PHOSPHORUS NITROGEN YLIDS

by

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ABSTRACT

The preparation of a series of new iminophosphoranes, the imino-1, 2, 5-triphenylphospholes or phospholimines is described and some of their chemistry has been investigated. The preparative studies have involved the reaction of 1, 2, 5-triphenylphosphole both with azides and with nitrenes and nitrenoid species.

The thermolysis of \( \text{N-}(\alpha\text{-nitrophenyl})-1, 2, 5\text{-triphenylphospholimines}\) at 150° has been found to provide a novel route to benzofurazans. This reaction is not found with the corresponding triethylphosphorimidates of triphenylphosphinimines. Kinetic and mechanistic studies of this reaction are described and a mechanism postulated.

The reaction of the phospholimine diene system with dienophiles has also been studied. When the dienophile is dimethyl acetylenedicarboxylate, extrusion of the phosphorus bridge occurs. Attempts to trap this fragment, a P\(^{V}\) analogue of nitrene, however, met with no success.

Potential routes to \( \alpha\text{-nitrenophenylcarbene}\) by thermolysis of \( \text{N-}(\alpha\text{-acylphenyl})\text{iminophosphoranes}\) have been investigated. The products isolated, however, suggest that inter- rather than intra-molecular Wittig-type reactions take place.
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INTRODUCTION

Preamble

The first recorded preparation of elemental phosphorus is due to a German alchemist named Brand in 1669. He obtained a sample of a liquid which emitted light as a residue from the distillation of large volumes of human urine. Boyle repeated and published this work in 1680. Boyle's assistant Hankwitz is of note as he must probably be considered the first commercial manufacturer of elemental phosphorus, a market which he monopolised for the next fifty years.

It was believed originally that phosphorus was the element, fire. However Lavoisier showed that phosphorus gained weight on burning in air and used this as part of his evidence to explode the Phlogiston theory.

The first large scale use of phosphorus was probably in the manufacture of matches, which led Arthur Albright in 1850 to introduce the first large capacity commercial plant. However it was not until the large expansion of the plastics industry and the discovery of the fire retardant, insecticide and other properties of phosphorus compounds that manufacture mushroomed.

This thesis is concerned with phosphorus nitrogen ylides, compounds which, themselves, have found some commercial application as light stabilisers, fungicides, bactericides, fire retardants and pigments. Polymeric phosphinimines have been found to possess useful properties as lubricants, fibres, varnishes and dielectric materials. Phosphinimines have also been used as oil additives. As most of the work in this present study has been concerned with the phosphinimines of 1, 2, 5-triphenylphosphole (phospholimines) the introduction which follows will describe the preparation and properties of both the phosphole nucleus and the phosphorus-nitrogen imine bond.
Phosphole chemistry is only twenty years old, the first derivative, 9-phenyl-9-phosphafluorene (1), being prepared by Wittig and Giesler\(^1\) in 1953. The first simple phosphole, 1, 2, 3, 4, 5-pentaphenylphosphole was reported simultaneously by two groups in 1959.\(^2,^3\) The parent phosphole (2) has not been prepared although the parent of (1), 9-phosphafluorene has recently been reported.\(^4\)

\[(\text{1})\]

\[(\text{2})\]

Several reports of 1-H-phospholes containing pentavalent phosphorus have been made,\(^5,^6,^7,^8,^11\) but largely due to Tebby and co-workers\(^9,^{10},^11\) none now remain unchallenged.

The following sections are concerned exclusively with the preparation and properties of simple 1-H-phospholes containing trivalent phosphorus.

**Preparation of Simple Phospholes.**

As mentioned above the preparation of 1, 2, 3, 4, 5-pentaphenylphosphole was reported independently by two groups in 1959. Leavitt, Manuel and Johnson\(^2\) prepared 1, 4-dilithio-1, 2, 3, 4-tetraphenylbuta-1, 3-diene (4) and allowed it to react with dichlorophenylphosphine to yield the phosphole (3). The same group later extended the reaction, with Matternas and Lehmann,\(^12\) to prepare the corresponding arsoles, stiboles, stannoles and germanoles.

Braye and Hubel\(^3\) reported a second route to (3) in the same year by the reaction of the iron carbonyl complex of diphenylacetylene,
$\text{Fe}_2(\text{CO})_6(\text{PhC} \text{CPh})_2$ with dichlorophenylphosphine.

Braye, Hubel and Caplier\textsuperscript{13} later reported a third synthesis of (3) by the action of disodium phosphide on 1,4-diodo-1,2,3,4-tetraphenylbuta-1,3-diene.

Most of the recent syntheses of phospholes fall into one of two main groups: these starting with the McCormack reaction\textsuperscript{14} and those using the method of Märkli and Potthast.\textsuperscript{15}

The McCormack reaction is the reaction between a dihalophosphine and a buta-1,3-diene to yield a 1,1-dihalophosphol-3-ene (5) which on hydrolysis gives the phosphol-3-ene-1-oxide (b). Howard and Donadio\textsuperscript{16} have developed a bromination and dehydrobromination procedure which converts the phosphol-3-ene-1-oxide to the phosphole-1-oxide. A similar approach has been reported by Westheimer\textsuperscript{17} using N-bromosuccinimide to brominate the phosphol-3-ene in the 2-position. Dehydrobromination again gives the phosphole oxide.

Quin\textsuperscript{18} and Märkli\textsuperscript{19} have extended the Howard and Donadio procedure in their preparations of 1-methyl (8a) and 1-phenylphosphole (8b) respectively. This involves the deoxygenation of the intermediate 3,4-dibromophospholane-1-oxide (7) with a silicon reagent such as trichlorosilane or phenylsilane. Dehydrobromination of the resulting 3,4-dibromophospholane (9) yields the phosphole (8).

A more direct synthesis from a McCormack adduct has been reported by Mathey\textsuperscript{20,37} involving the dehydrobromination of 1,1-dibromo-1-phenylphosphol-3-ene (10) with 1,5-diazabicyclo[5,4,0]-undec-5-ene (DBU). When butyl lithium was used as base the product was the 1-phenylphospholene (11).
Cookson et al. have reported a synthesis of 1, 2, 5-triphenylphosphole by heating 1, 4-diphenylbuta-1, 3-diene with dichlorophenylphosphine at 210-220°. The authors claim that the first step is 1,4-addition to the butadiene followed by spontaneous dehydrochlorination. In support of this they demonstrated that no reaction took place when the diene was heated under the same conditions with dichlorophenylphosphine oxide. Against this mechanism Hughes reports that all attempts to perform the reaction using other dichlorophosphines on the diene, or to pyrolyse other McCormack adducts have met with no success. Similarly all attempts to isolate the
intermediate phospholene failed. As will be seen results obtained in this laboratory cast further doubt on the simple scheme proposed.

The second general method is due to Märkl and Potthast following similar known preparations for pyrroles and thiophenes. The synthesis involves the treatment of 1,4-diaryl or 1,4-dialkylbuts-1,3-diyynes with phenylphosphine in benzene or benzene/tetrahydrofuran in the presence of catalytic quantities of butyl or phenyl lithium. Replacement of the phenylphosphine with bis-(hydroxymethyl)phenylphosphine in pyridine was also found to give phospholes, but in lower yield.

\[
\begin{align*}
R_1\text{C} \equiv \text{C} &- \text{C} \equiv CR_2 \\
&\xrightarrow{\text{PhPH}_2/C_6\text{H}_6}\text{ or } \text{Ph(CH}_2\text{OH)}_2/C_5\text{H}_5\text{N} \\
\end{align*}
\]

\text{Scheme 1}

The first phosphole containing only alkyl groups on the ring, 2,5-dimethyl-1-phenylphosphole was prepared in this way.

1-Phenylphospholes are reported to react with potassium in dioxan and lithium in tetrahydrofuran forming the phosphacyclopentadienide anion (12).

\[
\begin{align*}
R^3 &\xrightarrow{2\text{Li}} R^3 \text{P}^- & R^3 = R_1 = \text{Ph} \\
R^2 &\xrightarrow{\text{H}_2\text{O}} R^2 \text{P}^+ & R^2 = R^3 = \text{Ph}, \text{H} \\
R^1 &\xrightarrow{\text{RX}} R^1 \text{P}^- & R^1 = R^4 = \text{Ph} \\
\end{align*}
\]
The ion will react with water to produce a 1-H-phosphole (13) or with an alkyl halide to form a 1-alkyl phosphole (14).

