In the Wittig reaction a ketone or aldehyde is reacted with a phosphorane to give an olefin and a phosphine oxide. The carbonyl compound may contain any of the following groups: - hydroxy, acetoxy, methoxy, acetal, tetrahydropyranyl, dimethylamino, terminal acetylenic, halogen, ester and nuclear halogen and nitro.

The reaction has probably found most use in polyene synthesis. Squalene, Vitamin A ester, lycopene, 15,15'-dehydro-lycopene, 15,15'-cis-lycopene, 15,15'-dehydro-β-carotene and norbixin and crocetin diesters have been prepared using the Wittig reaction.
The reaction has been used extensively in the Vitamin D field. Calciferol and other related steroids have been prepared for use in light absorption studies by methods involving Wittig reactions.\(^{62,63}\)

Bestmann \(^{26}\) has used the Wittig reaction to synthesise tritiated olefins with phosphoranes having a tritium atom as the methylene carbon atom. These phosphoranes were prepared by treating the corresponding non-tritiated phosphonium salt with sodium ethoxide in tritiated ethanol:

\[
\begin{align*}
\text{Ph}_3\text{P}^+ - \text{CH}_2\text{R} & \xrightarrow{\text{EtONa}, \text{EtOT}} \text{Ph}_3\text{P} = \text{CHR} + \text{EtOH} \\
\text{Ph}_3\text{P} = \text{CTR} & \xrightarrow{\text{R'CHO}} \text{Ph}_3\text{P}^+ - \text{CHTR} + \text{EtO}^-
\end{align*}
\]

Allenèes have also been prepared. Staudinger \(^{71}\) and Wittig \(^{72}\) reacted ketenes with phosphoranes, while Gilman used the phosphorane (37) and ketones to give allenèes.

\[
\text{Ph}_3\text{P} = \text{C} = \text{CR}^2\text{R}^2 + \text{R}^3\text{R}^4\text{C} = \text{O} \rightarrow \text{R}^3\text{R}^4\text{C} = \text{C} = \text{CR}^2\text{R}^2 + \text{Ph}_3\text{PO}
\]

\(37\)

Levine,\(^{73}\) Wittig\(^{74}\) and Zbiral\(^{75}\) have shown that
the Wittig reaction can be used as an alternative to the
glycidic ester synthesis, for the conversion of an aldehyde
or ketone into its next higher homologue. Aldehydes and
ketones react with methoxymethylenetriphenylphosphoranes to
give vinyl ethers, which are readily hydrolysed by acid to
aldehydes.

\[
\text{Ph}_3\text{P} = \text{CHCOCH}_3 + \text{R}^1\text{R}^2\text{C} = \text{O} \rightarrow \text{R}^1\text{R}^2\text{C} = \text{CHCOCH}_3
\]

\[
\text{R}^1\text{R}^2\text{CH} \cdot \text{CHO} \uparrow \text{H}^+ 
\]

Siemiartycki\(^7\) has used certain substituted benzylidene-
phosphoranes as selective reagents for the determination of
aldehydes.

Recently fluoroolefins have been prepared by a
method which involves the Wittig reaction.\(^7\)^\(^7\),\(^7\)\(^8\) When a
phosphine, a carbonyl compound and sodium difluorochloro-
acetate are heated in a polar solvent difluoroolefins are
produced. The difluorocarbene produced from the sodium salt
presumably reacts with the phosphine to give the phosphorane
(38) which then undergoes a normal Wittig reaction to give
the products.

\[
\text{ClCF}_2 \cdot \text{CDONa} \rightarrow \text{CO}_2 + \text{NaCl} + :\text{CF}_2 \xrightarrow{\text{Ph}_3\text{P}} \text{Ph}_3\text{P} = \text{CF}_2
\]

(38)

\[
\text{R}_2\text{C} = \text{CF}_2 + \text{Ph}_3\text{PO}
\]
(b) Other Reactions of Phosphorus Ylids Proceeding via Intermediate Betaines.

The Wittig reaction is a specific example of a general reaction of phosphorus ylids proceeding through an intermediate betaine (39).

\[ R_3P = CHR + X = Y \rightarrow R_3P^+CHRX^-Y \]

Although phosphoranes react by the normal Wittig route with \( \alpha,\beta \)-unsaturated ketones in most cases, some anomalies, involving 1,4-addition, have been found. In these cases the betaine (40) is initially produced, which can decompose in various ways depending upon the groups R.
When (40) is derived from the reaction of 1 oxo-1,5 diphenylpent-2,4-diene (41) and styrylmethylenetriphenylphosphorane it decomposes to give the triene (42), phenylacetylene and triphenylphosphine oxide.

\[
\begin{align*}
&\text{Ph} \quad \text{C} \quad \text{H} \quad \text{O} \\
&\text{Ph} \quad \text{CH}=\text{CH} \quad \text{CH} \quad \text{PPh}_3 \\
&\text{CH} \quad \text{C} \quad \text{O} \\
&\text{Ph} \quad \text{CH}=\text{CH} \quad \text{CH} \quad \text{PPh}_3
\end{align*}
\]

When (40) is derived from 2-methylene cyclohexanone and cyclohexylideneethylidenetriphenylphosphorane any rearrangement similar to that above would produce cyclohexyne. As this is unfavourable the decomposition follows a different path leading to the triene (43) and triphenylphosphine oxide, products which can be explained by a 1,3 hydride shift.
The third and final recorded example of conjugate addition of a phosphorane to an $\alpha,\beta$ unsaturated ketone has been demonstrated by Freeman. \textsuperscript{81} When methylenetriphenylphosphorane reacts with benzylideneacetomesitylene (44), triphenylphosphine is eliminated and the cyclopropane derivative (46) is produced. This may be explained by electron shifts as shown in (45).
Considerable work has been carried out on the reactions of epoxides with phosphorus ylids. Denney and Boskin\textsuperscript{82} have shown that ethoxycarbonylmethylenetriphenylphosphorane and styrene oxide give, at 200°C, triphenylphosphine oxide (90%) and the cyclopropane (47) (21%).

\[
\text{Ph}_3\text{P} = \text{CH-} \text{COOEt} + \text{Ph-CH-CH}_2 \rightarrow \text{Ph-CH-CH}_2 + \text{Ph}_3\text{PO} \]

McEwan\textsuperscript{83} found that when the optically active phosphonium
salt (48) was converted to the phosphorane, and treated with styrene oxide, a precipitate was formed. This was shown to be the lithium iodide adduct of the betaine (49).

When this was heated to 190-200°C for three hours a complex mixture of products resulted, including racemic ethylmethylphenylphosphine (35%) and benzylacetophenone (50) (12-30%). Use of isotopically labelled carbon in the phosphonium salt (48), at the position starred, proved that this ketone could not have arisen via the symmetrical intermediate (51) since the labelled carbon was found only at the position β to the carbonyl group.
When benzylidenetriphenylphosphorane was used in this reaction, very little of the ketone (50) was produced, the main products being triphenylphosphine oxide (80%) and 1,3-diphenylpropene. Work by Zbiral has confirmed this and also shown that p-methoxyphenylethylene oxide reacts with this phosphorane to give 1-p-methoxyphenyl-3-phenylpropene, thus establishing the position of the double bond in relation to the phenyl groups.

\[
\text{Ph}_3\text{P} = \text{CHPh} + \text{p-MeO-C}_6\text{H}_4 - \text{CH} - \text{CH}_2
\]

\[
\rightarrow \text{p-MeO-C}_6\text{H}_4 - \text{CH} = \text{CH} - \text{CH}_2 - \text{Ph}
\]

Zbiral has also shown that cyclohexene oxide reacts with
benzyldenetriphenylphosphorane to give the olefin \((52)\) and the hydrocarbon \((53)\)

\[
\text{Ph}_3\text{P} + \text{CHPh} \rightarrow \text{Ph-CH} = \text{CH} + \text{Ph-}
\]

\[
\text{Ph-}
\]

All these results may be explained in the following manner. The initial reaction in all cases is nucleophilic attack of the \(\alpha\)-carbanion in the phosphorane on the epoxide to give the betaine \((54)\). When \(R^1 = \text{alkyl}\) the electrophilic character of the phosphorus in the betaine is decreased, thus hindering attack of \(O\) sufficiently to allow a 1,3 hydride shift to take place, leading to the ketone \((55)\) and the phosphine \(R^1_3\text{P}\).

\[
R^1_3\text{P} = \text{CHR}^2 + \text{R}^3\text{CH} - \text{CHR}^4 \rightarrow R^1_3\text{P} + \text{CHR}^2 - \text{CHR}^3
\]

\[
\text{R}^1_3\text{P} + \text{R}^2\text{CH}_2\cdot\text{CHR}^3\cdot\text{COR}^4
\]
A similar reaction has been reported by Wittig and Boll.\textsuperscript{85} Butyraldehyde reacts with butoxymethylenetriphenylphosphorane to give the betaine (56) which undergoes a 1,2 hydride shift to give the ketone (57) and triphenylphosphine.

\[
\begin{align*}
\text{Ph}_3\text{P} &= \text{CH} - \text{OBu} \\
\text{Ph}_3\text{P}^+ - \text{CH} - \text{OBu} + &\xrightarrow{R^A} \text{Ph}_3\text{P}^+ \\
\text{C}_3\text{H}_7 - \text{CHO} &\xrightarrow{\text{C}_3\text{H}_7} \text{C}_3\text{H}_7 \text{O} = \text{C} \\
&\xrightarrow{\text{C}_3\text{H}_7} \text{CH}_2 - \text{O} - \text{Bu} \\
&\xrightarrow{\text{C}_3\text{H}_7} (57)
\end{align*}
\]

In all other cases cyclisation occurs to give (58) which can then undergo either P—C or O—C fission.
When stable phosphoranes are used $R^2$ will be an electron withdrawing group and will be able to stabilise the carbanion (59), thus in the case of stable phosphoranes path (A) to give the cyclopropane would be expected. In other cases path (B) will be followed producing the olefin (60), except where $R^2$ and $R^3$ are held in a fixed conformation such that $R^3$ is trans to the $O-C$ bond. This is the case in the intermediate (61) from cyclohexene oxide, and the rearrangement shown can take place leading to the olefin (62)

![Diagram](image)

Certain phosphoranes can themselves exist in a betaine form. This is the basis of the acetylene synthesis of Trippett and Gough. One contributing structure in $\beta$-ketophosphoranes can be considered to be the phosphobetaine form (63) (see p. 3) and on heating to $\sim 200^\circ C$ these compounds eliminate phosphine oxide to give the corresponding acetylene.
For the yields to be good in these reactions $R^1$ or $R^2$ must be able to conjugate with the double bond in the betaine ($R_1$ or $R_2 = -\text{Ph}, -\text{COR}, -\text{COOR}, -\text{CN}$), this is probably because the acetylene formed requires to be stabilised somewhat to survive the reaction conditions.

Zimmerman has pyrolysed the phosphorane (64) at 220-260°C to give the expected acetylene (65) and the muconic ester (66).

The reaction of phosphines with $p$-benzoquinones leads to betaine (67) analogous to (63). These are extremely
thermally stable and will not eliminate phosphine oxide even at temperatures $>280^\circ$C.

\[ \text{67) } \]

The reaction of phosphoranes with phenylisocyanate was first reported by Staudinger, and has since been fully investigated by Trippett. The general reaction may be formulated as a typical Wittig reaction proceeding via the betaine (68). When $R^1$ and $R^2$ are phenyl, the betaine (68) eliminates phosphine oxide to give 1,1-diphenyl-2-phenylimidoethylene (69; $R^1 = R^2 = \text{Ph}$).

\[ \text{68) } \]

\[ \text{69) } \]
However if $R^1$ or $R^2$ are hydrogen a proton transfer to nitrogen occurs, to give the more stable phosphorane (70).

Nitrosobenzene also reacts with phosphoranes via an intermediate betaine (71) to give phosphine oxide and Schiff's base.\(^9\)

\[
\begin{align*}
\text{Ph}_3\text{P} = \text{CHR} & \quad \rightarrow \quad \text{Ph}_3\text{P}^+ \\
\text{O} = \text{N} - \text{Ph} & \quad \rightarrow \quad \text{Ph}_3\text{PO} \\
\text{Ph}_3\text{P}^+ & \quad \rightarrow \quad \text{CHR} \\
\text{O} & \quad \rightarrow \quad \text{NPh} \\
\text{NPh} & \quad \rightarrow \quad \text{CHR} \\
\text{NPh} & \quad \rightarrow \quad + \\
\end{align*}
\]

This reaction appears to be general for stable and unstable phosphoranes, however p-dimethylaminonitrosobenzene has been shown to give phosphine, and what is thought to be the nitrone (72), with phosphorus ylids.\(^9\) This is presumably due to the $+M$ effect of the p-dimethylamino group facilitating the electron shifts shown in (73).

\[
\begin{align*}
\text{(CH}_3\text{)}_2\text{N} & \quad \rightarrow \quad \text{Ph}_3\text{P} + \text{(CH}_3\text{)}_2\text{N} \\
\text{CHR} & \quad \rightarrow \quad \text{CHR} \\
\text{N} & \quad \rightarrow \quad \text{CH}_3 \\
\text{N} & \quad \rightarrow \quad + \\
\end{align*}
\]

Carbon disulphide reacts with phosphoranes to give triphenylphosphine sulphide and thietenes.\(^9\) Presumably...
via the betaine (74).

\[
\begin{align*}
\text{Ph}_3\text{P} &= \text{CR}_2 + \text{CS}_2 \rightarrow \text{Ph}_3\text{P} - \text{CR}_2 \\
-\text{S} &\quad \text{C} = \text{S} \rightarrow \text{R}_2\text{C} = \text{C} = \text{S} \\
+&\quad \text{Ph}_3\text{PS}
\end{align*}
\]

(74)

Bestmann and Seng have shown that phosphoranes react with Schiff's bases by two different routes depending on the phosphorane. When phosphoranes of the type (75), with a \(-\text{CH}_2-\) group in the \(\beta\)-position of the side chain, were reacted with benzylideneaniline the products were phosphine, aniline and allenes of the type (76).

\[
\begin{align*}
\text{Ph}_3\text{P} &= \text{CH} - \text{CH}_2 - \text{R} + \text{Ph} - \text{CH} = \text{NPh} \rightarrow \text{Ph}_3\text{P} + \text{PhNH}_2 \\
&\quad + \text{PhCH} = \text{C} = \text{CHR}
\end{align*}
\]

(75) (76)

As yet no mechanism has been postulated for this reaction.

When the phosphorane is of the type (77), with no \(\beta-\text{CH}_2-\) group, the elimination proceeds via the betaine (78) to give the iminophosphorane (79) and the olefin (80).
Bestmann has also studied the autoxidation of phosphorus ylids. Benzyldenetriphenylphosphorane (81; R = Ph) reacts with oxygen to give triphenylphosphine oxide (80%), cis-stilbene (20%) and trans-stilbene (35%). The initial step is possibly the formation of the betaine (82), decomposition of which leads to phosphine oxide and benzaldehyde which can then react with the original phosphorane, by a normal Wittig reaction, to give stilbene (83; R = Ph).
Styrylmethylenetriphenylphosphorane (81; \( R = \text{Ph} - \text{CH} = \text{CH}^- \)) similarly gave 1,6-diphenylhexatriene (83; \( R = \text{Ph} - \text{CH} = \text{CH}^- \)). This reaction has considerable applications in polyene synthesis and Bestmann has converted vitamin A into \( \beta \)-carotene in 35% yield by the following method.

\[
\begin{align*}
\text{CH}_2\text{OH} & \quad \text{Ph}_3\text{P} \\
\text{HX} & \quad \rightarrow \\
\end{align*}
\]

Cyclic olefins, including acenaphthylene (84), have been prepared by autoxidation of bis-phosphoranes. \(^{96}\)
The analogous reaction of phosphoranes with sulphur leads to phosphine sulphides and thio ketones.

Stable phosphoranes (85) have also been oxidised with peracetic acid to give olefins, providing \( R^1 = \text{H} \).

Thus ethoxycarbonylmethylenetriphenylphosphorane (85; \( R^1 = \text{H}, R^2 = -\text{COOEt} \)) gave diethylfumarate (41%), but \( \alpha \)-ethoxycarbonylethylidenetriphenylphosphorane (85; \( R^1 = \text{Me}, R^2 = -\text{COOEt} \)) gave only 7% of the expected olefin. When less stable, more basic, phosphoranes were used in this reaction phosphonium acetates were formed, which underwent hydrolysis to the phosphine oxide.

When benzoyl peroxide was used as the oxidising agent, acid anhydrides of the type (86) were formed.
A possible mechanism for this reaction involves the initial production of the phosphonium salt (87), attack of benzoate on this to give the betaine (88) and elimination of phosphine leading to (89), which rearranges to the product (86).

The triphenylphosphine is oxidised by the second molecule.
of peroxide and isolated as the oxide. An alternative explanation is that the betaine (88) eliminates phosphine oxide to give an olefin, which is epoxidised by the second molecule of peroxide to (89).