1-t-Butylphospholes have been prepared by Mathey\textsuperscript{34} from 3- and 3,4-dimethyl phospholes by reaction with t-butyl lithium:

\[
\begin{array}{c}
\text{Me} & \text{Me} \\
\text{P} & \text{t-BuLi} \\
\text{Ph} & \text{t-BuLi} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{Me} & \text{Me} \\
\text{P} & \text{t-Bu} \\
\text{PhLi} & \text{PhLi} \\
\end{array}
\]

\textbf{Scheme 2}

Similarly the phenyl group may be replaced by n-butyl.

The Aromatic Character of Simple Phosphole Systems.

Since the first preparation of the phosphole system it has attracted much attention as a potential aromatic system. At first glance it would appear to be structurally and electronically similar to pyrrole which is considered to have aromatic character by virtue of delocalisation of the nitrogen lone pair.

The chemical behaviour of phospholes has been taken to indicate a lack of aromatic character. They readily form oxides, sulphides, selenides and quaternary salts. Triphenylphosphole has also been shown to form imines\textsuperscript{24} although more forcing conditions are required than for triphenylphosphine. Similarly the diene system will undergo Diels-Alder reactions,\textsuperscript{3,13,21} but again forcing conditions are required; more drastic, in fact, than for furan derivatives which are considered to possess aromatic character. Quin,\textsuperscript{18} in his study of 1-methylphosphole, found that it was considerably less basic than would be expected for a tertiary phosphine. The phosphole was not extracted from pentane even with 2N hydrochloric acid while the 1-methyl-3-phospholene was readily extracted. When 6N acid was used the phosphole was destroyed presumably by initial protonation followed by ring opening and polymerisation.
Brown\textsuperscript{25} has pointed out, basing his calculations on a planar aromatic model of phosphole, that the energy required for quaternary salt and oxide formation would be considerably higher for pyrrole than for phosphole. X-Ray measurements\textsuperscript{29,30} have since shown phospholes to be puckered but the basis of the argument may still have some validity. Thermochemical measurements by Millar\textsuperscript{26} show the dissociation energy of the $P=O$ bond in 1, 2, 3, 4, 5-pentaphenyl phosphole to be considerably lower than for other phosphine oxides, and this, it has been suggested, may be a measure of the enhanced stability of the phosphole system due to conjugation of the phosphorus lone pair with the diene system.

Several groups have attempted to estimate the aromaticity by use of N. M. R. Märkl\textsuperscript{15} has noted the similarity in proton magnetic shifts in 2, 5-dimethyl-1-phenyl phosphole and the corresponding dimethylfuran, thiophene and pyrrole and concludes that the phosphole may be aromatic. Märkl\textsuperscript{19} has also noted the similarity between the spectra of 1-phenylphosphole and $N$-phenyl pyrrole. In agreement Quin\textsuperscript{18} has shown the similarity between the spectra of 1-methyl phosphole and $N$-methylpyrrole. Quin also states that the low field $^3P$ N. M. R. may be considered as resulting from delocalisation of the lone pair.

Mislow et al.\textsuperscript{27} have measured the barriers to inversion in a series of substituted phospholes, a phosphindole and a 9-phosphafluorene by N. M. R. and compared these with model compounds. The simple phospholes showed an extremely low inversion barrier which is attributed to the favourable planar transition state due to increased $(3p-2p)\pi$ delocalisation. The benzophosphole and dibenzophosphole showed higher inversion barriers and thus it is concluded that while simple phospholes show evidence for some conjugation, annulation by benzene rings disrupts the aromatic character. If the assertion, that lowering of inversion barriers is a measure of the aromaticity of the phosphole nucleus, is correct, then Bundgaard and Jakobsen\textsuperscript{28} have shown that it is possible to
rationalise the $^{13}$C N.M.R. of 1-phenylphosphole to indicate aromatic character.

Two phospholes have been examined by X-ray crystallography. Quin et al. $^{29}$ have compared the structure of 1-benzylphosphole with the structures of furans, pyrroles and thiophens. He concluded that the P-C$_2$ bond was significantly shorter than the sum of the single bond radii and that the contraction was of similar magnitude to that of the other heteroaromatics. Similarly the C$_2$-C$_3$ and C$_3$-C$_4$ bonds are comparable in length with those found for the other systems. However they have also shown by microwave spectroscopy that the ring is puckered, while the pyrrole ring is flat, but attribute this to the conformational stability of phosphorus compared to nitrogen which has a low inversion barrier. On the other hand, Ozbirn et al. $^{30}$ have measured the bond angles and lengths of 1, 2, 5-triphenylphosphole and state that the P-C$_2$ bond shortening is not significant although it differs by only 0.04 Å from Quin's $^{29}$ 'significantly' shortened bond. It is also shown $^{30}$ that the ring of 1, 2, 5-triphenylphosphole is puckered and these authors conclude that the structural evidence would indicate little or no delocalisation.

Perhaps the most significant evidence produced to date is due to Märlkl et al. who have studied the photoelectron spectra of two phospholes and shown that they are non-aromatic. Comparison was made between the spectra of 1-phenylphosphophole, 1-phenylphospholane, 2, 5-dimethyl-1-phenylphosphole and 2, 5-dimethyl-1-phenylphospholane. The addition of methyl substituents caused the ionisation potential of the diene system to change but in all cases the ionisation potential attributed to the lone pair on phosphorus remained constant. Hence, the authors conclude that the phosphole nucleus exists as a diene unconjugated to the phosphorus atom.

Thus, in spite of the N.M.R. evidence, it would seem that the phosphole ring is non-aromatic. Mathey $^{35}$ has described the photoelectron spectral evidence as 'practically irrefutable that phospholes possess very little aromatic character at least in the ground state.'
However, if there is no involvement of the lone pair, then it is difficult to explain the reduced nucleophilicity and basicity of phospholes as compared with phosphines. The conclusion of Quin\textsuperscript{18} that 1-methylphosphole 'may be properly included in the family of heteroaromatics with suitable allowance for the unique character of phosphorus' may still be a useful viewpoint when examining certain aspects of phosphole chemistry but it is now clear that the extent of aromaticity is not of the same order as pyrroles, thiophenes and furans.

The Reactions of Simple Phospholes

It is convenient to divide the reactions of phospholes into two groups: reactions at phosphorus and reactions involving the diene system.

a. Reactions at Phosphorus

Many of the reactions involving the phosphorus atom are paralleled by familiar reactions of simple phosphines. Phospholes like phosphines form oxides, sulphides, quaternary salts, imines, inorganic complexes and there is one report of P-dibromide formation.\textsuperscript{21}

Oxidation of simple phospholes is normally carried out with hydrogen peroxide\textsuperscript{13, 19, 21} although solutions of phospholes lacking phenyl substituents such as 1-methylphosphole and 1-benzylphosphole oxidise spontaneously in air.\textsuperscript{13} Sulphides and selenides are prepared by heating the phosphole with the element in benzene or xylene.\textsuperscript{13, 19, 21} Sulphides may also be prepared by heating the phosphole with sodium polysulphide in ethoxyethanol.\textsuperscript{3, 13}

There is one report of a P-dibromide.\textsuperscript{21} This was prepared by heating 1, 2, 5-triphenylphosphole with bromine in carbon tetrachloride. No bromination of the ring was observed. The dibromide, isolated as a red solid, rapidly hydrolysed in air to the phosphole oxide.

Quaternary salts have been formed by the reaction of methyl
iodide and ethylbromoacetate with 1, 2, 5-triphenylphosphole and methyl iodide with 1, 2, 3, 4, 5-pentaphenylphosphole. An attempt to quaternise 1, 2, 5-triphenylphosphole with p-nitrobenzenediazonium fluoroborate was unsuccessful and the phosphole was recovered unchanged. The alkaline decomposition of 1, 2, 5-triphenyl- and 1, 2, 3, 4, 5-pentaphenylphosphonium iodides has been studied by Bergesen. The reaction was found to proceed with ring opening being kinetically first order in phospholium salt and first order in hydroxyl ion. The mechanism is believed to proceed via an unstable hydroxyphosphorane (15) which then ring opens with proton migration to give (1, 4-diphenylbuta-1, 3-dienyl)methyl phenylphosphine oxide (16).

Treatment of 1-(ethoxycarbonylmethyl)-1, 2, 5-triphenylphosphonium bromide with 4N sodium hydroxide gives rise to a stable phosphonium ylid. Campbell et al. state that this ylid is stable in boiling cyclohexanone. Hocking has shown that reaction does take place but much more slowly than with the triphenylphosphine analogue. This, of course, may be a steric effect and not due to any essential difference in the nature of the PC bond. It was also found to be less reactive and less stereospecific in its reactions with other ketones and aldehydes. Hocking, however, does suggest that it might have some synthetic value in selective alkene formation in dicarbonyl compounds.

Matthey has described a rearrangement which is also likely to involve the intermediacy of a phosphonium salt. Treatment of certain phospholes with benzoyl chloride followed by an aqueous work-up gives 2-phenyl-2-hydroxyphosphorin oxides (17).
presence of catalytic quantities of sodium hydride this latter compound ring-expands to a (7-phenyl)-1-oxa-2-phosphacyclohepta-4, 6-diene (18).

\[
\begin{align*}
R^1 &= \text{Ph}, \quad R^3 = R^4 = \text{Me}. \\
R^1 &= \text{Me}, \quad R^3 = R^4 = \text{Me}. \\
R^1 &= \text{n-Bu}, R^3 = R^4 = \text{Me}. \\
R^1 &= \text{Ph}, \quad R^3 = R^4 = \text{H}. \\
R^1 &= \text{Ph}, \quad R^3 = \text{Me}, R^4 = \text{H}. 
\end{align*}
\]

The reaction was found not to work in the case of \( R_1 = \text{t-butyl} \) and this will be discussed at the end of this section. (Page 15)

The metal complex formation of 1, 2, 5-triphenylphosphole and 1, 2, 3, 4, 5-pentaphenylphosphole has been studied in some detail. The products of the reaction of the phospholes with iron carbonyls give both \( \sigma \) and \( \pi \) complexes. The reaction of 1, 2, 5-triphenylphosphole with the hexacarbonyls of Cr, Mo, W and the tetracarbonyl of Ni gives the \( \sigma \) phosphine-type complex exclusively.

Imines of 1, 2, 5-triphenylphosphole (19) and 2, 5-di-t-butyl-1-phenylphosphole (20) have been reported by Gee by the reaction of
the phosphole with azides (19a, b) and by the reaction of chloramine T. (19c)

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{N} \quad \text{Ph} \\
19 & \\
\text{Ph} & \quad \text{t-Bu} \\
\text{t-Bu} & \quad \text{Ph} \\
20 & \\
\end{align*}
\]

\(X = (a) \text{ Ar} \)
\( (b) -\text{CO}_2\text{Et} \)
\( (c) -\text{SO}_2-\text{p-Tolyl} \)

Formation of phospholimines requires temperatures of 80-100° which are considerably more severe than the conditions required for phosphinimine formation which in the absence of \(\alpha\)-carbonyl or nitro groups will react with loss of nitrogen at room temperature. In the presence of these groups the phosphatriazene is formed at room temperature. The corresponding intermediate phosphatriazene (21) was not observed

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{N} \quad \text{N}_2\text{R} \\
21 & \\
\end{align*}
\]

This is because the reduced nucleophilicity of the phosphorus in 1, 2, 5-triphenylphosphole, to which reference has already been made, makes necessary the use of conditions under which the corresponding phosphatriazene will decompose readily.

As has already been mentioned 1, 2, 5-triphenylphosphole and 1, 2, 3, 4, 5-pentaphenylphosphole react with alkali metals to form phosphacyclopentadienide anions. Besides the preparation of parent 1-H-phospholes and 1-alkylphospholes the reaction has been used to
prepare spiro (22a, b) and bispiro (22c) phosphonium salts by alkylation with dibromides.

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

\[
\begin{align*}
\text{Br} & \quad \text{(CH}_2\text{)_nBr} \\
n=2 & \quad n=4 \\
\end{align*}
\]

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

\[
\begin{align*}
\text{Br}^{-} & \quad 2\text{Br}^{-} \\
n=5 & \quad n=2 \\
\end{align*}
\]

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

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

In the cases \( n = 3, 6 \) polymeric material is formed.

Hughes and Srivanavit have reported a preparation of 3, 4, 5-triphenyl-4-phosphabicyclo[3, 1, 0]hex-2-ene-4-oxide (23) by the alkaline hydrolysis of 1-iodomethyl-1, 2, 5-triphenylphosphonium iodide (24).

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

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

The authors proposed three schemes for this reaction but could not differentiate between them. They postulate the formation of an intermediate hydroxyphosphorane followed by either a 1, 2 or a 1, 3 shift of the iodomethyl group. They point out that if this is the case, an intermediate of the type (25a, b) may be isolable.
Mathey reported two reactions which he proposed were electrophilic attack on the ring carbons of the phosphole ring. He proposed that the 2-position might be electron rich by virtue of the resonance form (26).

The reactions are protonation of 3, 4-dimethyl-1-phenylphosphole or 3, 4-dimethyl-1-alkylphosphole and attack of benzoyl chloride or 3, 4-dimethyl-1-t-butylphosphole. It is now believed in the light of the work of Märkl and Hughes that the mechanism of each of these reactions involves initial attack on the phosphorus followed by a 1, 2-shift. (Scheme 3,4).
When the 3-methyl-1-t-butylphosphole was used the product was 1-t-butyl-3-(benzoyloxy, phenyl methylene)-4-methyl phospho]ene. (27).

The authors propose a stepwise transfer of the benzoyl group from phosphorus to the 2- and finally 3-position on attack of hydroxide ion. Enolisation and attack by further benzoyl chloride gives the final product.

Nucleophilic displacement of phenyl from phosphorus in various phospholes by n-butyl and t-butyl lithium has been discussed in part a of this section. 34, 37

The reactions of phospholes and their derivatives with dienophiles will be considered in the second part of this section. However, dimethyl acetylenedicarbonylate has been shown by Hughes and Uaboonkul 5 to react with 1, 2, 5-triphenylphosphole to give a 2:1 adduct for which they proposed the spiran structure (28) based on earlier reports of pentavalent phosphole formation. 6, 7, 8 Warming the adduct was reported to give (29) via (30) which then underwent an
internal Diels-Alder reaction.

Tebby,\textsuperscript{10} in a more detailed study refuted this and showed that the initial adduct is (31) and argues that the intermediate is a zwitterionic species. The product found after rearrangement was shown to be the 9-membered cyclic phosphine (32). (Scheme 5)
b. Reactions of the Diene System

For convenience these will be further subdivided into 1, 2 and 1, 4-additions.

1, 2-Additions

Cookson et al. 21 have investigated the reactions of 1, 2, 5-triphenylphosphole with methyl diazoacetate and diazomethane. When methyl diazoacetate is left for prolonged periods in a slurry with triphenylphosphole or its oxide a 2-pyrazoline (33) was obtained. This compound decomposed in a solvent above 140° in the presence of copper to give either (34) or (35) with (34) seeming to the authors the most likely structure. One of the authors Hughes, 40 however, states categorically that the product has the structure (35) in a subsequent paper without presenting further evidence.

![Structures](image)

When heated in boiling dioxan 1, 2, 5-triphenylphosphole oxide reacts with methyl diazoacetate to give (35) directly. This is the only reported case of ring expansion of a simple phosphole to give a simple phosphorin.