Zbiral \(^9^9\) has oxidised phosphoranes with lead tetraacetate to give phosphine oxides and carbonyl compounds.

\[
\text{Ph}_3 = C - CO - R \xrightarrow{\text{Pb(OAc)}_4} RCO\cdot COOMe + \text{Ph}_3\text{PO}
\]

Ozonolysis of \(\beta\)-ketoalkylenephosphoranes leads to \(\alpha\)-diketones. \(^1^0^0\) When treated with ozone at \(-70^\circ\text{C}\) in methylene chloride, phenacylidene-triphenylphosphorane gave 96\% of triphenylphosphine oxide and 88\% of phenylglyoxal (90).

\[
\text{Ph}_3\text{P} = CH - CO - Ph \xrightarrow{O_3} \text{Ph}_3\text{PO} + \text{PhCO} \cdot \text{CHO}
\]

Markl \(^1^0^1\) has carried out the reaction of benzylidene-triphenylphosphorane with aliphatic diazocompounds. The betaine (92) was initially formed, elimination of triphenylphosphine then gave the azine (93). The triphenylphosphine eliminated was able to react with another mole of diazo compound to give the phosphineazine (94).
Markl claimed that the more stable phosphoranes (91; R = −COOCH₃, −CO−Ph, −CO−CH₃) did not react with aliphatic diazo compounds. Stryelecka, Siemiatycki, and Prevost have, however, reported that benzoyldiazo-methane and phenacylidenetriphenylphosphorane (91; R = −COPh) react to give 4-benzylidene-2,6-diphenylpyran (95) and triphenylphosphine oxide.

\[
2\text{Ph}_3\text{P} = \text{CHCO} - \text{Ph} + \text{PhCO} \cdot \text{CHN}_2 \rightarrow \text{Ph} + \text{Ph}_3\text{PO} + \text{Ph}_3\text{P} \cdot \text{CHR} + \text{R}^2\text{CO} \cdot \text{CR} = N = N \rightarrow \text{Ph}_3\text{P} \cdot \text{CHR} + \text{R}^2\text{CO} \cdot \text{CR} = N = N = \text{CR}^4\text{COR}^2
\]

(91)

Markl claimed that the more stable phosphoranes (91; R = −COOCH₃, −CO−Ph, −CO−CH₃) did not react with aliphatic diazo compounds. Stryelecka, Siemiatycki, and Prevost have, however, reported that benzoyldiazo-methane and phenacylidenetriphenylphosphorane (91; R = −COPh) react to give 4-benzylidene-2,6-diphenylpyran (95) and triphenylphosphine oxide.

\[
2\text{Ph}_3\text{P} = \text{CHCO} - \text{Ph} + \text{PhCO} \cdot \text{CHN}_2 \rightarrow \text{Ph} + \text{Ph}_3\text{PO} + \text{Ph}_3\text{P} \cdot \text{CHR} + \text{R}^2\text{CO} \cdot \text{CR} = N = N \rightarrow \text{Ph}_3\text{P} \cdot \text{CHR} + \text{R}^2\text{CO} \cdot \text{CR} = N = N = \text{CR}^4\text{COR}^2
\]

(91)

Pyrilium salts (96) have been shown to react with phosphorus ylids to give substituted benzene derivatives by a mechanism involving a Wittig type elimination.
Dimroth, Wolf and Wache have extended this reaction to the preparation of azulene derivatives by using only half a mole equivalent of phosphorane.
\[
\begin{align*}
\text{[Diagram showing chemical reactions and structures]} & \quad \text{(97)} \\
\text{[Diagram showing chemical reactions and structures]} & \quad \text{(98)}
\end{align*}
\]
The authors suggest that the intermediate (97) is initially formed, which, on ring opening, aldol condensation, transannular rearrangement and loss of water leads to the azulene (98).

Phosphoranes also give adducts with electron deficient compounds, \(^{105,106}\) e.g. diborane reacts with methylenetriphenylphosphorane to give \(\text{Ph}_3\text{P}^-\text{CH}_2^-\text{BH}_3\). These adducts are stable to water, but liberate hydrogen on treatment with dilute acid. Decaborane and boron trifluoride give similar salts.

(c) Reactions of Phosphorus Ylids not Proceeding via Intermediate Betaines.

Reactions of this type may be represented by:

\[
\text{R}_3\text{P} = \text{CHR} + \text{X} - \text{Y} \rightarrow \text{R}_3\text{P}^-\text{CHR}^-\text{X} + \text{Y}^-
\]

All phosphorus ylids are Lewis bases and as such will react with inorganic acids to give the corresponding phosphonium salt.

\[
\text{Ph}_3\text{P} = \text{CH}_2 + \text{HCl} \rightarrow \text{Ph}_3\text{P}^-\text{CH}_2^-\text{Cl}^-
\]

Bestmann \(^{107}\) has studied the stability of phosphoranes and shown that an equilibrium is established between a phosphorane and a phosphonium salt:
This reaction is known as transylidation (see p. 6) and the equilibrium lies towards the most stable, least basic, phosphorane.

Phosphorus ylids undergo hydrolysis, the least stable in cold water, the more stable in boiling water or alkali, to give the corresponding hydrocarbon of that group attached to the phosphorus which is most stable as an anion, and a phosphine oxide.

\[
\text{Ph}_3\text{P}^- + \text{H}_2\text{O} \rightarrow \text{Ph}_3\text{P} = \text{CHR}^+ + \text{R}^+ + \text{H}_2\text{O}^-
\]

Only cyclopentadienylidenetriphenylphosphorane is uneffected by treatment with hot alkali.

The alkylation of phosphoranes has already been discussed (p. 6). Work has also been carried out on systems where alkylation and Wittig elimination should be competing reactions. In most cases the Wittig reaction is more favourable. When 4-halomethylbenzaldehyde is reacted with substituted benzylidenetriphenylphosphoranes, substituted stilbenes are formed. \(^{108}\)
Similarly α-bromopropionaldehyde reacts with ethoxycarbonylmethylenetriphenylphosphorane to give the α,β-unsaturated ester (99) in 61% yield.

\[
\text{CH}_3\cdot\text{CHBrCHO} + \text{Ph}_3\text{P} = \text{CH} - \text{COOEt} \rightarrow \text{CH}_3\cdot\text{CHBrCHCH} = \text{CH} - \text{COOEt} + \text{Ph}_3\text{PO}
\]

Bestmann has carried out a series of reactions with α-bromoketones and methoxycarbonylmethylenetriphenylphosphorane. Ketones will not undergo Wittig reactions with stable phosphoranes under the conditions of the reaction and so the first stage is alkylation of the phosphorane to give the phosphonium salt (100). A second mole of phosphorane then removes a β-proton to give the betaine (101), which eliminates triphenylphosphine to give the olefin (102) in 60-80% yield.

\[
\text{R} - \text{CO} - \text{CH}_2\text{Br} + \text{Ph}_3\text{P} = \text{CH} - \text{COOCH}_3 \rightarrow \text{Ph}_3\text{P}^+\text{Br}^- \text{CH} - \text{CO} - \text{R}
\]

\[
\text{Ph}_3\text{P} + \text{RCOCH} = \text{CHCOOCH}_3 \leftarrow \text{Ph}_3\text{P}^+\text{CH} - \text{COOCH}_3
\]
Siemiatycki and Stryelecka have carried out the analogous reaction between phenacylbromide and phenacyldienetriphenylphosphorane. They found that as well as the expected olefin (1,2-dibenzylethylene) and phenacyltriphenylphosphonium bromide, a 7% yield of the cyclopropane (103) was formed.

\[
\text{Ph}_3\text{P} = \text{CHCOPh} + \text{PhCOCH}_2\text{Br} \rightarrow \text{PhCO.CH} = \text{CH.COPh}
\]

\[
\text{Ph}_3\text{P} - \text{CH}_2 - \text{COPh} + \text{Br}^-
\]

A possible explanation of the formation of the cyclopropane derivative is that the 1,2 dibenzylethylene first formed reacts with the original phosphorane to give the betaine (104). Electron shifts as shown will give the cyclopropane and triphenylphosphine, which would be expected to form the phenacylphosphonium salt with the phenacylbromide present in the reaction mixture.

\[
\text{Ph}_3\text{P} = \text{CHCOPh} + \text{PhCO.CH} = \text{CH.COPh}
\]

\[
\rightarrow \text{Ph}_3\text{P} \rightarrow \text{Ph}_3\text{P} \rightarrow \text{Ph}_3\text{P} + \text{PhCOCH} \rightarrow \text{CHCOPh}
\]
The normal reaction path for betaines of the type (104) is a 1,3 proton transfer to give the stable phosphorane (105) (See p. 54) however the cyclopropane is only produced in very low yield.

$$\text{Ph}_3\text{P} = \text{CR-CHR-CH}_2\text{R} \quad \text{R} = \text{-CO-Ph}$$  

(105)

An alternative explanation involves the production of the carbene PhCO-\text{CH}, possibly by the action of the phosphorane on phenacyl bromide, and attack of this on the 1,2-dibenzoyl-ethylene. Bestmann \(^{112}\) has shown that while bromoacetates give olefin and phosphine, as above, chloroacetates give the cyclopropane derivatives corresponding to (103), with phosphoranes.

Trippett \(^{59}\) has shown that 2-bromocyclohexanone reacts with the phosphorane (106) to give the triene (107).

\[ \text{Br} \text{PhCO} \quad \text{Ph}_3\text{P} = \text{CH-CH} \quad \text{C} \rightarrow \text{CH} \quad \text{Br} \text{PhCO} \]

(106)  

(107)
As yet no mechanism has been suggested for this reaction, but it is possible that the diene (108) is first formed by a normal Wittig reaction and this is then dehydrohalogenated by the phosphorane (106).

\[
\begin{align*}
\text{Ph}_3\text{P} &= \text{CHR} + \text{CHCl}_2\cdot\text{NMe}_2 \\
&\rightarrow \text{Ph}_3\text{P} = \text{CHR} \\
(109) &+ \text{CHCl} - \text{NMe}_2 \\
&\rightarrow \text{Ph}_3\text{P} = \text{CHR} \\
(110) &+ \text{Cl}^- \\
&\rightarrow \text{Ph}_3\text{P} = \text{CHR} \\
(111) &+ \text{CN} - \text{NMe}_2 \\
&\rightarrow \text{Ph}_3\text{P} = \text{CHR} \\
&+ \text{Ph}_3\text{P} - \text{CH}_2 - \text{R} \\
&+ \text{Cl}^- \\
&+ \text{Cl}^-
\end{align*}
\]

Markl has reacted phosphoranes with chloroamines of the type (109). The phosphonium salt (110) is initially formed, and undergoes dehydrohalogenation by the original phosphorane to give the enamine phosphonium salt (111).

These compounds can be used to produce a wide range of
phosphonium salts.

Seyferth et al. \textsuperscript{114} have shown that phosphoranes
will react with metallic, and organometallic, halides to give
substituted phosphonium salts of the type (112).

\[
\text{Ph}_3\text{P} = \text{CR}^2\text{R}^2 + \text{M} - \text{Br} \rightarrow \text{Ph}_3\text{P}^+ - \text{CR}^2\text{R}^2 - \text{M} - \text{Br}^-
\]

(112)

This occurs when \(\text{M} = \text{(CH}_3\text{)}_3\text{Si}^-, \text{Ph}_2\text{P}^-, \text{Ph}_3\text{Sn}^-, \text{and Ph}_3\text{Ge}^+. \text{\textsuperscript{114}}\)

When dihalides are used the reaction gives the
diphosphonium salts (113) for \(\text{M} = \text{Zn}^{++}, \text{Hg}^{++}, \text{and (CH}_3\text{)}_2\text{Sn}. \text{\textsuperscript{114}}\)

\[
\text{PhP}^{115} \text{ and (CH}_3\text{)}_2\text{Sn}. \text{\textsuperscript{114}}
\]

\[
\text{Ph}_3\text{P} = \text{CR}^2\text{R}^2 + \text{Br} - \text{M} - \text{Br} \rightarrow \text{Ph}_3\text{P}^+ - \text{CR}^2\text{R}^2 - \text{M} - \text{CR}^2\text{R}^2 - \text{PPh}_3
\]

\(2\text{Br}^-
\)

(113)

Stable phosphoranes react with halogens to give,
initially, the phosphonium salt (114), which then undergoes
transylidation to give the phosphorane (115). \textsuperscript{25,117,118}

\[
\text{Ph}_3\text{P} = \text{CH} - \text{COOCH}_3 + \text{X}_2 \rightarrow \text{Ph}_3\text{P}^+ - \text{CHX} - \text{COOCH}_3 \quad \text{X}^-
\]

(114)

\[
\text{Ph}_3\text{P} = \text{CX} - \text{COOCH}_3
\]

(115)
Halogenated phosphoranes are useful for the preparation of vinylhalides by a Wittig reaction. If excess halogen is used the phosphorane (115) reacts further to give the phosphonium salt

$$\text{Ph}_3\text{P}^+\text{CX}_2-\text{COOC}_3 \quad X^-$$

Diazonium salts will react with stable phosphoranes to give salts (116), which may be converted to highly coloured phosphoranes (117) by treatment with aqueous sodium hydroxide. 119

$$\text{Ph}_3\text{P} = \text{CHR} + \text{R}^i \rightarrow \text{Ph}_3\text{P}^+\text{CHR}=\text{N} \quad \text{X}^- \rightarrow \text{Ph}_3\text{P}^+\text{CHR}=\text{N}=\text{N} = \text{R}^i \quad \text{X}^-$$

(116)

$$\text{OH}^- \rightarrow \text{Ph}_3\text{P} = \text{CR}=\text{N}=\text{N} = \text{R}^i$$

(117)

However, when benzylidenetriphenylphosphorane was reacted with diazonium salts the salt (118) was produced.

$$\text{Ph}_3\text{P}^+\text{C}=\text{N}=\text{N} = \text{Ph} \quad \text{X}^-$$

(118)

Cyclopentadienylidenetriphenylphosphorane also behaves differently in that substitution takes place at the β-position to give the azo dye (119), with benzene diazonium
chloride in a sodium acetate buffer.\(^{120}\)

According to Saunders and Burchmann,\(^{121}\) phosphorus ylids can be reduced with lithium aluminium hydride to phosphines.

\[
\text{Ph}_3\text{P} = \text{CHR} + \text{LiAlH}_4 \rightarrow \text{OH}^- \rightarrow \text{Ph}_2\text{PCH}_2\text{R} + \text{PhH}
\]

Even \(\beta\)-ketophosphoranes can be reduced in this way without reduction of the carbonyl group.

Zinc and acetic acid appears to work differently, reducing \(\beta\)-ketophosphoranes to triphenylphosphine and a ketone.\(^{122,123}\) The reaction is thought to proceed by attack of zinc on the carbonyl group of the initially formed, transient, phosphonium acetate.
Attempts to extend this reaction to the preparation of $\beta$-keto esters have failed. $^{124}$
Activated multiple bonds are highly susceptible to nucleophilic attack. Various phosphorus containing nucleophiles have been used in this way, notably phosphines and phosphoranes.\textsuperscript{125} Johnson and Tebby\textsuperscript{126} have shown that phosphines react readily with a variety of unsaturated compounds, with initial formation of the Michael addition products. Triphenylphosphine reacted with the diester of acetylene-dicarboxylic acid to give (120), which then reacted with a further molecule of acetylene to give the 1,5-dipole (121), which was isolated as its hydroiodide.

\[
\begin{align*}
\text{Ph}_3\text{P} + & \quad \text{COOR} \quad \text{Ph}_3\text{P}^+ \quad \text{COOR} \quad \text{Ph}_3\text{P}^+ \quad \text{COOR} \\
& \quad \text{COOR} \quad \text{COOR} \quad \text{COOR} \quad \text{COOR} \\
\quad \text{COOR} & \quad \text{COOR} \quad \text{COOR} \quad \text{COOR} \quad \text{COOR} \\
\quad \text{(120)} & \quad \text{(121)}
\end{align*}
\]

Oda\textsuperscript{27} and Hoffmann\textsuperscript{28} have shown that phosphines react readily with activated double bonds, again initially forming the Michael addition precursor, analogous to (120.)
In the reactions of phosphoranes with activated olefins, three possible paths have been suggested, all of which initially involve Michael addition of the phosphorane carbanion to the double bond to give (122).

\[
R_3P = CHR^4 + R^2R^3C = CR^4R^5 \rightarrow R_3P^+ - CHR^4 - CR^3R^3 - CR^4R^5
\]

(122)

This can then react further by;

(a) a proton shift from the \(\alpha\)-carbon to the \(\gamma\)-carbon to give the phosphorane (123)

\[
R_3P = CR^4 - CR^3R^3 - CHR^4R^5
\]

(123)

(b) ring closure and elimination of phosphine to give the cyclopropane (124),

\[
\begin{align*}
R_3P & \xrightarrow{\text{CHR}^4} CR^4R^6 & \xrightarrow{\text{CHR}^3} CR^2R^3 & \rightarrow R_3P + CR^4R^5 \xrightarrow{\text{CHR}} CR^2R^3
\end{align*}
\]

(124)

and (c) if \(R^a\) can form a stable anion, the loss of \((R^a)^-\) and formation of (125) which loses a proton to give the phosphorane (126).
All these paths have been observed.