The phosphole oxide reacted with diazomethane to give the 1-pyrazoline (36). This decomposes readily to give the cyclopropane (37). 21 Hughes 40 reports that deoxygenation of the phosphorus atom with trichlorosilane gives the 2-pyrazoline (38), the acid conditions promoting a prototropic shift. The cyclopropane (37) can also be obtained directly by photolysis of diazomethane in the presence of phosphole oxide. 21
Attempts to add dichlorocarbene and dibromocarbene have not succeeded. ⁴⁰

Hughes and Srivanavit ⁴⁰ have investigated the photolysis and pyrolysis of (37) in search of further routes to the phosphorin system. The products they obtained were derivatives of the 4,4'-biphosphorin system, (39) and (40) by pyrolysis and photolysis respectively.

Barton and Nelson ⁴⁷ have observed a [2+2] photodimerisation of 1, 2, 5-triphenyl phosphole to give (41a, b) and a [2+2] cycloaddition with 1, 1-dimethyl-2, 5-diphenylsilacyclopentadiene. The oxide also gives a photodimer but it is implied ⁴¹ to be a Diels Alder [2+4] adduct.
Kashman and Awerbouch\textsuperscript{46} have reported a thermal [4+2] addition of 3,4-dimethyl-1-thio-1-phenylphosphole with tropone (Scheme 6).

\begin{center}
\textbf{Scheme 6}
\end{center}

1,4-Additions

1,4-Additions are Diels-Alder reactions with dienophiles and the diene system of the phosphole ring. In some cases stable adducts have been isolated but especially where acetylenic dienophiles are concerned cheletropic extrusion of the bridgehead phosphorus fragment, and aromatisation of the remaining part of the molecule occurs.

Phosphole oxides and sulphides with no aryl substituents show a strong tendency to dimerise, in analogous fashion to cyclopentadiene, one molecule reacting as diene, the other as dienophile. Westheimer\textsuperscript{41} was only able to identify 1-ethoxyphosphole-1-oxide by trapping it with cyclopentadiene. Phosphole oxides and sulphides with aryl substituents tend to be more stable. However, Campbell
et al.\textsuperscript{21} have reported that 1, 2, 5-triphenylphosphole oxide forms a photodimer, and the sulphide also forms a dimer on exposure to daylight. Similar dimers have, very recently, been reported by Quin\textsuperscript{154} from phosphonium salts where there are no C-substituents. It appears, however, that salts of 1, 3-dimethyl phosphole may also be dimeric.\textsuperscript{154}

The first report of a diels-Alder reaction of a simple phosphole was due to Braye, Hübel and Caplier.\textsuperscript{13} They reacted 1, 2, 3, 4, 5-pentaphenylphosphole with dimethyl acetylenedicarboxylate and maleic anhydride in a sealed tube at 150°. The maleic anhydride formed the expected adduct (42) while the reaction with the acetylene resulted in extrusion and the formation of dimethyl 3, 4, 5, 6-tetraphenylphthalate (43) presumably via the intermediacy of (44). In this latter reaction no well defined phosphorus compound was isolated.

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

Campbell et al.\textsuperscript{21} have reported the reactions of various dienophiles with 1, 2, 5-triphenylphosphole and its oxide. When heated with maleic anhydride 1, 2, 5-triphenyl phosphole gave 3, 6 diphenylphthalic anhydride (45) but in low yield. Extrusion was also observed in the reaction of the phosphole, and the phosphole
oxide, with dimethyl acetylenedicarboxylate to give the phthalate (46). When the phosphole oxide was heated with dimethyl fumarate, 3,6-diphenylcyclohexa-3,5-diene-trans-1,2-dicarboxylate (47) was obtained.

![Chemical Structures](image)

The phosphole oxide was found to give the normal adducts with maleic anhydride and acrylonitrile.

Schmidt has observed extrusion in the reaction between 1,2,5-triphenylphospholes and benzyne, obtaining as product 1,4-diphenylnaphthalene (48).

![Chemical Structure](image)

He has also reported the preparation of the expected adduct from acetylene dicarboxylate (49) and triphenylphosphole oxide by the elegant route shown. (Scheme 7)

Attempts to produce the analogous adduct of 1,2,5-triphenylphosphole by deoxygenation on phosphorus of (48) with silanes gave the dihydrophthalates (50) or (51) depending on the silane employed.
Westheimer$^{43,44}$ has found that 3,4-dimethyl-1-ethoxyphosphole-1-oxide will react with maleic anhydride to give the normal adduct (52a) which was characterised by hydrolysis, to the acid (52b). 3,4-Diphenyl-1-ethoxyphosphole oxide is less reactive towards dienophiles but reacts with dimethyl acetylene dicarboxylate with extrusion of the metaphosphite fragment to give the phthalate (53).
Gee has investigated the reactions of phospholimines with dimethyl acetylenedicarboxylate. The products were found to depend on the nature of the group X. When X was electron withdrawing the phthalate (54) was formed. When X was electron releasing attack was found also at the P-N bond yielding ethylphosphinidenes (55).

This latter reaction is discussed elsewhere.

This section has been concerned solely with the chemistry of simple 1-H-phospholes and in particular the more recent work on such systems. No attempt has been made to discuss the preparation or reactions of other phosphorus heterocyclic systems.

The chemistry of phosphole as it stood in 1969 has been comprehensively reviewed by Hughes and Srivanavit. Earlier work on phosphorus heterocycles has been reviewed by Mann and Märkl, more recent developments by Mann and Berlin and Hellwege.
The Chemistry of Iminophosphoranes

Iminophosphorane is the generic term for compounds of structure (56). They are isoelectronic with phosphonium ylids and can be represented also by the resonance structure (57), the exact nature of the P-N bond being determined by the degree of overlap between the nitrogen and the phosphorus d-orbitals.

\[
\begin{align*}
R_3P=NR' & \rightleftharpoons R_3P-\overline{NR}' \\
56 & 57
\end{align*}
\]

a. Preparation

Iminophosphoranes were first prepared in 1919 by Staudinger and Meyer, by the action of azides on tertiary phosphines, and the reaction has become known as the Staudinger reaction. The reaction is known to go via an intermediate triazene (58), some of which are isolable. Such phosphatriazenes are known as Staudinger adducts.

\[
\begin{align*}
R_3P=N(N_2)R' & \quad R_3P=N-N=N-R' \\
58 & 58a
\end{align*}
\]

Isolable adducts have been prepared from sulphonyl azides. Two structures have been proposed for this adduct (58a, b), but infrared studies on \({}^{15}\text{N}\) labelled compounds have shown that the structure of the compound derived from tosyl azide and triphenylphosphine is of the type (58a). No azide absorption is found in the infrared. Franz and Osuch, however, found that the adduct with triphenyl phosphine and benzenesulphonyl azide shows an azide absorption in the infrared in solution but not in the solid state. Leffler, however, has postulated that triazine formation is reversible, and this would explain this observation. Leffler has
also postulated a mechanism for phosphinimine formation (Scheme 8).

\[
\begin{align*}
R_3P\equiv N\equiv N\equiv N\equiv R' & \rightarrow R_3P\equiv N\equiv N\equiv N\equiv R'
\end{align*}
\]

\[
\begin{align*}
R_3P\equiv N\equiv N\equiv N\equiv R' & \rightarrow R_3P\equiv N\equiv N\equiv N\equiv N_2
\end{align*}
\]

\textbf{Scheme 8}

Isotopic labelling studies have shown that the two terminal azide nitrogens are always lost.

Thayer and West, \textsuperscript{54} however, report that the adduct formed with triphenylsilyl azide and triphenylphosphine shows an azide absorption in both the solid and in solution. Johnson \textsuperscript{55} has suggested that the formation of the adduct formulated as (59) may be formed as a result of extra stability gained from delocalisation of the 3d-orbitals in both silicon and phosphorus. Thermal decomposition results in the formation of the phosphinimine (60).

\[
\begin{align*}
\text{Ph}_3P\equiv N\equiv \text{SiPh}_3 & \quad \text{Ph}_3P\equiv N\equiv \text{SiPh}_3
\end{align*}
\]

59

60

Support for the unusual structure of (59) comes from the work of Leffler, \textsuperscript{56} who has observed that triphenylmethyl azide and 9-azidofluorene, form adducts with triphenylphosphine, which show no azide absorption. The triazenes decompose at almost the same temperature as the free azide and give azide decomposition products rather than phosphinimines. Leffler has rationalised this by stating that there is too much steric crowding to form the necessary four membered transition state in order to permit elimination of nitrogen. Were (59) a similar, linear adduct the same would
probable apply.

Stable triazenes may also be formed where there is an aryl with an ortho-group, capable of interacting with the nitrogens, as in the phosphatriazine derived from o-azidobenzoic acid and triphenylphosphine. The triazene is stable in the solid state to 150° but decomposes smoothly to the phosphinimine if heated in toluene under reflux. The infrared spectrum shows the OH stretching frequency to have moved to longer wavelength, indicating hydrogen bonding. It is probable that the best representation is (61).

\[
\text{Ph}_3\text{P}-\text{N} = \text{N} + \text{H}^-\text{O}^-
\]

Chemical support for the linear triazine structure has been found by Mosby and Silva. The reaction of 2, 3-bisazidonaphthoquinone with triphenylphosphine gives in addition to the expected bisphosphinimine a phosphinyl derivative of naphtho (2, 3-d)triazole-dione, the formation of which can only be rationalised by assuming a linear triazine intermediate. (Scheme 9.)

The Staudinger reaction has fairly general application and has been used to prepare compounds of the type (56) R' - alkyl, aryl, acyl, sulphonyl, carboalkoxy, carbamoyl, organophosphorus, organometallic and polymers with the P=N function incorporated in the backbone. (Scheme 10)

The rate of the Staudinger reaction is determined by the nucleophilicity of the phosphorus reactant and the electrophilicity of the azide. \(^{54,57,58,59}\) Hence studies have shown that \((\text{C}_5\text{H}_{10}\text{N})_3\text{P} > \text{Et}_3\text{P} > \text{Ph}_3\text{P} > (\text{EtO})_3\text{P} > (\text{PhO})_3\text{P} > \text{PCl}_3\) phosphorus trichloride giving no reaction. Similarly in the case of phenyl and benzoyl azides it has been shown that \(p-\text{NO}_2 > p-H > p\text{MeO}\).
Many routes to iminophosphoranes involve the intermediacy of a phosphonium salt. Tetraphenyolphosphonium chloride (62) is converted to triphenylphosphinimine (64) via the intermediate triphenylphosphonium amide (63).
Chloramine and its derivatives also react with phosphines to give the intermediate phosphonium salt (65) which in the presence of base yields the phosphinimines. Bases used in this reaction have included ammonia, pyridine, triethylamine, sodamide, magnesium hydride, tetramethylguanidine and lead tetraacetate. Salts of structure (65) have also been prepared by other means and reacted to give the phosphinimine.

\[
\text{Ph}_3\text{P} + \text{ClNHR} \rightarrow [\text{Ph}_3\text{PNHR}]^+ \rightarrow \text{Ph}_3\text{P}=\text{NHR}
\]

When the sodium salt of the chloramine is used the addition of base is not necessary. A third variation on the use of N-chloro-compounds is due to Schönberg and Singer who have prepared sulphonylphosphinimines by treating N,N-dichlorosulphonamides and triphenylphosphine in the presence of copper powder.

N-Chloriminocarboxylic acid derivatives have also been used to form phosphinimines. The reaction again goes via an intermediate phosphonium salt (66).
Similarly, N-chloroamidines react with triphenylphosphine.  

\[
\text{Ph}_3\text{P} + \text{Ph}_3\text{PN}=\text{CR} \rightarrow \text{Ph}_3\text{P}=\text{NCR} \quad \text{Cl}^- \quad \text{NH}_2 \quad \text{NH}
\]

Perhaps the most convenient procedure is due to Horner and Odiger.  The method involves reacting a primary amine with a dihalotriphenylphosphorane. The reaction probably proceeds by two intermediate phosphonium salts (67) and (68). Base is required to remove the hydrogen halide evolved. In the case of anilines triethylamine is sufficient but when alkylamines are employed the reaction stops at the salt (68), unless a very strong base such as sodamide in liquid ammonia is used.

\[
\text{Ph}_3\text{PX}_2 + \text{H}_2\text{NR} \rightarrow \left[\text{Ph}_3\text{P}^+\text{NH}_2\text{R}^{-}\right] \text{Cl}^- \quad \text{Cl} \quad \text{67}
\]

\[
\text{Ph}_3\text{P}=\text{NR} \leftarrow \left[\text{Ph}_3\text{P}^+\text{NHR}^{-}\right] \text{Cl}^- \quad \text{68}
\]

The reaction has also been applied to the preparation of bisimines such as (69) from hydrazine and (70) from p-phenylene diamine.

\[
\text{Ph}_3\text{P}=\text{N-N=PPPh}_3 \quad \text{Ph}_3\text{P}=\text{N} \quad \text{N=PPPh}_3
\]

69 70
A one step route to phosphinimines has been reported, by addition of halogens to a mixture of phosphine and amine. The mechanism is presumed to go by initial reaction of the phosphine with the halogen to form the dihalophosphorane which then reacts with the amine as described above.

On heating in a solvent with phosphorus pentachloride, amides of sulphinic and carboxylic acids and anilines yield P,P,P-trichlorophosphinimines. These will react with alkoxides and Grignard reagents yielding the phosphorimidates and phosphinimines respectively.

\[
\text{Cl}_3\text{P}=\text{NSO}_2\text{Ph} \xrightarrow{\text{NaOMe}} \text{(MeO)}_3\text{P}=\text{NSO}_2\text{Ph} \\
\xrightarrow{\text{RMgX}} \text{R}_3\text{P}=\text{NSO}_2\text{Ph}
\]

The reaction of an aminophosphine with a tetrahalomethane is also believed to involve the intermediacy of a phosphonium salt. The initial product a P-halophosphinimine can be converted to the tertiary phosphinimine by use of a Grignard reagent.

\[
\text{Ph}_2\text{PNHPh} + \text{CX}_4 \rightarrow \left[\text{Ph}_2\text{PNHPh}\right] \text{CX}_3 \\
\text{Ph}_2\text{RP}=\text{NPh} \xrightarrow{\text{RMgX}} \text{Ph}_2\text{P}=\text{NPh}
\]

Two routes to phosphinimines have been reported involving a four membered transition state similar to the Wittig reaction. The driving force for such reactions is probably the formation of the P=N bond in analogous fashion to P=O bond formation in the Wittig reaction.
Phosphonium ylids of the structure (76) react with Schiff's bases to give phosphinimines and olefins.\(^{76}\)

\[
\begin{align*}
\text{Ar}_3\text{P} = \text{CHAr} & \quad \bigg[ \begin{array}{c}
\text{Ar}_3\text{P} \text{CHAr} \\
\text{R}^1\text{N} = \text{CHR}^2
\end{array} \bigg] + \text{ArCH} = \text{CHR}^2 \\
\text{Ar}_3\text{P} = \text{NR}^1
\end{align*}
\]

Similarly iminophosphoranes have been found as products in the reaction between ylids of structure (76) and nitriles.\(^{77}\) (Scheme 11).

\[
\begin{align*}
76 \text{+ PhCN} & \rightarrow \text{Ar}_3\text{P} \text{CHAr} \\
& \rightarrow \text{Ar}_3\text{P} \text{CHR}^2 \\
& \rightarrow \text{Ar}_3\text{P} \text{NCHR}^2
\end{align*}
\]

Aminophosphines have been found to react with suitably activated olefins to give phosphinimines.\(^{78}\) (Scheme 12)

\[
\begin{align*}
\text{Ph}_2\text{PNHPh} + \text{CH}_2\text{CHR} & \rightarrow \text{Ph}_2\text{P} \text{NHPh} \\
& \rightarrow \text{Ph}_2\text{P} \text{NPh}
\end{align*}
\]

N'-Tosyl phosphinimines (78) have been prepared by the reaction of triphenyl phosphine, its oxide and sulphide with N-sulphinyl-sulphonamides (77).\(^{79}\) (Scheme 13)