These three types of reaction also apply when phosphoranes react with activated acetylenes. However, in these cases there is the possibility of a further type of reaction involving the four membered transition state (127) and leading to the phosphorane (128).

\[
\begin{align*}
\text{R}_3\text{P} = \text{CHR}^4 & + X - C\equiv C - X \rightarrow \text{R}_3\text{P} + \text{CHR}^4 \\
\text{R}_3\text{P} & = CX - CX = \text{CHR}'
\end{align*}
\]

(127)

(128)

Trippett\textsuperscript{127} and Hendrickson\textsuperscript{129} have both carried out reactions of phosphoranes of the type (129) with dimethylacetylenedicarboxylate.

\[
\text{R}_3\text{P} = \text{CHR}^4
\]

(129)
Hendrickson found that phenacylidnetriphenylphosphorane (129; \( R = \text{Ph}; R^4 = -\text{CO}^-\text{Ph} \)) gave an adduct, for which he suggested the structure (130).

\[
\begin{align*}
\text{Ph} & \quad \text{O} \quad \text{COOCH}_3 \\
\text{P} & \quad \text{COOCH}_3 \\
\text{R}_3 & \quad \text{R}_3
\end{align*}
\]

(130)

He also showed that on pyrolysis the adduct gave an acetylene of structure (131).

\[
\begin{align*}
\text{Ph} & \quad \text{C} = \text{C} - \text{C} = \text{CH} \\
/ & \quad \text{CH}_3\text{COOC} \\
\text{COOCH}_3 & \quad \text{COOCH}_3
\end{align*}
\]

(131)

The acetylene synthesis of Trippett and Gough\(^8\) involving phosphobetaines of the type (132) has already been discussed (See p. 3). Application of these results to Hendrickson's

\[
\begin{align*}
\text{R}_3\text{P} & \quad \text{R}_4 \\
\text{O} & \quad \text{R}_2
\end{align*}
\]

(132)

compound suggest a structure (133),\(^8\) which would presumably
give the acetylene (131) on pyrolysis.

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{COOMe} \\
\text{C} & \quad \text{O} = \text{CH} - \text{COOMe} \\
\text{O} & \quad \text{Ph}
\end{align*}
\]

(133)

This adduct would be formed by a path analogous to (a) above. Trippett \(^{127}\) obtained similar adducts with other phosphoranes and dimethylacetylenedicarboxylate and suggested analogous structures for them all. In a later publication Hendrickson \(^{130}\) also suggests these structures.

Paths (a), (b) and (c) above have all been observed, but the fourth suggested path, which can only work for the acetylene case, had not. However, Huebner and Dorfmann, \(^{131}\) and a number of other workers, \(^{132},^{133},^{134}\) have shown that the addition of both activated and non-activated acetylenes to enamines involved a cyclobutene intermediate (134), which could even be isolated in certain cases. This can be readily seen to be analogous to the fourth possible reaction path in the phosphorane case.
This reaction has been used to expand Ring A of the steroidal nucleus. \(^{134}\)

To increase the possibility of the fourth reaction path the other reaction paths were made impossible or, at least, difficult.

The possibility of path (a) was easily removed by substitution of the \(\alpha\)-hydrogen by alkyl in the phosphorane. Elimination of path (b) was far more difficult, although Bestmann \(^{128}\) suggests that path (b) becomes less likely if the phosphorane has electron withdrawing groups on the \(\alpha\)-carbon atom. Fortunately, path (b), which would lead to a cyclopropane derivative, appears unimportant in the acetylene case. Path (c) cannot operate because no group which can form a stable anion is present.

Three phosphoranes were reacted with dimethyl acetylenedicarboxylate, \(\alpha\)-ethoxycarbonylthylidenetriphenylphosphorane (135), \(\alpha\)-benzoylthylidenetriphenylphosphorane (136) and \(\alpha\)-cyanoethylidenetriphenylphosphorane (137).

\[
\begin{align*}
\text{Me} & \quad \text{Me} & \quad \text{Me} \\
\text{Ph}_3\text{P} = \text{C} - \text{COOEt} & \quad \text{Ph}_3\text{P} = \text{C} - \text{CO} - \text{Ph} & \quad \text{Ph}_3\text{P} = \text{C} - \text{CN} \\
(135) & \quad (136) & \quad (137)
\end{align*}
\]

It was originally intended that the methyl ester
would be used in place of (135). However, although the phosphonium salt from methyl α-bromopropionate and triphenylphosphine was readily prepared, all attempts to form the phosphorane from this led to decarboxylation and the formation of the ethyltriphenylphosphonium salt. The phosphonium salt of the ethyl ester, however, readily formed the corresponding phosphorane on treatment with one equivalent of aqueous sodium hydroxide at 0°C. A possible explanation of this involves the case of hydrolysis of the ester groups. Considerable previous work ¹³⁵,¹³⁶,¹³⁷ has demonstrated the instability of phosphonium salts containing an α-carboxylate anion. If this anion is produced, by the hydrolysis of the ester group being faster than the formation of the phosphorane, decarboxylation will rapidly take place. This appears to be the case with the methyl ester, while the ethyl ester presumably loses an α-proton more rapidly. These results are in agreement with the general reactivity of esters towards hydrolysis.

The phosphoranes (135), (136) and (137) all reacted with dimethylacetylenedicarboxylate to give, after chromatography, pale yellow, crystalline adducts.

The N.M.R. spectra of these adducts were taken.
The compound from α-benzylethylidenetriphenylphosphorane and the acetylene gave a spectrum which could be explained on the basis of compound (138; R = −CO−Ph), which would be the expected product from a rearrangement analogous to (127). A doublet at 7.8\(\tau\)(\(J_p=3\) c.p.s.) due to the terminal methyl, a singlet at 7.2\(\tau\) due to one ester methyl, and the other ester methyl at 6.5\(\tau\) (a diffuse singlet), could be distinguished.

However, when the spectrum of the adduct from α-cyanoethylidenetriphenylphosphorane was studied, it appeared that a mixture of two compounds was present. The first, present in 60\%, had a doublet at 8.0\(\tau\), \(J_p=3\) c.p.s., and two singlets, one at 6.6\(\tau\) and the other at 6.7\(\tau\). The second, present in 50\%, had a similar spectrum, but the doublet was at 8.3\(\tau\), \(J_p=4\) c.p.s., and the two singlets at 6.5\(\tau\) and 6.65\(\tau\) respectively. This could possibly be explained by geometrical isomerization across the C−C double bond in (138; R = −CN), the doublets at 8.0\(\tau\) and 8.3\(\tau\)
being due to the terminal methyls in the two isomers and the singlets at 6.6γ and 6.7γ, and 6.5γ and 6.65γ, to the ester methyl groups.

The case of the adduct from α-ethoxycarbonyl-ethyldenetriphenylphosphorane (138; R = -COOEt) a mixture of compounds again appeared to be present, although one predominated (> 90%). One isomer had a singlet at 6.5γ due to the two ester methyl groups, while this was at 6.6γ in the other isomer. The terminal methyl showed as a doublet, at 8.1γ (Jp = 4 c.p.s.) in one isomer, and at 8.2γ (Jp = 4 c.p.s.) in the other.

The proportions of the isomers present in each case is further evidence for geometrical forms being present. The phenacyl case (138; R = -COPh) was a pure compound, and while the ester phosphorane adduct (138; R = -COOEt) was a 9:1 mixture, the nitrile phosphorane adduct (138; R = -CN) was a 3:2 mixture. As the size of R decreases in this order the effect appears to be steric, and may be due to the large phosphorus-containing substituent at the double bond allowing the R group to become cis to it in the case of R = -CN, and to a lesser extent when R = -COOEt.

By repeated recrystallisation pure samples of the major isomer of each adduct were prepared. However, when these
samples were treated with perchloric acid, the N.M.R. spectra of the salts produced showed them also to be mixtures. Assuming that the adducts are of the form (138), protonation could take place in two ways, at the α-carbon, to give the perchlorate (139), or at the γ-carbon, to give (140).

\[
\begin{align*}
\text{COOMe} & \quad \text{α protonation} \\
\text{Ph}_3\text{P} & \quad \text{CH} = \text{C} \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
\text{COOMe} & \quad \text{γ-protonation} \\
\text{ClO}_4^- & \quad \text{Ph}_3\text{P} \quad \text{CH} = \text{C} \quad \text{CH}_3
\end{align*}
\]

There are several recorded examples of electrophilic attack at the γ-carbon in allylic phosphoranes. Bestmann has shown that treatment of the allylic phosphorane (141) with chlorocarbamates \(^{23}\) leads to a γ-substituted product, as does treatment with tritiated water. \(^{26}\)

\[
\begin{align*}
\text{Ph}_3\text{P} & \quad \text{CH} = \text{CH} = \text{CH}_2 \quad \text{T} \quad \text{Cl} \quad \text{COOMe}
\end{align*}
\]

Treatment of the perchlorate mixtures with aqueous sodium hydroxide gave back the original adducts,
however, they again appeared to be mixtures of geometrical isomers, even though pure samples were used in the preparation of the salts.

In the hope of obtaining further information from N.M.R. spectra attempts were made to hydrogenate the perchlorates of the adducts. Adam's catalyst, palladium on charcoal, platinum on charcoal, and Raney Nickel were all tried under various conditions with a singular lack of success. A control experiment showed that it was impossible to hydrogenate cinnamic acid in the presence of phosphonium salt, presumably because the salt poisoned the catalyst in some way. Since our work, Hendrickson has succeeded in hydrogenating the adducts themselves.

Attempts to methylate the adducts using methyl iodide were unsuccessful, the adduct being reobtained in high yield.

Although the adducts were only reobtained in low yield from attempted acid hydrolysis reactions using concentrated hydrochloric acid, no other crystalline product was isolated. However, treatment of the mother liquors of these reactions with dilute alkali gave a further small amount of adduct, showing that some conversion of the adduct to its salt had taken place.
The adducts reacted readily with bromine to give compounds which could not be satisfactorily purified.

Degradation of the adducts was found to be difficult, prolonged refluxing with concentrated alkali being necessary. The adduct from \( \alpha \)-benzylethylidenetriphenylphosphorane (138; \( R = -\text{COPh} \)) was degraded both because it was easiest to purify and contained a phenacyl group, which is stable to hydrolysis. The products were triphenylphosphine oxide, in high yield, a crystalline acid in very low yield and traces of propiophenone and a compound which had an infrared spectrum similar to that of fumaric acid.

The ultraviolet spectrum of the crystalline acid showed a definite similarity to that of \( \beta \)-benzoylacrylic acid (142).

\[
\text{Ph} - \text{CO} - \text{CH} = \text{CH} - \text{COOH}
\]

The compound analysed for \( C_{12}H_{12}O_3 \) and showed two carbonyl groups (one of which appeared to be due to a carboxylic acid), a double bond and a mono-substituted benzene ring, in the infrared. On hydrogenation the compound took up 1.7 moles of hydrogen per mole and titration with alkali gave an equivalent weight of 194 ± 10.
The mass spectrum of the acid showed what appeared to be a mass peak at m/e = 193, and strong peaks at m/e = 77 (phenyl) and m/e = 105 (Benzoyl).

This evidence points to two possible structures for the acid, (143) and (144), one of which (144), could have been formed by decarboxylation of the original hydrolysis product of the adduct.

Attempts to carry out the N.M.R. spectrum of the sodium salt of this acid in deuterium oxide led to deuterium exchange, although the individual ortho, meta and para protons of the monosubstituted benzene ring could be picked out. The acid was not very soluble in deuterochloroform, but spectra were obtained at 50°C. The quality was poor, but a doublet, due to a methyl group, at 8.37 (J_H = 7 c.p.s.) and a multiplet, probably due to a -CH2-, at 6.17 could be distinguished. The peak at 6.17 integrating for two hydrogens and the splitting of 7 c.p.s. of the methyl group suggest that structure (143) is the
correct one.

Since this work has been carried out a considerable amount has been published on adducts of this type,¹³⁸,¹³⁹ adducts of iminophosphoranes with acetylenedicarboxylate¹⁴⁰ (which appear to be analogous) and adducts of phosphoranes with benzyne.¹⁴¹ The evidence from this work is that phosphoranes without α-hydrogens, and phosphaimines, react with dimethylacetylenedicarboxylate via a four membered transition state leading to phosphoranes of the type (145).

\[
\begin{align*}
\text{Ph}_3\text{P} & = \text{C} \quad \text{R}^1 \quad + \quad \begin{array}{c} \text{COOMe} \\ \text{COOMe} \end{array} \\
\text{Ph}_3\text{P} & = \text{C} - \text{C} = \text{CR}^2\text{R}^3 \\
\text{COOMe} & \quad \text{COOMe}
\end{align*}
\]

(145)

Zbiral suggests that the first stage in the reaction of phosphoranes with benzyne is identical with that above, attack of the ylid carbanion at one end of the benzyne
"triple" bond to give the betaine (146). This carbanion then attacks one of the phenyl groups on the phosphorus to give the phosphine (147).

\[
\text{Ph}_3\text{P} = \text{CH} - \text{Ph} + \text{Ph}_3\text{P} = \text{CH} - \text{Ph} \quad \rightarrow \quad \text{Ph}_2\text{P} - \text{CH} - \text{Ph}
\]

(146)

This rearrangement is analogous to that in the reaction of triphenylphosphine with dimethyl acetylenedicarboxylate (See p. 53), where the initially formed 1,5-dipole can rearrange to give (148) by the attack of the carbanion as a phenyl group.
McEwen has studied the reaction of benzonitrile with phosphoranes. In the case of benzylidene triphenylphosphorane the products, (after alkaline hydrolysis) were deoxybenzoin and phosphine oxide. The following reaction path has been suggested.
It seemed possible that by replacing the α-hydrogen atom in the original phosphorane by an alkyl group, which cannot easily migrate, a rearrangement analogous to that above might be forced to take place to give (150).

\[
\text{Ph}_3\text{P} = \text{CR}_2 + \text{PhCN} \rightarrow \text{Ph}_3\text{P} = \overset{\hat{}}{\text{C}} \quad (149)
\]

\[
\rightarrow \text{Ph}_3\text{P} = \overset{\hat{}}{\text{N}} = \overset{\hat{}}{\text{C}} = \overset{\hat{}}{\text{C}} \quad (150)
\]
However, when isopropylidenetriphenylphosphorane was reacted with benzonitrile, although a vigorous reaction took place, no crystalline compounds could be isolated. Alkaline hydrolysis of the reaction mixture gave triphenylphosphine oxide and isopropylphenyl ketone. This ketone could have been formed by hydrolysis of either the intermediate (149) or the rearranged product (150).
Experimental

All experiments using phosphoranes, and similar unstable compounds, were carried out under an oxygen-free nitrogen atmosphere. All solvents were dried before use. Melting points were corrected.

Attempted preparation of α-Methoxycarbonyl ethylidene-triphenylphosphorane. - α-Methoxycarbonyl ethyltriphenylphosphonium iodide $^{143}$ (9.5 g.) was dissolved in ethanol-water (1:1) (80 ml.) and one equivalent of sodium hydroxide ($\text{IN}$; 20 ml.) added slowly with stirring. The solution remained clear and was extracted with chloroform. The chloroform solution was dried and evaporated to give ethyltriphenylphosphonium iodide (5.8 g.), m.p. and mixed m.p. (from chloroform-ethyl acetate) 166-167°.

Preparation of Cyanomethylenetriphenylphosphorane.$^{89}$ - The phosphonium salt $^{89}$ (15.7 g.) was dissolved in water (300 ml.) and one equivalent of aqueous sodium hydroxide ($\text{IN}$; 47 ml.) was added slowly at 0° with stirring. The solid precipitate was filtered and washed with water until the washings were neutral. Thorough drying and recrystallisation from ethyl
acetate gave the phosphorane (10.4 g.), m.p. (from ethyl acetate) 195-196° (lit. [89] 195-196°).

Preparation of α-Cyanoethyltriphenylphosphonium Iodide. - Cyanomethylenetriphenylphosphorane (12 g.) and methyl iodide (25 g.) were heated together, without solvent, at 100° for 16 hours. The reaction mixture was triturated with benzene (5 x 50 ml.). The benzene-insoluble oil crystallised from ethanol-water (12 g.), m.p. (from ethanol-water) 120-122°. [Found: C, 54.3; H, 4.3; Calc. for C_{21}H_{19}NI: C, 56.80; H, 4.3, Calc. for C_{21}H_{19}NI. HgO: C, 54.6; H, 4.8%].

Preparation of α-Cyanoethylidenetriphenylphosphorane. - The phosphonium iodide (7 g.) was dissolved in chloroform (60 ml.) and cooled to 0°. This solution was shaken in a separatory funnel with an ice-cold solution of sodium hydroxide (0.25 g.) in water (50 ml.) for one minute. The chloroform layer was separated, washed with water (4 x 30 ml.), dried and evaporated to give the phosphorane (4.1 g.), m.p. (from ethyl acetate-petrol) 173-174° [Found: C, 76.6, H, 5.7; N, 3.52%; Calc. for C_{21}H_{19}NP: C, 80.0; H, 5.76; N, 4.45%].
Preparation of α-Ethoxycarbonyl ethyltriphenylphosphonium Bromide. Ethyl α-bromopropionate (52 g.) and triphenylphosphine (75 g.) were dissolved in benzene (400 ml.) and refluxed together for 7 hours. The oil which separated was decanted off and triturated with ethyl acetate to give the phosphonium salt (89 g.) m.p. (from chloroform-ethyl acetate) 199-201° (lit. 199-200°).

Preparation of α-Ethoxycarbonyl ethyldienetriphenylphosphorane. The phosphonium salt (22 g.) was dissolved in ethanol-water (1:1, 200 ml.) and cooled to 0°. One equivalent of aqueous sodium hydroxide (1N; 50 ml.) was slowly added with stirring. The oil which separated crystallised on trituration (13 g.), m.p. (from ethyl acetate) 157-159° (lit. 156-157°).