Several more complex triphenyl phosphinimines have been prepared by reactions of triphenyl phosphinimine itself. This has been prepared from triphenyl phosphonium chloride or by the reaction
of triphenylphosphine with chloramine as already described. A third route is the cleavage of N-trimethylsilyl-P,P,P-triphenylphosphinimine (79) in methanolic sulphuric acid. Yet a fourth route to this compound is by treating triphenylphosphine in liquid ammonia with hydroxylamine-\text{-}O\text{-}sulphonic acid. (Scheme 14)

\[
\text{Ph}_3\text{P}=\text{NSiMe}_3
\]

79

\[
\text{Ph}_3\text{P} + \text{H}_2\text{NO}_2\text{SO}_3\text{H} \rightarrow \text{Ph}_3\text{P}^+\text{NH}_2\text{HSO}_4^- \text{NH}_3(1)
\]

Scheme 14

Ph$_3$P=NH

Kirsanov et al. have reacted the phosphinimine with various reagents to form N-substituted phosphinimines. (Scheme 15) Treatment of the parent imine with alkyl iodides and acid chlorides leads only to 50\% maximum conversion as the intermediate phosphonium salt (80) is deprotonated by another molecule of phosphinimine acting as base.
\[ \text{Ph}_3\text{P} = \text{NH} \xrightarrow{\text{RCN}} \text{Ph}_3\text{P} = \text{NCR} \]
\[ \xrightarrow{\text{NF}_3\text{CO}_2\text{Et}} \text{Ph}_3\text{P} = \text{NCCF}_3 \]
\[ \xrightarrow{\text{RC(NR)Cl}} \text{Ph}_3\text{P} = \text{NCR} \]
\[ \xrightarrow{\text{BrCN or PhOCN}} \text{Ph}_3\text{P} = \text{N-CN} \]

\text{Scheme 15}

\[ \text{Ph}_3\text{P} = \text{NH} \xrightarrow{\text{[Ph}_3\text{P-NHR] X}^{-} + \text{RX}} \text{180} \]
\[ \text{Ph}_3\text{P} = \text{NR} + \text{Ph}_3\text{P} = \text{NH}_2 \]

The imines unsubstituted on nitrogen will also react with lithium, zinc, cadmium, gallium, aluminium and indium alkyls.
The lithium phosphinimines (81) have been used in synthesis. (Scheme 16)

\[
\begin{align*}
\text{Me}_2\text{PCl} & \quad \rightarrow \quad \text{Me}_3\text{P}=\text{NPM}_{\text{Me}_2} \\
+ \quad \text{Me}_3\text{P}=\text{NLi} & \quad +\text{LiCl} \\
81 & \\
\text{Scheme 16}
\end{align*}
\]

Phosphorimidates have been isolated from the reduction of nitro- and nitroso-compounds with triethyl phosphite. Bunyan and Cadogan\(^{106}\) have isolated triethyl N-dimethylaminophenylphosphorimidate from the reaction of p-dimethylaminonitroso-benzene with triethyl phosphite.

Sundberg\(^{107}\) has isolated phosphorimidates in high yields (40-50%) from the deoxygenation of o-nitroalkylbenzenes with large excess of triethyl phosphite. The corresponding nitroso compounds also gave phosphorimidates but in lower yield (5-10%). (Scheme 17).

\[
\begin{align*}
\text{R} & \quad \text{P(OEt)}_3 \\
\rightarrow & \quad \left[ \begin{array}{c}
\text{R} \\
\text{N=PO(OEt)}_3
\end{array} \right] \\
\text{R'} & \quad = \text{NO or NO}_2 \\
\text{Scheme 17}
\end{align*}
\]

Sasaki et al.\(^{86}\) have studied phosphinimine formation from triphenylphosphine and tetrazolopolyazines such as (82) and (83). They conclude from kinetic studies that nucleophilic attack by phosphorus results in transition states identical to the adducts discussed above in connection with the Staudinger reaction (84), (85).

Stoker and Baier\(^{87}\) have reported the reaction of o-aminoaroxyl radicals (86) with triphenylphosphine to give N-(o-hydroxy-
An unusual route to a phosphinimine has been reported by Bailey. Treatment of benzotrifuroxan with triphenylphosphine did not result in deoxygenation to give the benzotrifurazan as happens with triethyl phosphite but instead yields a mixture of products, the principle being 1, 3, 5-trinitro-2, 4, 6-tris(triphenylphosphinimino)-benzene a result of attack by triphenylphosphine on the nitrogen without the oxygen on each of the three rings (Scheme 18).

\[ \text{Ph}R_1 \text{N=N=PPh}_3 \]

\[ \text{Ph} \text{Ph} \text{R}_2 \text{N=N=PPh}_3 \]

\[ \text{Ph} \text{R}_3 \text{N=N=PPh}_3 \]

\[ \text{X or } Y = N \]
The Reactions of Iminophosphoranes

The iminophosphoranes react in many ways like phosphonium ylids with which they are isoelectronic. The reactivity of such compounds is dependent upon the nucleophilicity of the nitrogen and the driving force for the reaction often the formation of a phosphorus oxygen bond. It is proposed to discuss the reactions under the headings: hydrolysis, reactions involving formation of a phosphorus oxide, reactions with triple bonds and 1,3-dipoles and finally a summary of previous work on phospholimines.

a. Hydrolysis

The initial step in hydrolysis is believed to be protonation of the nitrogen atom to give a phosphonium salt (88).\textsuperscript{52b, 58} A pentavalent transition state (89) has been proposed as the hydrolysis of optically active phosphinimines goes mainly but not exclusively with inversion.\textsuperscript{88}
The ease of hydrolysis is dependent upon the basicity of the phosphinimine. Hence the parent triphenylphosphinimine which is very basic, requiring sodamide in liquid ammonia to prepare it from its conjugate acid, is hydrolysed on exposure to the atmosphere while the N-phenyl triphenylphosphinimine which is readily converted from its conjugate acid by triethylamine requires dilute acid.

Allen, Mann and Tebby have suggested the hydrolysis of N-tosyl triphenylphosphinimines as a step in the reaction between hydrated chloramine-T and triphenylphosphines to give complexes of structure (90). This seems unlikely, however, as the N-Tosyl triphenylphosphinimines are known to be weakly basic and extremely stable to hydrolysis. Purification of such compounds has even been effected by recrystallisation from ethanol/water mixtures. It is more probable, therefore, that the hydrolysis to the sulphonamide and phosphine oxide which occurs, is a reaction of some intermediate rather than of the phosphinimine itself.
Phosphorimidates $^{90}$ and iminotrichlorophosphoranes $^{72}$ hydrolyse by nucleophilic displacement on phosphorus to give phosphoramidates (91) and aminodichlorophosphine oxides (92) respectively.

Siklanch-Sohnen and Foucaud $^{91}$ have found $\alpha$-bromo-$\alpha'$-dicyanonitriles (93) will react with triphenylphosphite to form the corresponding phosphorimidate (94).

Under hydrolytic conditions a mixture of three products is found the expected phosphorimidate, the $\alpha'$-dicyanonitrile by decomposition of the phosphorimidate and a $\Delta^2$-pyrroline (96) presumed to be formed as shown (Scheme 19).
b. **Reactions Involving Loss of the Phosphorus Moiety as its Oxide.**

Appel, Bergman, and Horner have shown that phosphinimines will react with carbonyl compounds in analogous fashion to phosphonium ylides forming an imine bond with loss of the phosphine. A summary of these reactions is given below (Scheme 20).

\[
\begin{align*}
\text{Ph}_3\text{P} = \text{NPh} + \text{Ph}_2\text{CO} & \rightarrow \text{Ph}_2\text{CNPh} + \text{Ph}_3\text{PO} \\
+ \text{PhCHO} & \rightarrow \text{PhCH} = \text{NPh} + \text{Ph}_3\text{PO} \\
+ \text{PhNCO} & \rightarrow \text{PhN=C=NPh} + \text{Ph}_3\text{PO} \\
+ \text{CO}_2 & \rightarrow \text{PhNCO} + \text{Ph}_3\text{PO} \\
+ \text{S}_2\text{C} & \rightarrow \text{PhNCS} + \text{Ph}_3\text{PS}
\end{align*}
\]