Preparation of α-Methylphenacyltriphenylphosphonium Bromide. α-Bromopropiophenone (32 g.) and triphenylphosphine (40 g.) were refluxed together in benzene (200 ml.) for 16 hours. The oil which separated crystallised (62 g.) on trituration with ethyl acetate, m.p. and mixed m.p. (from chloroform-ethylacetate) 242-243°.
Preparation of α-Methylphenacylidene triphenylphosphorane. - The phosphonium salt (25 g.) was dissolved in ethanol-water (1:1; 300 ml.). One equivalent of aqueous sodium hydroxide (1N; 53 ml.) was added slowly with stirring. The precipitate was filtered, washed with water and dried (20 g.), m.p. and mixed m.p. (from ethyl acetate) 161-163°.

Reaction of Dimethyl Acetylenedicarboxylate with α-Ethoxycarbonylethylidene triphenylphosphorane. - The phosphorane (12 g.), in ethyl acetate (150 ml.), was added to a solution of the diester (5 g.) in ethyl acetate (50 ml.). The deep red reaction mixture was refluxed for 3 hours. Evaporation and chromatography on Woelm neutral alumina using benzene as the eluent gave yellow crystals (5 g.) m.p. [from light petroleum (b.p. 100-120°)] 137-138° (Found: C, 68.90; H, 5.90; P, 6.30; Calc. for a 1:1 adduct C₂₉H₂₇PO₆: C, 69.0; H, 5.75; P, 6.1%).

Preparation of the Perchlorate of this Adduct. - The adduct (1.2 g.) was dissolved in methanol (10 ml.) and an aqueous solution of perchloric acid (70%) added dropwise until the original yellow colour of the solution was discharged.
Addition of water to turbidity gave crystals (0.9 g.),
m.p. (methanol–water) 179-181° (Found: C, 56.0; H, 5.00; P, 5.39; Calc. for C$_{29}$H$_{30}$ClFe$_{10}$: C, 57.60; H, 4.97; P, 5.13%).

Reaction of α-Cyanoethylidenetriphenylphosphorane with
Dimethyl Acetylenedicarboxylate. - The phosphorane (11g.), in chloroform (120 ml.), was added to a solution of the diester (5 g.) in chloroform (20 ml.). The reaction mixture was refluxed for 3 hours. Evaporation and chromatography on Woelm neutral alumina, using benzene as the eluent, gave yellow crystals (4 g.) m.p. [from carbon tetrachloride–light petroleum (b.p. 60-80°)] 149-151° (Found: C, 70.80; H, 5.22; P, 7.01; Calc. for a 1:1 adduct C$_{27}$H$_{24}$PO$_{4}$: C, 70.9; H, 5.25; P, 6.78%).

Preparation of the Perchlorate of this Adduct. - The adduct (2 g.) was dissolved in methanol (10 ml.) and an aqueous solution of perchloric acid (70%) was added dropwise until the original yellow colour of the solution was discharged. Addition of water to turbidity gave crystals (1.7 g.), m.p. (from methanol–water) 184-185° (Found: C, 57.5; H, 4.39; P, 5.56; Calc. for C$_{27}$H$_{25}$ClNPO$_{6}$: C, 58.1; H, 4.48; P, 5.5%).
Reaction of α-Methylphenacyldenetriphenylphosphorane with Dimethyl Acetylenedicarboxylate. - The phosphorane (8 g.), in ethyl acetate (100 ml.), was added to a solution of the diester (3 g.) in ethyl acetate (30 ml.). The reaction mixture was refluxed for 3 hours. Evaporation and chromatography on Woelm neutral alumina, using benzene as the eluent, gave yellow crystals (8.4 g.) m.p. (from carbon tetrachloride-petrol) 191-192° (Found: C, 73.79; H, 5.08; Calc. for a 1:1 adduct C_{33}H_{29}O_6P: C, 73.80; H, 5.40%).

Preparation of the Perchlorate of this Adduct. - The adduct (1 g.) was dissolved in methanol (8 ml.) and an aqueous solution of perchloric acid (70%) was added dropwise until the solution became colourless. Addition of water gave crystals (0.6 g.) m.p. (from methanol-water) 202-204°.

Attempted Methylation of the Adduct from α-Cyanoethylidene-triphenylphosphorane and Dimethyl Acetylenedicarboxylate. - (a) The adduct (0.8 g.), in benzene (10 ml.), and methyl iodide (5 ml.) were refluxed together for 20 hours. Evaporation gave the adduct (0.6 g.). (b) The adduct (0.5 g.), and methyl iodide (4 ml.), were heated together on a steam bath for 2 days. Evaporation gave the adduct (0.3 g.)
Similar results were obtained from analogous experiments with the adducts from α-methylphenacylidene-triphenylphosphorane and α-ethoxycarbonylethylene-triphenylphosphorane.

Reaction of the Adduct from α-Methylphenacylidenedetriphenylphosphorane and Dimethyl Acetylenedicarboxylate with Hydrochloric Acid. — The adduct (1 g.) and concentrated hydrochloric acid (2 ml.) were heated in a steam bath for 12 hours. Water (5 ml.) was added and the solution filtered. Extraction of this solution with ethyl acetate gave a small amount of oil. Addition of aqueous sodium hydroxide solution (2N.) to the aqueous extract until alkaline gave the original adduct (0.1 g.), m.p. and mixed m.p. 191-192°.

Similar experiments with other adducts gave analogous results.

Reactions of the Adducts with Bromine. — All the adducts reacted with bromine. A typical experiment was: the adduct (0.8 g.), in benzene (10 ml.), was slowly added to a solution of bromine (0.28 g.) in benzene (5 ml.) and the mixture warmed for 5 minutes. The oil which separated
was tritutrated with ethyl acetate to give a solid which could not be satisfactorily purified.

Alkaline Hydrolysis of the Adduct from α-Methylphenacylidene-triphenylphosphorane and Dimethyl Acetylenedicarboxylate. - The adduct (2 g.), in methanol (25 ml.), was added to a solution of sodium hydroxide (2 g.) in water (10 ml.). The solution was refluxed for 60 hours, cooled and water (30 ml.) added. The solid was filtered off (0.8 g.) m.p. and mixed m.p. 157-158°, with an infrared spectrum identical with that of triphenylphosphine oxide. The filtrate was extracted with ether (3 x 20 ml.), and the ether extract on g.l.c. (6 m. apiezon L column at 220°) showed propiophenone (1%). Evaporation of the ether extract gave a small quantity of oil (10 mg.) which had $\lambda_{\text{max}}$ 5.98 $\mu$. The alkaline extract was then made acid to Congo Red and the resulting suspension extracted with ether (4 x 30 ml.). The ether solution was dried (MgSO$_4$) and evaporated to give an oil. The oil crystallised from methanol-water (38 mg.) m.p. 141-142°, $\lambda_{\text{max}}$ 5.88, 5.98, 8.0, 8.25, 13.25, 14.6$\mu$. (Found: C, 70.51; H, 6.02; Calc. for C$_{12}$H$_{12}$O$_3$: C, 70.60; H, 5.88%).
Hydrogenation of Acid from Hydrolysis of Phenacyl Adduct. - The acid (7 mg.), in ethanol (3 ml.) was hydrogenated using palladium on charcoal (3 mg.) as catalyst. The uptake after 10 minutes was 1.2 ml. of hydrogen. Theoretical uptake for one mole of hydrogen per mole, 0.70 ml.

Determination of the Equivalent Weight of the Acidic Hydrolysis Product by Alkali Titration. - The acid (5.9 mg.) was dissolved in water (5 ml.) and the resulting solution titrated with aqueous sodium hydroxide solution (N/100) using phenolphthalein as the indicator.

5.9 mg. of acid was equivalent to 3.05 ml. of N/100 sodium hydroxide solution, giving an equivalent weight of 194. This titration was repeated using similar conditions and tabulating the p.H. of the solution (See Table I).
Table I

<table>
<thead>
<tr>
<th>Titre (ml.)</th>
<th>p.H.</th>
<th>Titre (ml.)</th>
<th>p.H.</th>
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<td>3.10</td>
<td>7.40</td>
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<td>0.50</td>
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<td>3.20</td>
<td>8.40</td>
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<tr>
<td>3.00</td>
<td>6.70</td>
<td>6.00</td>
<td>10.05</td>
</tr>
</tbody>
</table>

Reaction of Isopropylidenetriphenylphosphorane with Benzonitrile. - (a) Isopropyltriphenylphosphonium iodide (15 g.), suspended in ether (200 ml.), was stirred and LiBu in ether (1N; 35 ml.) was added. The solution was stirred for 1 hour at room temperature. To this solution benzonitrile (10 ml.), in ether (20 ml.), was slowly added, the solution turning from deep red to black, and stirring continued at room temperature for 16 hours. The solution was evaporated, dissolved in chloroform (150 ml.), washed with water (3 x 60 ml.) and dried. Evaporation gave an oil which crystallised on trituration with light petroleum.
(b.p. 40-60°) to give triphenylphosphine oxide (1.3 g.) m.p. and mixed m.p. 157-158°.

(b) To a solution of isopropylidenetriphenylphosphorane, from the phosphonium iodide (15 g.) and BuLi (1N; 35 ml), was slowly added a solution of benzonitrile (10 ml.) in ether (20 ml.). The resulting solution was stirred for 20 hours at room temperature. To this solution methyl iodide (2 ml.), in ether (10 ml.), was added and the reaction mixture refluxed for 4 hours. The solution was evaporated, dissolved in chloroform (200 ml.) and washed with water (3 x 70 ml.). Drying (MgSO₄) and evaporation gave an oil which crystallised on trituration with ethyl acetate to give t-butyltriphenylphosphonium iodide (2.3 g.) m.p. and mixed m.p. (from chloroform-ethyl acetate) 204-206° (d).

(c) To a solution of isopropylidenetriphenylphosphorane, from the phosphonium iodide (8.6 g.) and BuLi (1N; 20 ml.), was slowly added a solution of benzonitrile (8 ml.) in ether (20 ml.) and the resulting solution refluxed for 5 hours. The ether was distilled off and sodium hydroxide (10 g.) in methanol-water (9:1; 100 ml.) added. The solution was refluxed for 1 hour, cooled and evaporated. The
residue was extracted with light petroleum (40-60° b.p.) (5 x 50 ml.). The petrol extract was dried (MgSO₄) and distilled to give three fractions (a) b.p. 100-120°, (b) 122-144° and (c) 144-180°. These fractions were chromatographed on preparative g.l.c. (20 ft. Silicon oil column at 180°). Three pure compounds were isolated (a) dimethyl-n-butylicarbinol (0.7 g.), (b) isopropyl phenyl ketone (0.7 g.) and (c) n-butyl phenyl ketone (1.4 g.) all having infrared spectra identical to that of authentic samples.
Some Reactions of Phosphorus-Containing Betaines in Wittig Reactions

The Mechanism of the Wittig Reaction

Although the reaction of phosphoranes with aldehydes and ketones was discovered by Staudinger and Meyer in 1919, it was not until 1953 that Wittig developed it into a general method of olefin synthesis.

The scope and limitations of the synthesis have been discussed in a large number of papers and reviews and recently more attention has been directed to the mechanism of the reaction.

The suggestion that the reaction proceeded via an intermediate of the type (151), or its covalent equivalent (152), was put forward by Wittig in his earliest publications. He supported this theory with the isolation of 2-hydroxy-2,2-diphenylethyltriphenylphosphonium iodide (153).
from the reaction mixture of methylenetriphenylphosphorane and benzophenone after quenching with hydriodic acid.

\[
\begin{align*}
\text{Ph}_3\text{P} & \xrightarrow{\cdot} \text{Ph}_3\text{P} - \text{CH}_2 \xrightarrow{\text{HI}} \text{Ph}_3\text{P} - \text{CH}_2
\end{align*}
\]

The same type of betaine intermediate (151) was also postulated in the reaction of triphenylphosphine with styrene oxide to give styrene and triphenylphosphine oxide.

\[
\begin{align*}
\text{Ph}_3\text{P} & \xrightarrow{\cdot} \text{Ph}_3\text{P} - \text{CH}_2 \xrightarrow{\text{HI}} \text{Ph}_3\text{P} - \text{CH}_2
\end{align*}
\]

If the above formulation is correct we have two possibilities for the rate determining step, betaine formation or betaine decomposition.

In betaine formation, assuming that this involves nucleophilic attack of the \(\alpha\)-carbanion of the phosphorane on the carbonyl group, the rate will depend on both the nucleophilicity of the \(\alpha\)-carbon and the reactivity displayed...
towards nucleophiles by the carbonyl group.

Substituents on the α-carbon which can delocalise the negative charge will decrease the reactivity of the phosphorane, while electron-donating substituents on the phosphorus will increase the reactivity of the phosphorane, by stabilising the dipolar form.

Betaine decomposition is usually assumed to proceed via a four-membered cyclic transition state, although there is no real evidence for this. Any electron-donating group on the phosphorus will decrease its positive charge and thus hinder the decomposition, in fact when the phosphorus has three p-methoxyphenyl substituents elimination will not take place and the betaine is stable. On the other hand any substituents on the carbon atoms of the betaine which can conjugate with the double bond to be formed will help the elimination step; thus intermediate betaines have never been isolated when stable phosphoranes of the type (154) have been used.

\[ \text{R}_3\text{P} = \text{CH} - \text{CO} - \text{R} \]

(154)

The stereochemistry, of the olefins resulting from a Wittig reaction, is determined by the stereochemistry of
the intermediate betaines. In the reaction of the phosphorane (155; $R^2 \neq H$) and the aldehyde (156) we have the possibility of two stereoisomeric betaines (157) and (158), which lead to cis and trans-olefins respectively after the elimination step.

If the betaine formation step is slow, then (158) is the predominant isomer and the olefin formed is mainly trans, while a fast betaine forming step produces a more nearly equal mixture of (157) and (158), and consequent amounts of cis and trans-olefins.
Thus stable phosphoranes give mainly trans olefins when reacted with aldehydes, while p-nitrobenzaldehyde and p-methoxybenzylidenetriphenylphosphorane, a reactive aldehyde and phosphorane, give a mixture of cis and trans-stilbenes. However, anisaldehyde and p-nitrobenzylidenetriphenylphosphorane, where both the aldehyde and phosphorane are deactivated by the substituents, react slowly to give mainly the trans-stilbene.

Reactions of Intermediate Betaines in the Wittig Reaction other than Olefin Formation.

Since the suggestion of a betaine intermediate leading to olefins in the Wittig reaction, a number of other reactions of the betaine have been postulated.

Results obtained from a variety of Wittig reactions had usually been rationalised by the assumption that the betaine-formation step was reversible. However, it was not until 1963 that evidence for this was reported. Speziale and Bissing allowed ethyl trans-phenylglycidate and tributylphosphine to react, in the presence of m-chlorobenzaldehyde, and obtained both ethyl cinnamate and ethyl
m-chlorocinnamate. They assumed that the betaine (159) was the intermediate, and that it could eliminate phosphine oxide (the normal Wittig path) to give cinnamate, or dissociate to benzaldehyde and phosphorane which could then react with the more reactive m-chlorobenzaldehyde. Betaine reversibility has since been demonstrated in the case of unstable phosphoranes.\(^{150}\)

\[
\begin{align*}
Bu_3P &\quad + \quad Ph-CH-CH-COOEt &\rightarrow &\quad Bu_3P-CHCOOEt \\
&\quad + \quad PhCHO &\rightarrow &\quad Bu_3PO + Ph-CH=CH-COOEt \\
&\quad + \quad m-ClC_6H_4-CH=CH-COOEt
\end{align*}
\]

The corresponding reactions of cis and trans-but-2-ene epoxides with tributylphosphine\(^^{151}\) do not appear to be completely stereospecific, the trans-epoxide gives 72% cis and 28% trans-butene, and the cis-epoxide gives
81\% \textit{trans} and 19\% \textit{cis}-butene. Thus it seems likely that betaine reversibility is taking part to give the unexpected stereoisomer.

A further example of betaine reversibility is to be found in the reaction between diphenylphosphine and styrene oxide.\textsuperscript{162} The products from this reaction are extremely dependent upon the conditions, but at 140°, without solvent, benzaldehyde and methyldiphenylphosphine oxide are formed together with other products. Presumably the reaction proceeds \textit{via} the betaine (160) (further evidence for this assumption is given below; p.\textsuperscript{164}) dissociation and rearrangement giving benzaldehyde and methyldiphenylphosphine.

\[
\begin{align*}
\text{Ph}_2\text{PH} + \text{Ph}-\text{CH}-\text{CH}_2 & \rightarrow \text{Ph}_2\text{P} \underset{\text{CHPh}}{\overset{\text{H}}{\longrightarrow}} \text{PhCHO} \\
& \quad \downarrow \quad \text{Ph}_2\text{P} \underset{\text{CH}_2}{\overset{\text{H}}{\longrightarrow}} \\
& \quad \text{Ph}_2\text{P}-\text{CH}_3
\end{align*}
\]

In this case it was possible to observe betaine reversibility because the phosphorane formed is readily able to rearrange to the phosphine, thus removing any possibility of reforming the betaine. A similar reaction takes place if the product
from the opening of trans-stilbene oxide with sodium diphenylphosphide, the phosphine (161), is protonated with ethanol. The products are benzaldehyde and benzyldiphenylphosphine.

Although it is possible that this reaction proceeds via an intermediate betaine similar to (160), as there is an equivalent amount of base present, in the form of ethoxide, once protonation of the oxygen has taken place, protonation of the phosphorus would seem unlikely. An alternative explanation is that the β-hydroxyporphosphine (162) undergoes a base catalysed reverse aldol reaction.

\[
\begin{align*}
\text{Ph}_2\text{P}^- + \text{Ph} \rightarrow & \text{Ph}_2\text{P}^- \text{CHPh}^- \text{C(OH)Ph} \\
& \text{EtOH} \\
& \text{(161)} \\
\text{Ph}_2\text{P}^- \text{CHPh}^- \text{C(OH)Ph} \rightarrow & \text{Ph}_2\text{PCH}_{\text{Ph}} + \text{PhCHO} \\
& \text{EtO}^- \end{align*}
\]
A thorough discussion of betaine reversibility is given in reference 150.

Although reversible betaine formation must be invoked in reactions like that of diphenylphosphine with styrene oxide, where this reversibility is used to explain betaine interconversion there is a possibility of a further explanation. There could be direct interconversion of one stereoisomeric betaine to the other without dissociation to aldehyde and phosphorane. 60

The two isomeric betaines, which can be produced by the reaction of a phosphorane and an aldehyde, are interconvertible via the phosphorane (163), formed by the removal of a proton from the α-carbon of the isomeric betaines. Obviously this proton will be most readily removed when \( R^1 \) is an activating group; thus direct interconversion is most likely to be found in Wittig reactions involving stable phosphoranes.
As all the steps shown may be operating at any given time it is not usually possible to distinguish between them. However, Trippett $^{150}$ has shown that in the system including the betaine (165) direct interconversion is relatively unimportant. When this betaine was produced from its corresponding phosphonium iodide (164) in the presence of an excess of m-chlorobenzaldehyde, $49\%$ of cis and $5.9\%$ of trans-stilbene was formed. The amount of trans-stilbene was reduced to $4\%$ by further increasing the excess of m-chlorobenzaldehyde.
Under these conditions betaine interconversion via betaine dissociation is impossible because the benzylidene-phosphorane (166) will be irreversibly captured by the m-chlorobenzaldehyde to give m-chlorostilbenes. Thus the small percentage of trans-stilbene formed can only come from direct interconversion of the betaines via a phosphorane of the type (163).

Another reaction of intermediate betaines has been described by Hands and Mercer.\textsuperscript{153} When β-hydroxyethyltriphenylphosphonium salts (167) were treated with sodium ethoxide, in ethanol, β-ethoxyethyltriphenylphosphine oxide (169) and benzene were formed. A similar reaction using
aqueous potassium hydroxide gave β-hydroxyethyldiphenylphosphine oxide. Hands suggested that these reactions involve attack by alkoxide on the β-carbon of the betaine (168), the formation of a phosphorus oxygen bond and the expulsion of a phenyl group as its anion, which takes up a proton from the solvent.

However, consideration of the alcoholysis of phosphonium salts \(^\text{154}\) makes this mechanism appear unlikely. Under conditions of alcoholysis it is suggested that the five valent phosphorus intermediate (170) is formed initially, by attack of alkoxide on phosphorus. Further attack of alkoxide on this leads to the formation of an ether and phosphine oxide by displacement of the anion (R^1)^-.
Alcoholysis, however, will only take place when $R^2 = \text{benzyl}$ or substituted benzyl, not when $R^2 = \text{phenyl}$. If we write (168) as (171) it is readily seen that the mechanism suggested by Hands is analogous to alcoholysis.

There appears to be no valid reason why a phenyl group should leave in this case when it will not in normal alcoholysis.

A possible alternative to this mechanism is the removal of a proton from the $\alpha$-carbon atom in the betaine (168) by alkoxide, followed by the electron shifts shown
(172) to give a vinylphosphine oxide, which can readily add ethanol to give Hands' product.

In the reaction with aqueous potassium hydroxide it is possible that simple hydrolysis of the phosphonium salt is taking place.

A further example of this type can be found in the reaction of diphenylphosphine with styrene oxide. The diphosphine dioxide (175) is one of several products isolated and could be formed by the addition of diphenylphosphine oxide, or its anion, to the vinyl phosphine (174), which in turn may be formed by
protonation on oxygen of the betaine (173) and subsequent loss of water, with or without loss of a proton from the phosphorus. Subsequent air oxidation gives the product (175).
Abnormal Reactions of the Betaines $\text{R}_3\text{P}^+\text{CH}_2\text{CH(O)R}$

Wittig\(^{165}\) has shown that benzyldenetriphenylphosphorane with benzaldehyde in ether gives $>80\%$ of stilbene. The equivalent reaction using sodium ethoxide in ethanol as the base to produce the phosphorane gives $>96\%$ yield of stilbenes. However, methyltriphenylphosphonium halides in alcoholic-alkoxide give only poor yields of olefins and, unlike the benzyl salts, do not undergo alcoholysis.\(^{164}\) Obviously reactions other than alcoholysis must be successfully competing with olefin formation in this case.

Methyltriphenylphosphonium bromide, or iodide, on standing at room temperature, with benzaldehyde in ethanolic sodium ethoxide, formed styrene (11\%) and a highly crystalline, insoluble compound. This was shown to be 1,2-diphenylethylidiphenylphosphine oxide (176; $\text{R} = \text{Ph}$). Fusion of this compound with alkali gave a high yield of stilbene and not 1,2-diphenylethane as previously reported.\(^{166}\) Compound (176) is presumably formed from the betaine (177) by simultaneous migration of a phenyl group from phosphorus to $\alpha$-carbon and of hydrogen from $\alpha$ to the $\beta$-carbon.
Replacement of benzaldehyde by substituted benzaldehydes gave the corresponding phosphine oxides (176; R = m-chlorophenyl, p-tolyl, piperonyl, m-nitrophenyl) whose structures were determined both by fusion with alkali, and identification of the resulting stilbenes, and by synthesis from benzyl halides and metallated benzylidiphenylphosphine oxide.

As the betaine (177; R = Ph) is the expected intermediate in the reaction of triphenylphosphine with styrene oxide it would seem reasonable that the phosphine oxide (176; R = Ph) would be the major product, although Wittig and Haag have reported that this reaction in the absence of solvent gives styrene (50%) and triphenylphosphine oxide (86%). However, when the reaction was carried out in refluxing ethanol the rearranged oxide (176; R = Ph) was
formed in high yield.

This led us to believe that the reaction was highly dependent on solvent, and further work showed this to be true. Although reaction in di-n-butyl ether gave the rearranged oxide (176; R = Ph) in somewhat reduced yield, reaction in benzene was extremely slow to give styrene (36%) and triphenylphosphine oxide (40%), after a week, and no trace of the rearranged oxide (176). Even in methanol the yield of the oxide (176) was reduced and that of styrene consequently increased.

The migratory aptitudes of substituted phenyl groups in the above rearrangement were investigated using both the reactions of the iodides MePh₂PC₆H₄X·I⁻ with benzaldehydes in ethanolic sodium ethoxide, and the reactions of the phosphines Ph₂PC₆H₄X with styrene oxide in refluxing ethanol. In all reactions the order of migration was m-chlorophenyl>phenyl>p-anisyl, that group migrating which is the more stable as the anion. Therefore, it appears that the migrating group, with its bonding electrons, is being "pushed" from the phosphorus, the electron shift (I; formula 177) being in advance of the others and the driving force for the reaction being the formation of the P–O bond. This is analogous to the benzil-benzilic acid
rearrangement, which involves attack of hydroxide anion on one carbonyl of benzil, followed by migration of a phenyl as an anion from this carbon to the other carbonyl carbon.

The search for rearrangements of this type in slightly different systems was greeted with varying success. When propionaldehyde was treated with methyltriphenylphosphonium iodide in ethanolic sodium ethoxide, no olefin or rearranged oxide was formed. This is presumably due to neither of these reactions being able to compete with base catalysed polymerisation of the aldehyde. Ethyltriphenylphosphonium iodide with benzaldehyde in ethanolic sodium ethoxide gave high yields of β-methylstyrene, and even higher yields in methanolic sodium methoxide, no rearranged oxide being detected.

The reaction of diphenylphosphine with styrene oxide was far more profitable. Here it was possible to observe, depending upon the conditions used, the majority of the
reaction of betaines. Without solvent at 120° the products were β-phenylethylidiphenylphosphine oxide (178) (25%), presumably formed by a rearrangement (a), analogous to that of the betaine (177) to give the oxide (176), but involving the migration of hydride rather than phenyl anion, together with benzaldehyde (24%) and methyldiphenylphosphine (isolated as the oxide) (34%), these last two presumably being formed by dissociation (b) of the intermediate betaine (179). When the reaction was carried out in refluxing ethanol the products were styrene (60%), probably resulting from a conventional Wittig elimination (c) from the betaine (179), benzaldehyde and methyldiphenylphosphine (from betaine dissociation) and the diphosphine dioxide (180), the possible mode of formation of which has already been discussed (p. 97).
Authentic dioxide (180) was synthesised by the thermal rearrangement of the phosphinite (181) obtained from chlorodiphenylphosphine and 2-hydroxy-2-phenylethyl- diphenylphosphine oxide (182).

\[
\text{Ph}_2\text{PCl} + \text{Ph}_2\text{P}-\text{CH}_2-\text{CH(OH)Ph} \xrightarrow{\text{Py}} \text{Ph}_2\text{P} \quad \text{CH}_2
\]

\[
\text{Ph}_2\text{P}-\text{O} \quad \text{CHPh}
\]

Heat 120°

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

\[
\text{Ph}_3\text{P} \quad \text{CHPh}
\]

(180)

(181)

A number of other epoxides were reacted with tri- and diphenylphosphine. It was found that all the reactions required far more vigorous conditions than those of styrene oxide and phosphines, mainly sealed tubes and high temperatures. This is a little surprising as a search of the literature showed no evidence of extra reactivity towards nucleophiles in the case of styrene oxide when compared with other epoxides. 1,2-Epoxyhexane gave hex-1-ene as the major product on reaction with either
di- or triphenylphosphine, presumably by a normal Wittig elimination. No betaine dissociation products could be detected in either case. However, with diphenylphosphine, 1,2-epoxyhexane did give a small yield (1/3) of hexyldiphenylphosphine oxide (183) presumably by a mechanism similar to (a) above.

\[
\text{Ph}_2\text{PH} + \text{CH}_2\text{CH}-(\text{CH}_2)_3-\text{CH}_3 \rightarrow \text{Ph}_2\text{PCH}_2\text{CH}-(\text{CH}_2)_3-\text{CH}_3
\]

(183)

trans-Stilbene oxide gave only poor yields of stilbene, and phosphine oxide, when reacted without solvent with triphenylphosphine at 180° for four days and no other isolatable product. This was equally true of cis-stilbene oxide.\textsuperscript{156}

The reaction of 1,2-epoxycyclohexane with diphenylphosphine gave cyclohexene (6%) and cyclohexyl-diphenylphosphine oxide (3%) as the only isolatable products. However, with triphenylphosphine, or methyldiphenylphosphine,
although the yield of olefin was not improved, the corresponding cyclohexenylphosphonium salt (185) was formed. This is probably produced by elimination of $^\cdot$OH from the intermediate betaine (184).

\[
\begin{align*}
\text{R} &= \text{Ph or Me} \\
\text{(184)} &
\end{align*}
\]

This may be a consequence of the high energy of a transition state for olefin formation, involving a four-membered ring fused diequatorially to a six-membered ring. Benzene (20%) was also formed in these reactions, probably by decomposition of the phosphonium hydroxide (185).

In an attempt to rationalise these results cyclooctene oxide was reacted with triphenylphosphine.

The problems of a high-energy transition state for olefin formation should not arise in this case because the system will consist of a four-membered ring fused to an eight-membered. Although the reaction required even more
vigorous conditions than the cyclohexane case, the only products were phosphine oxide and cyclooctene (38%), no phosphonium salt being formed.

It can be seen from this discussion that intermediate betaines in Wittig reactions can undergo a number of reactions other than elimination of phosphine oxide to give olefins; They may;

(a) dissociate to phosphorane and carbonyl compound,
(b) rearrange to phosphine oxide by migration of phenyl from phosphorus to α-carbon,
(c) suffer further attack by nucleophiles to give β-substituted phosphine oxides, and
(d) eliminate hydroxide to give vinyl phosphonium salts.

Experimental

All experiments involving phosphoranes and similar unstable compounds were conducted under an oxygen-free nitrogen atmosphere. All aromatic aldehydes were freshly distilled under an oxygen-free nitrogen atmosphere. All solvents were dried before use. Melting points were corrected.

Reaction of Methyltriphenylphosphonium Iodide with Benzaldehyde in Ethanolic Sodium Ethoxide. - A solution of
methyltriphenylphosphonium iodide (16.2 g.) and benzaldehyde (4.25 g.), in ethanol (60 ml.), containing sodium (0.97 g.), was set aside at room temperature under oxygen-free nitrogen. After 48 hr., g.l.c. (2m. Apiezon column at 130°) showed the presence of styrene (10%) and benzaldehyde (<5%), and filtration gave 1,2-diphenylethylidiphenylphosphine oxide (68%), m.p. and mixed m.p. (from ethanol) 232-233° (Found: C, 81.3; H, 5.9; P, 8.07. Calc. for C_{26}H_{23}OP: C, 81.6; H, 6.02; P, 8.12%).

The same experiment in methanol gave styrene (26%) and oxide (34%). The oxide (8 g.) was fused with sodium hydroxide (15 g.), to which water (1 ml.) had been added, for 2 hr. and the cooled mixture dissolved in water (200 ml.). Extraction with chloroform gave a solution which g.l.c. (2m. Apiezon column at 250°) showed to contain cis (40%) and trans (8%) stilbenes. The aqueous layer gave, on acidification, diphenylphosphinic acid (81%), m.p. and mixed m.p. 192-193°.

Similar experiments in ethanol using substituted benzaldehydes gave the following phosphine oxides.

1-Phenyl-2-\textsubscript{m}-chlorophenylethyldiphenylphosphine oxide, (48%), m.p. and mixed m.p. (from ethanol) 212-213°.

1-Phenyl-2-\textsubscript{p}-tolylethylidiphenylphosphine oxide (40%), m.p. and mixed m.p. (from ethanol) 240-241°.
l-Phenyl-2-(3',4'-methylenedioxyphenyl) ethyldiphenylphosphate oxide (38%), m.p. (from ethanol) 204-205° (Found: C, 76.6; H, 5.6; P, 7.15. C_{27}H_{23}O_{3}P requires C, 76.2; H, 5.4; P, 7.3%).

l-Phenyl-2-m-nitrophenylethyldiphenylphosphate oxide (10%), m.p. (from ethanol) 203-204° (Found: C, 72.3; H, 5.2; P, 7.2; N, 3.4. C_{26}H_{22}NO_{3}P requires C, 73.0; H, 5.2; P, 7.25; N, 3.3%).

1-Phenyl-2-m-chlorophenylethyldiphenylphosphate Oxide. — Ethereal NE butyl-lithium (15 ml.) was added to a solution of benzyldiphenylphosphate oxide (4.2 g.) in ether (100 ml.) and the solution heated under reflux for 1/4 hr. m-Chlorobenzyl bromide (4 g.), in ether (40 ml.), was then added and the solution heated under reflux for a further 2 hr. It was then washed with water, dried and evaporated and the residue crystallised from ethanol to give the phosphine oxide (67%), m.p. 212-213°, (Found: C, 74.5; H, 5.0; Cl, 7.6; P, 8.65. C_{28}H_{22}ClO_{3}P requires C, 74.7; H, 5.3; Cl, 7.4; P, 8.7%), Fusion with sodium hydroxide gave (g.l.c.) cis (32%) and trans-3-chlorostilbene (12%), and diphenylphosphinic acid (74%).

A similar experiment using 4-methylbenzyl bromide gave 1-phenyl-2-p-tolylethyldiphenylphosphate oxide (62%), m.p. (from ethanol) 240-241° (Found: C, 81.7; H, 6.3; P, 7.8.
Fusion with sodium hydroxide gave (g.l.c.) *cis* (36%) and *trans*-4-methylstilbene (7%), and diphenylphosphinic acid (77%).

**Experiments using m-Chlorophenyldiphenylphosphine.**

A solution of chlorodiphenylphosphine (35 g.) in ether (150 ml.) was added slowly to the Grignard reagent from m-chloroiodobenzene (45 g.) and magnesium (4.6 g.) in ether (200 ml.) cooled to 0°, and the solution stirred at room temperature for 2 hr. 2 N-Hydrochloric acid (250 ml.) was then slowly added followed by chloroform (200 ml.). The organic layer was washed with water, dried, and evaporated. Distillation gave m-chlorophenyldiphenylphosphine (37 g.), b.p. 208-212°/2mm., which did not crystallise and was characterised as the methiodide, m.p. (from chloroform-ethyl acetate) 170-173° (Found: C, 52.0; H, 4.0; Cl, 7.95; P, 6.9. C_{19}H_{17}ClIP requires C, 52.0; H, 3.9; Cl, 8.1; β, 7.0%).

m-Chlorophenylmethylidiphenylphosphonium iodide (4.4 g.) and benzaldehyde (1.2 g.) were added to ethanol (50 ml.) containing sodium (0.25 g.) and the solution set aside at room temperature for 5 days. Water was then added to turbidity. Crystallisation then gave 1-m-chlorophenyl-2-phenylethylidiphenylphosphine oxide (1.6 g.), m.p. and
mixed m.p. (from aqueous ethanol) 193-194°. A similar experiment using m-chlorobenzaldehyde (1.4 g.) gave 1,2-di-m-chlorophenylethylidiphenylphosphine oxide (1.8 g.), m.p. and mixed m.p. (from aqueous ethanol) 194-195°.