**Scheme 20**

Johnson and Wong have suggested that the first step is betaine (97) formation as in the Wittig reaction. Frøyen, however, has also performed kinetic studies and has concluded that the reaction is concerted and does not involve a betaine as a free species unlike the Wittig reaction where betaines have been detected and in some cases even isolated. In support of this, Frøyen has shown that solvent polarity has little effect on the reaction rate, while the reaction is catalysed by agents capable of hydrogen bonding, which, he states, can be explained by assuming stabilisation of the transition state (98). Johnson and Wong studied
a series of N-phenyltriphenylphosphinimes (a) p-NO₂, (b) m-NO₂,
(c) m-Cl, (d) p-Br, (e) H, (f) p-Me, (g) p-OMe. A Hammett
plot showed straight line behaviour (a)-(e), (e)-(g) however, gave
a plot of opposite sign. They argued that this indicated that the
rate determining step had changed from betaine formation, to betaine
decomposition. In view of the above results, substitution of phenyl
groups on phosphorus by alkyl groups should also make betaine
decomposition the rate determining step, and a similar slowing of
rate should be observed. However, an increase of $3 \times 10^3$ was
noted. In view of this Froyen has proposed the mechanism shown
below (Scheme 21).

\[ \begin{align*}
R_3P-NR & \\
\text{O-CR}_2 & 97 \\
R_3P=NR & \\
\text{O-CR}_2 & 98 \\
\text{R}_2CNR & \\
\text{R}_3PO &
\end{align*} \]

Scheme 21

Intramolecular reactions involving phosphorus imines and
carbonyl groups have been used in several syntheses.

N-Acyl phosphinimines (99) react on heating to give nitriles
and phosphine oxides. An identical reaction has been observed
in the trihalophosphinimines. (Scheme 22).

Saunders et al. have reported synthesis for benzoxazoles and 2-substituted quinolines from 2-azidophenyl esters and 2-
azidocinnamates by treatment with triethyl phosphite (Scheme 23).
Scheme 22

Scheme 23
Zbiral has used phosphinimines in the preparation of tetrazoles. Phosphinimines react with acyl halides to form \( N \)-acyl phosphonium salts. In aprotic media these salts react with sodium azide with loss of the phosphine oxide to give the tetrazole. (Scheme 24).

The acylation may, in some cases, be done using acyl azides. Acylation with acyl cyanides gives iminonitriles (100).

Pailer and Haslinger have neatly synthesised the alkaloid nigrifactine (101).

Zbiral and Stroh have also used 2-oxophosphinimines to synthesise pyrazines (Scheme 25).
One final reaction in this class, although of no synthetic importance is worthy of mention. N-Phenyliminotriphenylphosphorane reacts with nitrosyl chloride to form an N-nitrosophosphonium salt which spontaneously decomposes to give triphenyl phosphine oxide and benzenediazonium chloride which has been trapped with 2-naphthol.\(^{101}\) (Scheme 26).
c. Reactions with Triple Bonds and 1, 3-Dipoles

Brown et al.\textsuperscript{102} have shown the phosphinimines will react with dimethyl acetylenedicarboxylate to give a 1:1 adduct, providing strongly electron withdrawing groups, such as sulphonyl, were not attached to nitrogen. The adduct obtained from N-(p-bromophenyl)-iminotriphenylphosphorane has been studied by X-ray crystallography\textsuperscript{103} and found to have structure (102). The mechanism is believed to comprise nucleophilic attack by the imine nitrogen and rearrangement of the resulting betaine-like intermediate (103).

(Scheme 27).
As already mentioned, Gee has found this reaction to occur in the phospholimine series. Activated nitriles react in a similar way this time with formation of a new phosphorus-nitrogen bond to give (104). (Scheme 28)

\[
\begin{align*}
\text{Ph}_3\text{P}=\text{NPh} + \text{N}=\text{C}\text{CF}_3 & \rightarrow \text{Ph}_3\text{P}=\text{N}-\text{C}=\text{NPh} \\
\text{Ph}_3\text{P}=\text{N}-\text{C}=\text{NPh} & \rightarrow \text{Ph}_3\text{P}=\text{N}-\text{C}=\text{NPh} \\
\end{align*}
\]

Zbiral has used this reaction in the preparation of naphtho-1,3-thiazoles and naphtho-1,3-selenazoles (104b), from the imino-phosphoranes (105a,b).

\[
\begin{align*}
\text{X-CN} & \rightarrow \text{X-CN} \\
\text{N}=\text{PPh}_3 & \rightarrow \text{N}=\text{PPh}_3
\end{align*}
\]

\[
\begin{align*}
\text{X} = \text{S} & \quad \text{Se} \\
\end{align*}
\]

Phosphinimines react with 1,3-dipoles but no instance
of a cycloadduct isolation has been reported, and the products are those of adduct decomposition. Nitrile oxides (106) and nitrones (107) are believed to form transient cyclic intermediates of structure (108, 109) which lose the phosphine oxide, producing carbodiimides (110) and formamidines (111).

\[
\begin{align*}
\text{Ph.C} &= \text{NO} \\
106 + \text{Ph}_3\text{P} &= \text{NPh} \\
\text{PhCOCH} &= \text{NPh} \\
107 + \text{Et}_3\text{P} &= \text{NPh} \\
\text{PhN}_3\text{PNPh} \\
\text{Ph}_3\text{PNPh} \\
\text{Ph} \text{N}_3\text{PNPh} \\
\text{Et}_3\text{PNPh} \\
\text{OCPh} \\
\text{NPh} \\
\text{111} + \text{Et}_3\text{PO} \\
\end{align*}
\]

Nitrile imines (112) react with iminophosphoranes to give stable betaines (113).

\[
\begin{align*}
\text{R}_1\text{C} &= \text{N}\text{NR}_2 \\
112 + \text{R}_3\text{P} &= \text{NR}_3 \\
112 \\
\end{align*}
\]

d. **Phospholimines**

1, 2, 5-Triphenylphospholimines were first prepared by Gee in 1971. They are coloured crystalline compounds and appear to
show typical iminophosphorane character; they undergo acid hydrolysis, form \( \text{N-methyl phospholium salts with methyl iodide} \) and undergo ethylphosphinidene formation with dimethyl acetylene-dicarboxylate.

\( \text{N-Phenyl-1-phenyl-dibenzophospholimine (114) had been prepared by Wittig,}^{108} \) who converted it to the \( \text{N-methyl salt (115),} \) and by treatment with phenyl lithium to the phosphorane (116). An attempt by Gee\(^{24}\) to repeat this reaction with \( \text{N-phenyl-1, 2, 5-triphenyl phospholimine (117),} \) resulted in a product tentatively identified as 1, 2, 3, 5-tetraphenylphosphole (118). Direct attack of the phenyl anion on the phosphole ring is proposed. (Scheme 29).

Attempts to produce phenyl nitrene by photolysis of (117) also failed although decomposition was noted.\(^{24}\)
Phosphorus imine chemistry has been well reviewed by Johnson, 56 by Bestmann and Zimmermann, 109 and by Zimmer and Singh. 110

e. **Trivalent Phosphorus Analogues**

There is only one authenticated account of a P=N bond where the phosphorus is in the trivalent state. 111 This is [bis(trimethylsilyl)amino][trimethylsilylimino]phosphane (119). This compound undergoes reaction with carbon tetrachloride and with alcohols. (Scheme 30).

\[
\begin{align*}
\text{(Me}_3\text{Si)}_2\text{NPF}_2 + \text{Li}^+ \text{N(SiMe}_3)_2 & \rightarrow \\
\text{(Me}_3\text{Si)}_2\text{N-P=NSiMe}_3 & \quad (53\%) \\
\end{align*}
\]

\[\text{CCl}_4 \quad \text{ROH, D} \]

\[
\begin{align*}
\text{(Me}_3\text{Si)}_2\text{NP=NSiMe}_3 \quad \text{(Me}_3\text{Si)}_2\text{NP=NSiMe}_3 \\
\text{CCl}_3 \quad \text{H, D} \quad \text{OR} \end{align*}
\]

Scheme 30
In general however attempts to prepare phosphanes of this type have led to dimeric structures. \(^{112}\) (Scheme 31).

\[
\begin{align*}
\text{PCl}_3 & \quad \rightarrow \quad (\text{ArN-PCl})_2 \quad \rightarrow \quad (\text{ArNHP-NAr})_2 \\
+ \text{ArNH}_2
\end{align*}
\]

Scheme 31
Programme of Research

In the introduction have been described the preparation and properties of the phosphole ring system and of phosphorus-nitrogen ylides. Mention has been made of the work of Gee\textsuperscript{24} who, previous to this present study, has prepared the first reported members of the series which were designated the 1, 2, 5-triphenyl-phospholimines.