A solution of m-chlorophenyldiphenylphosphine (2.96 g.) and styrene oxide (1.2 g.) in ethanol (25 ml.) was heated under reflux for 24 hr. and water then added to turbidity. Crystallisation gave 1-m-chlorophenyl-2-phenylethylidiphenylphosphine oxide (3.1 g.), m.p. and mixed m.p. (from aqueous ethanol) 192-194°.

1,2-Di-m-chlorophenylethylidiphenylphosphine Oxide. - A solution of m-chlorobenzyl bromide (8 g.) in benzene (20 ml.) was added slowly to a cooled solution of methyl diphenylphosphinite (7.8 g.) in benzene (20 ml.) and the resulting solution heated under reflux for 1 hr. Addition of light petroleum (b.p. 40-60°) then gave m-chlorobenzyldiphenylphosphine oxide (7.5 g.), m.p. 162.5-163.5° (Found: C, 69.62; H, 4.79; F, 9.30. C_{19}H_{16}ClOP requires C, 69.80; H, 4.90; F, 9.49%).

Ethereal Li\textsubscript{n}-butyl-lithium (8 ml.) was added to m-chlorobenzyldiphenylphosphine oxide (2.2 g.) in benzene (100 ml.) and the solution heated under reflux for 1 hr. and then cooled during the addition of m-chlorobenzyl bromide
(4 g.) in benzene (20 ml.). The resulting solution was heated under reflux for 1 hr. and the solvent then removed under reduced pressure. A solution of the residue in chloroform was washed with water, dried, and evaporated. The residue crystallised on trituration with light petroleum to give 1,2-di-m-chlorophenylethylidiphenylphosphine oxide (2.3 g.), m.p. (from aqueous ethanol) 194-195° (Found: C, 69.05; H, 4.6; Cl, 15.65; P, 7.0. $C_{26}H_{21}Cl_2OP$ requires C, 69.2; H, 4.65; Cl, 15.75; P, 6.9%). Fusion with sodium hydroxide gave (g.l.c.) cis-3,3'-di-chlorostilbene (69%).

A similar experiment using benzyl bromide gave 1-m-chlorophenyl-2-phenylethylidiphenylphosphine oxide (65%), m.p. (from aqueous ethanol) 192-193° (Found: C, 74.85; H, 5.42; Cl, 8.45; P, 7.22. $C_{26}H_{22}ClOP$ requires C, 74.95; H, 5.28; Cl, 8.5; P, 7.22%). Fusion with sodium hydroxide gave (g.l.c.) cis-3-chlorostilbene (73%).

Experiments with p-Methoxyphenyldiphenylphosphine. - p-Methoxyphenylmethylidiphenylphosphonium iodide (4.34 g.) and benzaldehyde (1.2 g.) were added to ethanol (20 ml.) containing sodium (0.25 g.) and the solution set aside at room temperature for 4 days. Filtration then gave 1,2-diphenylethyl-p-methoxyphenyldiphenylphosphine oxide (1.7 g.), m.p. (from ethanol) 185-186° (Found: C, 78.45;
H, 5.9; P, 7.5. C_{27}H_{25}O_2P requires C, 78.8; H, 6.1; P, 7.5\%).

Fusion with sodium hydroxide gave (g.l.c.) cis (40\%) and trans-stilbene (8\%) with no trace of 4-methoxystilbenes.

A similar experiment with m-chlorobenzaldehyde (1.5 g.) gave 1-phenyl-2-m-chlorophenylethyl-p-methoxyphenylphenylphosphine oxide (1.9 g.), m.p. (from aqueous ethanol) 165-167\° (Found: C, 72.7; H, 5.5; Cl, 7.85; P, 6.9.

C_{27}H_{24}ClO_2P requires C, 72.5; H, 5.4; Cl, 7.9; P, 6.9\%).

Fusion with sodium hydroxide gave (g.l.c.) cis (49\%) and a trace of trans-3-chlorostilbene.

A solution of p-methoxyphenylidiphenylphosphine (5 g.) and styrene oxide (2.1 ml.) in ethanol (25 ml.) was heated under reflux for 24 hr. and water then added to turbidity. Crystallisation gave 1,2-diphenylethyl-p-methoxyphenylphenylphosphine oxide (3 g.), m.p. and mixed m.p. (from ethanol) 185-186\°.

Reaction between Triphenylphosphine and Styrene Oxide. - A solution of triphenylphosphine (7.5 g.) and styrene oxide (3.5 g.) in ethanol (50 ml.) was heated under reflux for 24 hr. Crystallisation then gave 1,2-diphenylethyldiphenylphosphine oxide (6.3 g.) m.p. and mixed m.p. 232-233\°. Styrene (8\%) was also formed (g.l.c.).
A similar reaction in dibutylether at 120° for 20 hr. gave 1,2-diphenylethyldiphenylphosphine oxide (40%) and styrene (20%).

A solution of triphenylphosphine (13 g.) and styrene oxide (6 g.) in benzene (80 ml.) was heated under reflux for 6 days. Styrene (32%) and unchanged styrene oxide (20%) were then present (g.l.c.). Methyl iodide (10 ml.) was then added and the solution heated under reflux for 1 hr. The syrup which separated gave, on trituration with ethyl acetate, methyltriphenylphosphonium iodide (7.7 g.), m.p. and mixed m.p. 189-190°. The mother liquors were evaporated and the residue chromatographed on alumina. Elution with benzene gave triphenylphosphine oxide (7 g.), m.p. and mixed m.p. 157-158°.

**Reaction of Ethyltriphenylphosphonium Iodide with Benzaldehyde in Ethanolic Sodium Ethoxide.** - A solution of ethyltriphenylphosphonium iodide (10.5 g.) and benzaldehyde (2.6 g.) in ethanol (100 ml.) containing sodium (0.51 g.) was set aside at room temperature for 4 days, when g.l.c. showed the presence of cis (16%) and trans-β-methylstyrene (46%). The solution was evaporated and the residue, in chloroform, washed with water, dried, and the solvent removed under reduced pressure. The residue was extracted with benzene
leaving undissolved ethyltriphenylphosphonium iodide (1.9 g.), m.p. and mixed m.p. 164-165°, and the extract chromatographed on alumina to give triphenylphosphine oxide (2.49 g.), m.p. and mixed m.p. 157-158°.

A similar reaction in methanol gave cis (26%) and trans-β-methylstyrene (54%).

Reaction of Diphenylphosphine with Styrene Oxide.

(a) without solvent. - Diphenylphosphine (6.5 g.) and styrene oxide (4.5 g.) were heated together under oxygen-free nitrogen at 140° for 12 hr. when g.l.c. showed the presence of benzaldehyde (24%) and styrene oxide (20%). The reaction mixture, in benzene, was chromatographed on alumina. Elution with benzene gave 3-phenylethyl diphenylphosphine oxide (2.6 g.), m.p. and mixed m.p. (from light petroleum; b.p. 100-120°) 103-105°; elution with benzene-ether (1:1) gave methyldiphenylphosphine oxide (2.4 g.), m.p. and mixed m.p. (from light petroleum, b.p. 80-100°) 109-110°.

(b) in ethanol. - A solution of diphenylphosphine (8.1 g.) and styrene oxide (8 g.) in ethanol (80 ml.) was heated under reflux for 40 hr. when g.l.c. showed the presence of styrene (60%) and benzaldehyde (13%). The solvent was evaporated and the residue, in benzene, chromatographed on alumina. Elution with benzene gave 1,2-di(diphenylphosphinyl)-1-phenylethane (3 g.), m.p. and mixed m.p. (from ethanol) 112-114°.
283-284°; elution with benzene-ether (1:1) gave methyldiphenylphosphine oxide (2 g.), m.p. and mixed m.p. 109-110°.

1,2-Di(diphenylphosphinyl)-1-phenylethane. - Chlorodiphenylphosphine (2.2 g.) was added to a solution of β-hydroxy-β-phenylethylidiphenylphosphine oxide (3.2 g.) in pyridine (10 ml.) and the solution heated under reflux for 3 hr., then cooled and poured into water. The precipitated syrup crystallised from aqueous ethanol to give 1,2-di(diphenylphosphinyl)-1-phenylethane (3.4 g.) m.p. 283-284° (Found: C, 75.8; H, 5.4; P, 12.0. C₃₂H₂₈O₂P₂ requires C, 75.9; H, 5.5; P, 12.2%).

β-Phenylethylidiphenylphosphine Oxide. - A solution of diphenylphosphine (3.4 g.) in tetrahydrofuran (30 ml.) was heated under reflux with sodium wire (6 g.) for 2 hr. The excess of sodium was then removed and β-bromoethylbenzene (3.49 g.) in tetrahydrofuran (6 ml.) added. The mixture was heated under reflux for 1 hr., the solvent then removed under reduced pressure and the residue, in chloroform, washed with water and then stirred at room temperature for 10 minutes with hydrogen peroxide (6%). The solution was then washed with water, dried, and evaporated. The residue crystallised
from light petroleum to give \( \beta \)-phenylethyl diphenylphosphine oxide (4 g.), m.p. 104-106° (Found: C, 78.3; H, 6.2; P, 10.1. \( \text{C}_{20}\text{H}_{19}\text{OP} \) requires C, 78.4; H, 6.2; P, 10.1%)

**Reactions of 1,2-Epoxyhexane with Phosphines.** - Triphenylphosphine (3.24 g.) and 1,2-epoxyhexane (1.2 g.) were heated together in a sealed tube at 220° for 7 days and the product dissolved in ethanol (25 ml.) g.l.c. (50 m. capillary column coated with polypropylene glycol, at 40°) showed the presence of hex-1-ene (61%). The ethanol was evaporated and the residue crystallised from ethyl acetate to give triphenylphosphine oxide (2.4 g.), m.p. and mixed m.p. 157-158°.

A similar reaction with diphenylphosphine gave hex-1-ene (38%) and hexyldiphenylphosphine oxide (4%) having an infrared spectrum identical with that of an authentic sample.

**Reaction of 1,2-Epoxycyclohexane with Phosphines.** - Methyl diphenylphosphine (4 g.) and 1,2-epoxycyclohexane (2 g.) were heated together at 120° for 30 hr., cooled, and the product extracted with ethyl acetate (3 x 50 ml.). The extract was treated with methyl iodide (5 ml.) and set aside at room temperature for 16 hr. Filtration then gave dimethyldiphenylphosphonium iodide (2.3 g.), m.p. and mixed
m.p. 256-257°. The mother liquor was evaporated and the residue crystallised from light petroleum to give methyldiphenylphosphine oxide (1.3 g.), m.p. and mixed m.p. 109-110°.

The residue from the extraction with ethyl acetate was dissolved in chloroform and the solution washed (4x) with saturated aqueous potassium iodide, dried, and evaporated. Crystallisation of the residue from chloroform/ethyl acetate gave cyclohex-1-enylmethyldiphenylphosphonium iodide (1 g.), m.p. and mixed m.p. 225-226°, having an infrared spectrum identical with that of an authentic sample.

A solution of triphenylphosphine (8.6 g.) and cyclohexene oxide (3.3 g.) in ethanol (40 ml.) was heated under reflux for 60 hr. G.l.c. (50 m. capillary column coated with polypropylene glycol, at 40°) showed the presence of cyclohexene (3%) and benzene (22%). The solution was evaporated and the residue extracted with ethyl acetate (2 x 50 ml.). The extract was heated under reflux with methyl iodide for ½ hr. to give methyltriphenylphosphonium iodide (1.1 g.), m.p. and mixed m.p. 188-189°.
The mother liquor, on evaporation, gave triphenylphosphine oxide (3 g.), m.p. and mixed m.p. (from chloroform/light petroleum) 157-158°.

The residue from the extraction with ethyl acetate was dissolved in chloroform and the solution washed (4x) with saturated aqueous potassium iodide, dried, and evaporated. The residue crystallised from chloroform/ethyl acetate to give what is probably cyclohex-1-enyltriphenylphosphonium iodide (0.4 g.), m.p. 228-233°. The compound could not be satisfactorily purified. Its n.m.r. spectrum showed a doublet at \(3.3\, \text{ppm}(J_{\text{PH}} 22 \text{ c/sec.})\) equivalent to one proton.

**Cyclohex-1-enylmethyldiphenylphosphonium Iodide.** - Chlorodiphenylphosphine (22 g.) in ether (50 ml.) was slowly added to a stirred, cooled, solution of cyclohex-1-enyl-lithium, prepared from lithium (6 g.) and 1-chlorocyclohexene (15 g.) in ether (150 ml.) and the solution heated under reflux for 1 hr. and then cooled during the addition of water (100 ml.). The ethereal layer was washed with water, dried, and heated under reflux for 2 hr. with methyl iodide (10 ml.). The resulting solid was recrystallised from chloroform/ethyl acetate to give cyclohex-1-enylmethyldiphenylphosphonium
iodide (16 g.), m.p. 225-226°.

Reaction of Triphenylphosphine with Cyclooctene oxide. - Triphenylphosphine (6.8 g.) and 1,2-epoxycyclooctene (3.2 g.) were heated together in a sealed tube at 210° for 6 days and the product extracted with ethanol (100 ml.). G.l.c. (6 m. apiezon L column, at 140°) showed the presence of cyclooctene (20%). The solution was evaporated, and the residue adsorbed on basic alumina. Elution with light petroleum (b.p. 40-60°) gave triphenylphosphine (2.3 g.), m.p. and mixed m.p. (from ethyl acetate-petrol) 78-79°; elution with ether-methanol (20:1) gave triphenylphosphine oxide (4.2 g.), m.p. and mixed m.p. (from ethyl acetate) 157-158°C.

Reaction of trans-stilbene oxide with Triphenylphosphine. - Triphenylphosphine (6.8 g.) and trans-stilbene oxide (4.9 g.) were heated together at 180° for 4 days and the product extracted with ethanol (80 ml.). G.l.c. (6 m. apiezon column, at 250°) showed the presence of trans-stilbene (9%) and cis-stilbene (2%). The solution was evaporated and the residue adsorbed on basic alumina. Elution with light petroleum (b.p. 40-60°) gave trans-stilbene (0.1 g.) m.p. and mixed m.p. 124-125°; elution with light petroleum-ether (4:1) gave triphenylphosphine (1.4 g.), m.p. and mixed
m.p. 78-79°; and elution with ether-methanol (20:1) gave triphenylphosphine oxide (4.5 g.), m.p. and mixed m.p. (from ethyl acetate) 157-158°.
Abnormal Quaternisation Reactions of Some Activated Alkyl Halides.

(a) Reactions Proceeding via Enol-Phosphonium Salts.

Most primary alkyl halides quaternise normally with tertiary phosphines, nucleophilic attack by the phosphine at carbon, leading to displacement of halide ion and the formation of a phosphonium salt.

\[ R_3P + R'-CH_2-X \rightarrow R_3P^+ - CH_2 - R' \ X^- \]

However, there are a number of examples of abnormal reactions between phosphines and organic halides. One group of these is the reaction of phosphines with alkyl halides containing activating groups attached to the \( \alpha \)-carbon atom.

When allowed to react with tertiary phosphines, certain \( \alpha \)-haloketones do not give the expected \( \beta \)-ketophosphonium salts, but instead, products, which on treatment with alcohols give tertiary phosphine oxides, de-halogenated ketones and alkylhalides.\(^{159,160}\)
Bromides show a greater tendency to react abnormally than the corresponding chlorides, although mono-halomethylketones do not usually show the abnormal reaction whatever the halogen.\(^{161}\) The abnormal reaction becomes more likely as the number of halogen substituents on the \(\alpha\)-carbon increases, for example, even when the halogen is chlorine, compounds like chloral undergo an abnormal reaction with triphenylphosphine in a violently exothermic manner.\(^{189}\)

The intermediate compound formed in these reactions has been formulated as the enol-phosphonium salt. (186)\(^{159,160}\)
Speziale and Partos\textsuperscript{162} finally established the structure of the intermediate (188) in the reaction of the chloroketone (187) with triphenylphosphine, by elemental analysis, the absence of a carbonyl stretching frequency in its infrared spectrum and the presence of a phosphonium salt like resonance in its P\textsuperscript{31} N.M.R. spectrum.

\[
\text{Ph}_3\text{P} + \text{Ph}_2\text{C} = \text{C} \cdot \text{Ph} \rightarrow \text{Ph}_2\text{C} = \text{C} \cdot \text{Ph}
\]

\[
\begin{array}{c}
\text{Cl} \\
\text{O} \\
\text{O} - \text{PPh}_3 \\
\text{Cl} \\
\end{array}
\]

(187) (188)

It seems likely that intermediates of the type (186) do not decompose because the likelihood of nucleophilic attack by halogen at a vinylic carbon atom is small. This can be compared with the Michaelis - Arbusov reaction.\textsuperscript{159,163,16}
The enol-phosphonium salt (188) is a Michaelis-Arbusov reaction intermediate and these will not decompose when halide attack is required on an aromatic nucleus, analogous to the vinylic system (188). The reaction of these systems with alcohols may be explained by transesterification to give an alkoxy-phosphonium salt (189), which can then undergo the second stage of the Michaelis-Arbusov reaction.

\[
\begin{align*}
\text{Hal}^- & \quad \text{ROH} \quad \text{Hal}^- \\
\text{PO + RHal} \\
(189) \\
\end{align*}
\]

Enol-phosphonium salts have not only been isolated from the reaction of α-haloketones with tertiary phosphines, ethyl trichloroacetate, chloroacetyl chloride, and bromomalonic ester have all been shown to give enol-phosphonium salts with tertiary phosphines.  

Many other reactions of tertiary phosphines with halogen compounds, to give products other than those expected by normal quaternisation, can be explained by the postulation of enol-phosphonium salt intermediates.
Desyl chloride and triphenylphosphine react to give diphenylacetylene, triphenylphosphine oxide and hydrogen chloride.

\[
\text{Ph}_3\text{P} + \text{Ph}-\text{CO}-\text{CHCl}-\text{Ph} \rightarrow \text{Ph}_3\text{PO} + \text{Ph}-\text{C}≡\text{C}-\text{Ph} + \text{HCl}
\]

This may be explained by initial formation of the enol-phosphonium salt (190), followed by decomposition as shown.

Enol-phosphonium salts may be postulated as intermediates in the reaction of N-bromo-amides (191) with triphenylphosphine, which lead to nitrile, phosphine oxide and hydrogen bromide.

\[
\text{RCONHBr} + \text{Ph}_3\text{P} \rightarrow \text{Ph}_3\text{PO} + \text{RCN} + \text{HBr}
\]
Speziale and Smith \(^{166}\) have studied the reaction of triphenylphosphine with N-chloro-N-ethylbenzamide (192), where any enol-phosphonium salt formed will not be able to deprotonate. They found that the products were triphenylphosphine oxide and N-ethylbenzimidoyl chloride (194). It is suggested that the enol-phosphonium salt (193) is initially formed and then attack of halide ion on this leads to the products.

\[
\begin{align*}
\text{Ph-CON} & \quad \xrightarrow{\text{Cl}} \quad \text{Ph}_3\text{P} \\
\text{Et} & \\
(192) & \\
\end{align*}
\]

\[
\begin{align*}
\left[ \begin{array}{c}
\text{Ph-} \\
\text{C}=\text{NEt} \\
\text{O-} \text{PPh}_3
\end{array} \right] & \\
\xrightarrow{\text{Cl}} & \\
\text{Ph}_3\text{PO} + \text{Ph-} \text{C}=\text{NEt} \quad \xrightarrow{\text{Cl}} (194)
\end{align*}
\]

Halide attack in this way offers an alternative explanation to deprotonation in the decomposition of the enol-phosphonium salts described above. The unstable unsaturated halogen compound (195) so formed, undergoing spontaneous dehydrohalogenation.
The reactions of $N,N$-disubstituted trichloroacetamides (196) with trialkyl phosphites and tertiary phosphines have been studied by Speziale and Freeman.\cite{166} The products are trichlorovinylamines (197) and the corresponding trialkyl phosphate or tertiary phosphine oxide.

\[ \text{Cl}_3\text{CONR}_2 + R'_3\text{P} \rightarrow \text{Cl}_3\text{C}=\text{C}-\text{NR}_2 + R'_3\text{PO} \]  \hspace{1cm} (196)  

\[ \text{Cl}_3\text{C}=\text{C}-\text{NR}_2 + \text{Hal} \rightarrow \text{Cl}_3\text{CONR}_2 + \text{Hal} \]  \hspace{1cm} (195)  

\[ \text{Cl}_3\text{CONR}_2 + R_3\text{P} \rightarrow \text{Cl}_2\text{C}=\text{C}-\text{NR}_2 + \text{products} \]  \hspace{1cm} (198)  

It is suggested that the enol-phosphonium salt (198) is initially formed, and this is decomposed by attack of halide ion at the activated vinylic carbon atom.
A possible alternative to this mechanism has been suggested. The lone pair of electrons on nitrogen may help to displace the phosphine oxide directly.

\[ \text{R}_3\text{P} = \text{N} \rightarrow \text{R}_3\text{P}^+ \text{Cl}^- \]

\[ \text{R}_3\text{PO} + \text{R}_2\text{N} = \text{C} = \text{CCl}_2 \]

\[ \text{Cl} \rightarrow \text{C} = \text{CCl}_2 \]

\[ \text{R}_2\text{N} \rightarrow \text{C} = \text{CCl}_2 \]

(b) The Mechanism of Enol-Phosphonium Salt Formation.

A comprehensive study of this has been carried out. Assuming that the attack of the phosphorus compound is nucleophilic, which has been verified by Speziale et al., there are five possible ways in which this initial attack may take place,

(a) at the halogen bearing carbon atom,
(b) at the carbonyl carbon atom,
(c) at the carbonyl oxygen atom,
(d) at the halogen atom, and
(e) in a five membered cyclic reaction to give a penta-covalent phosphorus intermediate.
Possibilities (a) and (b) have been shown to be unlikely. Distinction between the remaining possible modes of attack has been the subject of much discussion, and no absolute proof has yet been put forward as to the true mode of attack. However, it has been shown that the reaction can, in the α-haloketone case at least, proceed by either an acid catalysed, or a non-acid catalysed, mechanism depending upon the conditions used.

(c) The Reaction of Triphenylphosphine with 1-Bromo-1-Nitroalkanes.

In general 1-bromo-1-nitroalkanes react with triphenylphosphine to give phosphine oxide, nitrile and phosphine oxide hydrobromide. However, bromonitromethane and 1-bromo-1-nitroethane have been shown also to give salts, which were originally formulated as α-nitroalkyl-phosphonium bromides, mainly on the evidence that the salt from bromonitromethane and triphenylphosphine gave phosphine oxide and fulminic acid when treated with aqueous alkali at 0°. This reaction was thought to proceed via the phosphobetaine (199).
It was hoped to extend this reaction to the preparation of aliphatic nitrile oxides by treatment of the salt from triphenylphosphine and 1-bromo-1-nitroethane with aqueous sodium hydroxide. However, when this was carried out, no nitrile oxide could be detected, even in the presence of stilbene, which readily condenses with nitrile oxides to give $\Delta^2$-isoxazolines.

Reinvestigation of these reactions has led to different conclusions. Bromonitromethane, 1-bromo-1-nitroethane and 1-bromo-1-nitropropane have all been shown to give salts with triphenylphosphine (although that from 1-bromo-1-nitropropane was obtained in very small yield). If the homologous series is extended further the reaction gives no salt, but only phosphine oxide hydrobromide and nitrile, which are also formed in small yield together with
the above salts. The reaction appears to be extremely sensitive to temperature. If the addition of the bromo-compound, to the phosphine, is not carried out strictly at 5°, or below, the second reaction, to give nitrile and phosphine oxide hydrobromide, predominates even in the bromonitromethane case.

It was found that the optimum reaction was that between two moles of phosphine and one mole of bromo-compound to give the salt and phosphine oxide.

$$2\text{Ph}_3\text{P} + \text{RCHBr.NO}_2 \rightarrow \text{Salt} + \text{Ph}_3\text{PO}$$

These salts were shown to be $\alpha$-hydroxyiminophosphonium bromides (200).

$$\text{Ph}_3\text{P}^+ \text{OR} = \text{N} - \text{OH} \quad \text{Br}^-$$

(200)

The hydroxyl groups of the salts are apparent in the infrared at $\sim 2,750 \text{ cm}^{-1}$, and the N.M.R. spectrum of the salt (200; R = Me) shows the absence of hydrogen on the $\alpha$-carbon atom (doublet at $7.8 \text{Hz}$, $J_{\text{PH}} = 10 \text{ c.p.s.}$). The stability of the salts to alkaline hydrolysis increased markedly from R = H to R = Et. This made it possible to follow the reaction in the case of the salt (200; R = Me) using an
N.M.R. spectrometer. It was found that the ethyl and propyl salts (200; $R=\text{Me}$ and Et) were soluble in aqueous sodium hydroxide, from which solution they could be reprecipitated by the addition of acid. If allowed to stand at room temperature overnight, or warmed to $50^\circ$ for five minutes, these solutions decomposed to phosphine oxide and nitrile.

$$\begin{align*}
\text{Ph}_3\text{P}^+ \text{CR} = \text{NOH} & \quad \text{Br}^- \quad \text{NaOH} \\
\rightarrow & \\
\text{Ph}_3\text{PO} + \text{RCN}
\end{align*}$$

This reaction was carried out in the sample well of the N.M.R. spectrometer by dissolving the salt (200; $R=\text{Me}$) in NaOD/D$_2$O and taking a series of spectra at intervals of one minute at $40^\circ$. The doublet at 7.8 $\tau$ due to the methyl group steadily decreased in intensity and was replaced by a singlet at 8.05 $\tau$, due to acetonitrile.

The alkaline hydrolysis presumably involves the initial deprotonation of the hydroxyl group to give the intermediate (201), which then eliminates phosphine oxide to give the nitrile.

$$\begin{align*}
\text{Ph}_3\text{P}^+ \\
\text{CR} \\
\text{HO} \\
\text{Br}^- \quad \text{CH} \\
\rightarrow \\
\text{Ph}_3\text{P}^+ \\
\text{CR} \\
\text{O} \\
\rightarrow \\
\text{Ph}_3\text{PO} + \\
\text{RC}=\text{N}
\end{align*}$$

(201)
Acid hydrolysis of these compounds requires far more vigorous conditions, and the course depends to a large extent on acid concentration. In 2N hydrochloric acid refluxing for two or three hours leads mainly to phosphine oxide and nitrile, however, in 12N hydrochloric acid the major products are triphenylphosphine, hydroxylamine (isolated as benzaldoxime) and carboxylic acid. This is best explained by the competing reaction of hydrolysis by water.

The formation of hydroxylamine and carboxylic acid probably goes through the intermediate (202) which further hydrolyses to phosphine and carboxylic acid.

\[
\begin{align*}
\text{Ph}_3\text{P} - \text{CR} = N - \text{OH} + \text{H}^+ & \rightarrow \text{NH}_2\text{OH} + \left[ \text{Ph}_3\text{P} - \text{C} = 0 \right] \\
& \downarrow \\
& \text{Ph}_3\text{P} + \text{R} \cdot \text{COCH}
\end{align*}
\]

The mode of formation of these salts is, as yet, obscure. The reaction may in fact proceed via a true nitrophosphonium salt (203), which is then de-oxygenated by phosphine as shown to give the intermediate (204). Migration of a proton will then lead to the observed product.
The formation of nitrile and phosphine oxide could proceed via an enol-phosphonium salt of the type (205), which decomposes to give nitrile oxide and phosphine oxide, the nitrile oxide being de-oxygenated by further phosphine.
An alternative mechanism for the formation of these salts involves the initial formation of nitrile oxide and triphenylphosphine oxide via the intermediate (205). Attack of triphenylphosphine, or triphenylphosphine hydrobromide, on the nitrile oxide can then lead to (206) which may protonate more rapidly than it can eliminate under the acidic conditions.

\[
\begin{align*}
R&\overset{\text{Ph}_3\text{P}}{\text{C}}\overset{\text{+}}{\text{N}}\overset{\text{−}}{\text{O}} \rightarrow \text{Ph}_3\text{P}^+\overset{\text{C}}{\overset{\text{N}}{\text{R}}}\overset{\text{−}}{\text{O}} \\
&\downarrow \text{HBr} \\
&\text{Ph}_3\text{P}^+\overset{\text{S}}{\overset{\text{N}}{\text{R}}}\overset{\text{Br}^-}{\text{OH}}
\end{align*}
\]  

(206)

This is supported to some extent by the rapid decrease in yield of the salt in going from \(R = \text{H}\) to \(R = \text{C}_2\text{H}_5\), the inductive effect of the alkyl group decreasing the likelihood of nucleophilic attack on the carbon of the nitrile oxide and preferentially allowing deoxygenation to take place.
Zbiral has carried out the reaction of phosphoranes with ethyl nitrite and shown that, in the case of phosphoranes with a hydrogen on the α-carbon atom, nitriles and phosphine oxides are produced. This reaction presumably goes through an intermediate similar to (203). However, the anion will be ethoxide in this case, which can remove an α-proton to give the phosphobetaine (207). This can then eliminate as shown. In our case this type of elimination is hindered by lack of a sufficiently powerful base.

\[
\text{Ph}_3\text{P} = \text{CH} - \text{R} + \text{EtONO} \rightarrow \text{Ph}_3\text{P}^+\text{C} = \text{NR}\text{OEt} + \text{Ph}_3\text{PO}
\]

\[
\text{Ph}_3\text{P}^+\text{C} = \text{NR} + \text{EtOH}
\]

The reaction of aromatic nitroso compounds with phosphoranes is also analogous, the products being phosphine oxide and Schiffs base, probably formed via the
intermediate betaine (208).

$$\text{Ph}_3\text{P} = \text{CHPh} + \text{PhNO} \rightarrow \text{Ph}_3\text{P}^+ \text{Ph}^-\text{H}^-\text{NPh}^-$$

$$\text{Ph}_3\text{PO} + \text{PhCH} = \text{NPh}$$

In an attempt to prepare a true α-nitrophosphonium salt, ethyl nitrate was allowed to react with benzylidene-triphenylphosphorane. When this reaction was carried out in the presence of triphenylphosphine, triphenylphosphine oxide and benzonitrile were formed, presumably by a mechanism similar to that of Zbiral, with final deoxygenation of the nitrile oxide by phosphine.

$$\text{Ph}_3\text{P} = \text{CH} - \text{Ph} + \text{EtONO}_2 \rightarrow \text{Ph}_3\text{P}^+ \text{C}^-\text{H}^-\text{OEt}$$

$$\rightarrow \text{Ph}_3\text{P}^+ \text{C}^-\text{N}^-\text{O}^-$$

$$\rightarrow \text{Ph}_3\text{PO} + \text{Ph}^-\text{C}^-\text{N}^-\text{O}^-$$

$$\rightarrow \text{Ph}_3\text{PO} + \text{Ph}^-\text{C}^-\text{N}^-\text{O}^-$$
Other attempts to prepare α-nitrophosphonium salts were equally unsuccessful.

The reaction of sodium diphenylphosphide with bromonitromethane gave diphenylphosphinic acid as the only isolatable product, as did the reaction between the sodium salt of nitromethane and chlorodiphienylphosphine. Reactions of nitryl chloride (NO₂Cl) with phosphoranes gave no crystalline products.

This work means that, as yet, no α-nitroalkylphosphonium salts have been isolated, although Horner has made α-nitroarsoranes by the reaction of nitrophenylmethane with dichlorotriphenylarsorane in the presence of triethylamine.

\[
\begin{align*}
\text{Ph}_3\text{AsCl}_2 + \text{CH}_2\text{PhNO}_2 & \xrightarrow{2\text{Et}_3\text{N}} \text{Ph}_3\text{As} = \text{C} \text{PhNO}_2 + 2\text{Et}_3\text{NH}^+ \text{Cl}^- \\
\end{align*}
\]

The analogous reaction with dichlorotriphenylphosphorane gave only phosphine oxide and benzonitrile. This must be due to the much decreased oxygen affinity of arsenic when compared with phosphorus. This is borne out by the formation of epoxides from many arsenic betaines, where the analogous phosphorus betaines give olefins. Thus attack of
oxygen is on carbon rather than the positively charged arsenic atom, although certain arsenic betaines have been shown to give quite high yields of olefins.\textsuperscript{174}

\[
\begin{align*}
\text{Ph}_3\text{As} & \quad \xrightarrow{+} \quad \text{Ph}_3\text{As} + \quad \text{CR}_2 \quad \text{O} \\
\text{Ph}_3\text{P} & \quad \xrightarrow{-} \quad \text{Ph}_3\text{P} + \quad \text{CR}_2 = \text{CR}_2
\end{align*}
\]
Experimental

All experiments using phosphoranes, and similar unstable compounds, were carried out under an oxygen-free nitrogen atmosphere. All solvents were dried before use. Melting points were corrected.

Preparation of Bromonitromethane. - To a solution of sodium (3.5 g.) in ethanol (70 g.) was added a solution of nitromethane (10 g.) in ethanol (50 g.) with stirring. The solid sodium salt of nitromethane was filtered and washed with ether (3 x 30 ml.). (The sodium salt should be used directly, as an explosion occurred on drying and storage). To the solid sodium salt prepared in this way was slowly added, with ice cooling, a solution of bromine (22 g.) in carbon disulphide (100 g.) while the reaction mixture was vigorously stirred. The carbon disulphide solution was filtered and washed with water (3 x 40 ml.). Drying (Na₂SO₄), evaporation and distillation gave bromonitromethane (7 g.) b.p. 146-150° (lit.¹⁷⁵ b.p. 149°).

Similarly prepared were 1-bromo-1-nitroethane b.p. 145° (lit. 146-7) and 1-bromo-1-nitro-propane b.p. 163-166° (lit.¹⁷⁶ 160-165°).
Reaction of Bromonitromethane with Triphenylphosphine. -

A solution of bromonitromethane (7 g.) in benzene (15 ml.) was added slowly to a solution of triphenylphosphine (26 g.) in benzene (50 ml.) so that the temperature did not rise above 5°, and the resulting suspension set aside at < 5° for 1 hour. Filtration gave hydroxyiminomethyltriphenylphosphonium bromide (15 g.), m.p. (from nitromethane-ethyl acetate) 166°C (decomp.) (Found: C, 59.0; H, 4.5; N, 3.6. C₁₉H₁₇BrNOP requires C, 59.05; H, 4.4; N, 3.6%). Evaporation of the filtrate and recrystallisation from ethyl acetate gave triphenylphosphine oxide (12.5 g.), m.p. and mixed m.p. 157-158°.

In a similar way, 1-bromo-1-nitroethane gave α-hydroxyiminoethyltriphenylphosphonium bromide (65%), m.p. (from chloroform-ethyl acetate) 152-154° (Found: C, 59.85; H, 4.9; N, 3.5. C₂₀H₁₉BrNOP requires C, 59.9; H, 4.75; N, 3.5%), and triphenylphosphine oxide (80%);
1-bromo-1-nitropropane gave \( \alpha \)-hydroxyiminopropyltriphenylphosphonium bromide (16\%), m.p. 152-154° (Found: C, 60.76; H, 5.2; N, 3.3; P, 7.4. \( \text{C}_{21}\text{H}_{21}\text{BrNOP} \) requires C, 60.8; H, 5.1; N, 3.4; P, 7.5\%). The filtrate from the last reaction was shown by g.l.c. [Capillary column (50 m. x 0.5 mm.) coated with polypropylene glycol] to contain propionitrile (~60%).

Alkaline Hydrolysis of These Salts. - Hydroxyiminomethyltriphenylphosphonium bromide (4.92 g.) was dissolved in water (30 ml.) and ethanol (30 ml.), aqueous sodium hydroxide (1N; 13 ml.) added, and the suspension set aside at room temperature for 15 min. Filtration gave triphenylphosphine oxide (3.4 g.), m.p. and mixed m.p. 157-158°. Titration of the filtrate with silver nitrate showed the presence of cyanide ion (28%).

\( \alpha \)-Hydroxyiminoethyltriphenylphosphonium bromide and \( \alpha \)-hydroxyiminopropyltriphenylphosphonium bromide both dissolved in dilute alkali at room temperature to give stable solutions from which they could be recovered on acidification. Refluxing a solution of \( \alpha \)-hydroxyiminoethyltriphenylphosphonium bromide in aqueous sodium hydroxide solution (0.5N) for 10 min. gave, on cooling and filtration,
triphenylphosphine oxide (88%), m.p. and mixed m.p. 157-158°. Analysis of the filtrate by g.l.c. [capillary column (50 m. x 0.5 mm.) coated with polypropylene glycol] showed the presence of acetonitrile (50%). Similarly α-hydroxyiminopropyltriphenylphosphonium bromide gave triphenylphosphine oxide (91%) and propionitrile (60%).

**Acidic Hydrolysis of These Salts.** - A solution of the salt (1-2 g.) in hydrochloric acid (30 ml.) was refluxed for 2-3 hr., the resulting solution analysed directly for nitrile by g.l.c. [capillary column (50 m. x 0.5 mm.) coated with polypropylene glycol] and then extracted with chloroform. The extract was washed with water, dried and evaporated, and the residue set aside at room temperature overnight in benzene (10 ml.) containing methyl iodide (2 ml.). Filtration gave methyltriphenylphosphonium iodide, m.p. and mixed m.p. 190-192° (from chloroform-ethyl acetate). Evaporation of the filtrate gave triphenylphosphine oxide, m.p. and mixed m.p. 157-158° (from ethyl acetate). The yields are given in the Table.
A solution of hydroxyiminomethylphosphonium bromide (6.3 g.) in 12N-hydrochloric acid (15 ml.) was refluxed for 3 hr., cooled, filtered, and made alkaline at 0° by the addition of 5N-sodium hydroxide. Benzaldehyde (2 g.) was then added, the solution set aside at room temperature for 1 hr., and then acidified by the addition of solid carbon dioxide. Ether extraction and distillation of the extract at 110-120°/3 mm. gave a liquid (1.2 g.) whose infrared spectrum was a composite of equal parts of benzaldoxime and benzaldehyde. This was refluxed in acetic anhydride (2 ml.) for 15 min. Analysis by g.l.c. (6 m. apiezon L column) showed the presence of approximately equal quantities of benzaldehyde and benzonitrile.
Reaction of Benzylidenetriphenylphosphorane with Ethyl Nitrate. - To a solution of benzylidenetriphenylphosphorane, from the phosphonium bromide (12 g.) and BuLi (1 M; 29 ml.), in ether, was added triphenylphosphine (7 g.) and the solution stirred until the phosphine had dissolved. To this solution ethyl nitrate (2.6 g.), in ether (10 ml.) was slowly added. The reaction mixture was then stirred for 2 hours, when g.l.c. (6 m. apiezon L column at 180°) on the reaction mixture showed the presence of benzonitrile (28%). The reaction mixture was evaporated, dissolved in chloroform, washed with water and dried. Evaporation gave triphenylphosphine oxide (3.9 g.), m.p. and mixed m.p. 157-158°.

Reaction of Sodium Diphenylphosphide with Bromonitromethane. - Sodium diphenylphosphide was prepared from diphenylphosphine (18.6 g.) and sodium in tetrahydrofuran (100 ml.). To this solution was added bromonitromethane (13 g.) in tetrahydrofuran (15 ml.) and the solution stirred for 1 hr. at room temperature. The resulting solution was evaporated, dissolved in benzene washed with water and dried. Methyl iodide (15 g.) was added, and this solution allowed to stand at room temperature overnight. Filtration gave dimethyl-diphenylphosphonium iodide (5 g.), m.p. and mixed m.p.
246-249°. Evaporation of the filtrate gave, on trituration with petrol, diphenylphosphinic acid (12.8 g.), m.p. and mixed m.p. 191-192°.
The Reaction of Aldehydes and Ketones with Trivalent Phosphorus Compounds. — Considerable work has been carried out on the reactions of carbonyl compounds with trivalent phosphorus compounds containing a substituent capable of forming a stable anion.

Chlorophosphines have been shown to react readily with aldehydes. Conant found that chlorodiphenylphosphine and benzaldehyde reacted at room temperature to give a product which on treatment with water gave α-hydroxybenzylidiphenylphosphine oxide (209).

\[
\text{PhCHO} + \text{Ph}_2\text{PCl} \xrightarrow{\text{R.T.}} \text{[X]} \xrightarrow{\text{H}_2\text{O}} \text{Ph} \text{PhPO} \quad \text{Ph} - \text{CH} - \text{OH}
\]

(209)

Similar reactions with chloroacetaldehydes gave analogous products. Chlorodiethylphosphine and chloral at 0° gave a product which on treatment with water gave (210).
If hydrogen sulphide was used in place of water in the work up of these reactions the phosphine sulphide (211) analogous to (210) was obtained.

Phosphorus trihalides have also been shown to react with aldehydes and ketones. The products from these reactions depend upon the reaction conditions. When an aldehyde and phosphorus trichloride are allowed to react at R.T., and the reaction mixture treated with water, the product is the \( \alpha \)-hydroxyphosphonic acid (212).

The reaction of phosphorus trichloride with ketones is similar to give, after treatment with water, the phosphonic
However, when these reactions are carried out at elevated temperatures the products are different. If a mixture of benzaldehyde and phosphorus trichloride is heated, the phosphine oxide (214) is produced.\(^{180}\)

\[
\begin{align*}
\text{Heat} & \quad \text{PhCHO} + \text{PCl}_3 & \quad \text{Ph-CHCl-PCl}_2 \\
\end{align*}
\]

(214)

The reaction between ketones and phosphorus trichloride is analogous, heating in a sealed tube at 200° giving (215).\(^{183}\)

\[
\begin{align*}
\text{sealed tube} & \quad \text{R}_2\text{CO} + \text{PCl}_3 & \quad \text{R}_2\text{C} - \text{PCl}_3 \\
\end{align*}
\]

(215)

These results may be rationalised in the following manner. The initial step in all the reactions could be nucleophilic attack of phosphorus on the carbon of the carbonyl group in the ketone, or aldehyde, to give a betaine of the type (216).
If the reaction mixture is treated with water at this stage protonation and hydrolysis will give the phosphonic acid (213; Me = R). However, if the betaine (216) is heated it may rearrange, either by an intramolecular mechanism (217), or by an intermolecular mechanism (218), to give the phosphine oxide (219).
However, it is perhaps surprising that chlorophosphines are sufficiently nucleophilic to attack unactivated ketones and aldehydes at room temperature, although quite possible that they will attack aldehydes like chloral where the carbonyl group is highly susceptible to nucleophilic attack. In the cases of room temperature reactions with unactivated aldehydes and ketones acetic acid has invariably been used as a solvent, and this may well take part in the reaction. The initial step may be attack of the chlorophosphine on the acetic acid to give the acetoxyphosphine and hydrogen chloride, which will rapidly give secondary phosphine oxide and acid chloride. Secondary phosphine oxides are known to add readily to aldehydes and ketones to give hydroxyphosphine oxides. Conant has in fact isolated acetyl chloride from these reactions.

\[
\text{R}_2\text{PCl} + \text{CH}_3\text{COOH} \rightarrow \text{R}_2\text{P}-\text{O}-\text{C}-\text{CH}_3 + \text{HCl}
\]

The reaction with phosphorus trichloride may be similar to give the acetoxyphosphine initially, which gives the secondary
phosphine oxide (220) with hydrogen chloride. Attack of this on the carbonyl compound and finally hydrolysis with water giving the phosphinic acid (221).

\[
\begin{align*}
\text{PCl}_3 + \text{CH}_3\text{COH} & \rightarrow \text{Cl}_2\text{P} - \text{O} - \text{C} - \text{CH}_3 + \text{HCl} \\
& \rightarrow \text{Cl}_2\text{PH} + \text{CH}_3\text{COCl} \\
& \rightarrow \text{R}_2\text{CO} \quad \text{H}_2\text{O} \\
\text{Cl}_2\text{P} - \text{CR}_2 & \rightarrow \text{HO} - \text{P} - \text{OH} - \text{CR}_2
\end{align*}
\]

\( (220) \quad (221) \)

Tertiary phosphites also react with aldehydes and ketones. Trialkyl phosphites react with p-nitrobenzaldehyde to give phosphonates (223). Presumably the initial attack is at the carbonyl carbon to give the betaine (222), which then undergoes an internal Arbusov-type reaction to give the product.

\[
\begin{align*}
(\text{RO})_3\text{P} + \text{O}_2\text{N-CHO} & \rightarrow (\text{RO})_2\text{P} - \text{CH-CH-NO}_2 \\
(\text{RO})_2\text{P} & \rightarrow (\text{RO})_2\text{P} - \text{CH-CH-NO}_2
\end{align*}
\]

\( (222) \quad (223) \)
Similar reactions take place with aliphatic aldehydes under vigorous conditions.\footnote{187}

Aminophosphonites have been shown to react with aldehydes at 100\degree C to give rearranged products analogous to (219), the amino group migrating in preference to the alkoxy.\footnote{188}

\[
(R\text{O})_2\text{PNET}_2 + R'\text{CHO} \xrightarrow{20 \text{ mins.} \ 100\degree C} (R\text{O})_2\text{P}-\text{CH}-\text{NET}_2
\]

This reaction presumably takes place by a mechanism analogous to (217) or (218).

Aminophosphines have been shown to undergo a similar reaction with aldehydes. When dimethylaminodiphenylphosphine and benzaldehyde are heated to 120\degree C, a vigorous reaction takes place to give a highly crystalline compound which contains nitrogen and phosphorus and analyses for C_{21}H_{22}NOP. From its N.M.R. spectrum, which shows a singlet integrating for six protons at 7.65 \gamma (\text{NMe}_2) and a doublet (one proton; \(J_{PH} = 10 \text{ c.p.s.}\)) at 5.7 \gamma (P-\text{CH}-), and mass spectrum, which shows a mass peak at m/e = 335, and peaks at m/e = 201(Ph_{2}P), m/e = 134(Ph-\text{CH}-\text{NMe}_2) this compound appears to be \(\alpha\)-dimethylaminobenzylidiphenylphosphine oxide (224).
As a similar reaction with paraformaldehyde gave the phosphine oxide (228), an authentic sample of which was prepared by a Mannich type condensation between formaldehyde.
dimethylamine and diphenylphosphine, and subsequent oxidation.

\[
\text{Ph}_2\text{PNMe}_2 + \text{CH}_2\text{O} \rightarrow \text{Ph}_2\text{P}-\text{CH}_2-\text{NMe}_2
\]  
(228)

\[
\text{Ph}_2\text{PH} + \text{HCHO} + \text{Me}_2\text{NH} \rightarrow \text{Ph}_2\text{P}-\text{CH}_2-\text{NMe}_2
\]

An attempt to extend this reaction to acraldehyde gave only polymeric substances.

Dimethylaminodiphenylphosphine also reacts with acetophenone to give the phosphine oxide (229) and tetraphenylbiphosphine monoxide, presumably by a base catalysed aldol condensation of two molecules of acetophenone to give dypnone, which then adds diphenylphosphine oxide, produced by the action of water on dimethylaminodiphenylphosphine.

\[
\text{Ph}_2\text{PNMe}_2 + 2\text{PhCOCH}_3 \rightarrow \text{Ph}-\text{C}-\text{CH} = \text{C}-\text{Ph}
\]

\[
\text{Ph}_2\text{P} = \text{PPh}_2 \quad \text{Ph}_2\text{PH} \quad \text{Ph}_2\text{PH}
\]

\[
\text{Ph}-\text{C}-\text{CH} = \text{CHPh}
\]  
(229)
With cyclohexanone, dimethylaminodiphenylphosphine gives tetraphenylbiphosphine monoxide as the only isolatable product.

Benzoyldiphenylphosphine also reacts with aromatic aldehydes, although vigorous reaction conditions are required. Benzaldehyde and benzoyldiphenylphosphine gave benzyldiphenylphosphine oxide, while \( m \)-chlorobenzaldehyde gave \( m \)-chlorobenzyldiphenylphosphine oxide. As yet the mechanism of this reaction has not been established.

**Experimental**

All experiments using phosphines, and similar unstable compounds, were carried out under an oxygen-free nitrogen atmosphere. All solvents were dried before use. Melting points were uncorrected.

**Preparation of Dimethylaminodiphenylphosphine.** — A solution of dimethylamine (50 g.) in ether (250 ml.) was stirred and cooled in an ice bath while a solution of chlorodiphenylphosphine (100 g.) in ether (150 ml.) was added dropwise. After the addition the reaction mixture was allowed to warm up to room temperature and stirred for 1 hr. The amine
hydrochloride was filtered off, the solution evaporated and the residue distilled (130-132°C/0.9 mm.) to give dimethylaminodiphenylphosphine (80 g.).

Reaction of Dimethylaminodiphenylphosphine with Benzaldehyde. - The phosphine (9.5 g.) and benzaldehyde (4.5 g.) were heated together at 140° for 3 hrs. The reaction mixture was cooled to give a solid which was shown to be α-dimethylaminobenzyl-diphenylphosphine oxide (10 g.) m.p. (ethyl acetate) 195-196° (Found: C, 75.35; H, 6.55; P, 4.04; Calc. for C_{31}H_{22}NOP: C, 75.6; H, 6.57; P, 4.18).

Reaction of Dimethylaminodiphenylphosphine with Paraformaldehyde. - The phosphine (7.3 g.) and paraformaldehyde (1.2 g.) were heated together at 120° for 2 hours, after which the reaction mixture was solid. Recrystallisation gave dimethyaminomethylidiphenylphosphine oxide (4.9 g.), m.p. (ethyl acetate) 184-185° (Found: C, 69.41; H, 6.79; P, 5.64; Calc. for C_{15}H_{16}NOP: C, 69.5; H, 6.95; P, 5.40).

Preparation of Dimethylaminomethylidiphenylphosphine oxide. - A mixture of dimethylamine (30 g.) and aqueous formaldehyde
solution (37%; 60 g.) was stirred for 2 mins. Diphenylphosphine (15 g.) was added dropwise and the mixture stirred at room temperature overnight. Hydrogen peroxide (15 ml; 20 vol.) was added slowly. The solid was filtered off to give dimethylaminomethylidiphenylphosphine oxide (13.5 g.) m.p. and mixed m.p. (ethyl acetate) 184-185°.

Reaction of Dimethylaminodiphenylphosphine with Cyclohexanone. - The phosphine (4.3 g.) and cyclohexanone (1.25 g.) were heated together at 140° for 12 hrs. Trituration of the reaction mixture with light petroleum (60-80° b.p.) gave tetraphenylbiphosphine monoxide (2.4 g.) m.p. (acetone-ether) 166-167° (lit. 167°).

Reaction of Benzoyldiphenylphosphine with Benzaldehyde. - Benzoyldiphenylphosphine (1.7 g.) and benzaldehyde (1.2 g.) were heated together at 190° for 14 hrs. On cooling the reaction mixture crystallised to give benzylidiphenylphosphine oxide (0.85 g.), m.p. and mixed m.p. (ethyl acetate) 195-196°.

A similar reaction with benzoyldiphenylphosphine and m-chlorobenzaldehyde gave m-chlorobenzylidiphenylphosphine oxide (42%) m.p. and mixed m.p. (ethyl acetate) 162-163°.
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