The aim of the work described below has been to extend the series, investigate the limits of Gee's methods and develop new routes to the P=N bond. The remainder of the work has been concerned with two aspects of the chemistry of these compounds: firstly whether these compounds undergo any reactions which are specific to the phospholimines rather than common to iminophosphoranes in general, and secondly to investigate the diene nature of the phosphole moiety with special reference to exploiting the Diels Alder reaction as a source of reactive intermediates via cheletropic elimination.

The phospholimines were of interest also because they are highly and variously coloured. It was also, therefore, desirable that visible spectra of a series of these compounds be investigated.
EXPERIMENTAL SECTION

Abbreviations and Symbols.  

Instrumentation and General Procedures.  

1. Preparation of Azides
   (a) 1-Azido-2-nitrobenzene and analogous preparations. (Diazotisation of the amine in hydrochloric acid).  
   (b) 2,4-Dinitrophenyl Azide.  
   (c) 1,4-Diazidobenzene.  
   (d) 2-Azido-1-nitronaphthalene and analogous preparations. (Diazotisation of the amine in sulphuric acid/acetic acid mixture).  
   (e) 2-Azidobenzoic Acid.  
   (f) Tosyl Azide and other azides prepared from acid chlorides.  
   (g) Diphenylphosphinyl Azide.  
   (h) Other azides.  

   (a) N-Aminophthalimide.  
   (b) 4-Phenylurazole.  
   (c) 5-Aryl-1, 2, 5-dioxazolidin-2-ones.  

3. Preparation of Phospholes and Phosphole Oxides.
   (a) 1,4-Diarylbuta-1, 3-dienes.  
   (b) 1, 2, 5-Triphenylphosphole.  
   (c) Reaction of Dichlorophenylphosphine with 1-(4-methoxyphenyl)-4-phenylbuta-1, 3-diene.  
   (d) Reaction of Dichlorophenylphosphine with 1-Tolyl-4-phenylbuta-1, 3-diene.  
   (e) Reaction of Dichlorophenylphosphine with 1,4-Ditolybuta-1, 3-diene.
4. **Preparation of Phospholimines.**

(a) **Reaction of 1, 2, 5-Triphenylphosphole with Aryl Azides.**

1. \( \text{N}-(4-\text{Phenylazophenyl})-1,2,5\text{-triphenylphospholimine.} \)

2. \( \text{N}-(4-\text{Methoxyphenyl})-1,2,5\text{-triphenylphospholimine.} \)

3. \( \text{N}-(4-\text{Iodophenyl})-1,2,5\text{-triphenylphospholimine.} \)

4. \( \text{N}-(4-\text{Carboxyphenyl})-1,2,5\text{-triphenylphospholimine.} \)

5. \( \text{N}-(4-\text{Methoxy-2-nitrophenyl})-1,2,5\text{-triphenylphospholimine.} \)

6. \( \text{N}-(4-\text{Methyl-2-nitrophenyl})-1,2,5\text{-triphenylphospholimine.} \)

7. \( \text{N}-(2,4-\text{Dinitrophenyl})-1,2,5\text{-triphenylphospholimine.} \)

8. \( \text{N}-(2-\text{Nitro-4-trifluoromethylphenyl})-1,2,5\text{-triphenylphospholimine.} \)

9. \( \text{N}-(1-\text{Nitronaphthyl})-1,2,5\text{-triphenylphospholimine.} \)

10. \( \text{N}-(3-\text{Bromophenyl})-1,2,5\text{-triphenylphospholimine.} \)

11. \( \text{N}-m-\text{Tolyl}-1,2,5\text{-triphenylphospholimine.} \)

12. \( \text{N}-(4-\text{Cyanophenyl})-1,2,5\text{-triphenylphospholimine.} \)

13. \( \text{N}-2-\text{Benzimidazoly1}-1,2,5\text{-triphenylphospholimine.} \)

14. \( \text{N}-3-(\text{Phthalic anhydrido})-1,2,5\text{-triphenylphospholimine.} \)
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Symbols and Abbreviations

I. r. infrared
ν wavenumber
s singlet
d doublet
c complex
J coupling constant
U. V. ultraviolet
λ wavelength
m/e mass to charge ratio
b. p. boiling point
m. p. melting point
g. l. c. gas liquid chromatography
t. l. c. thin layer chromatography
h. s. l. c. high speed liquid chromatography
D. T. A. differential thermal analysis.
N. m. r. nuclear magnetic resonance.
Instrumentation and General Procedures

Infrared Spectroscopy: Perkin Elmer spectrometers 257 and 237 were most commonly employed for infrared spectroscopy. A polystyrene film was used as reference at 1603 and 1029 cm⁻¹. Liquids samples were examined as thin films, solids as nujol mulls or as a mix with potassium bromide pressed to 12 tons in a hydraulic press.

Nuclear Magnetic Resonance Spectroscopy: Spectra were obtained from a Perkin Elmer R-10 spectrometer and an A.E.I. EM360 spectrometer at a frequency of 60 MHz, and at 100 MHz from a Varian H.A. 100 instrument. Samples were examined as solutions in deuterochloroform, carbon tetrachloride or occasionally in hexadeuterodimethyl sulphoxide with tetramethylsilane as internal reference.

Mass Spectroscopy: Mass spectra were obtained with an A.E.I. MS-902 mass spectrometer.

Mass Spectroscopy/Gas Liquid Chromatography: These spectra were obtained from an A.E.I. MS-20 spectrometer coupled to a Pye 104 chromatograph using argon as carrier gas.

Ultraviolet Spectroscopy: A Unicam S.P. 800 spectrometer was used with a pair of matched 1 cm silica cells.

Gas Liquid Chromatography: For analytical work a Pye 104 chromatograph with flame ionisation detector and 1.5m x 4 mm packed columns or a Perkin Elmer F.11 chromatograph with a flame ionisation detector and 50m x 0.25 mm capillary columns was used. Stationary phases were supported on 100-120 mesh celite and included neopentylglycol succinate (N.P.G.S.), polyethylene glycol adipate (P.E.G.A.), polyethylene glycol (Carbowax), and Apiezon L grease (A.P.L.). Preparative work was performed on a Griffin and George D.6 gas density balance using a 10% Carbowax column. In all cases the carrier gas was nitrogen.
Column Chromatography: Alumina used was Laporte Industries Ltd. grade H 100-200 mesh. (Brockman activity 1-2).

Liquid-Liquid Chromatography: Chromatograms were obtained using a Du Pont 820 liquid liquid chromatograph with an ultraviolet detector with a Spherisorb A 20Y column and a 30% dioxan/petrol mobile phase.

Thin Layer Chromatography: Chromatograms were obtained using 0.25 mm layers of alumina (Merck Aluminium Oxide G type E) on glass plates and developed under U. V. light or by the action of iodine vapour.

Dry Column Chromatography: Alumina (Brockman activity 1) was deactivated with water to Brockman activity 3-4 and used as described by Loev and Goodman. 177

Elemental Analysis: Micro-analysis for carbon, nitrogen and hydrogen were performed by Mr. J. Grunbaum, University of Edinburgh using a Perkin Elmer 240 elemental analyser. Analyses were also obtained from National Physical Laboratory, Teddington and from the analytical service, Kodak Research Laboratories, Harrow.

Differential Thermal Analysis: Some decomposition temperatures were obtained by the technique of differential thermal analysis. The samples were examined at Kodak Research Laboratories, Harrow on a Du Pont instrument with Chromel Alumel thermocouples and a glass bead reference.

Solvents and Reagents: Benzene and petrol (light petroleum ether b.p. 40-60) were purified by distillation and stored over sodium. Ether (diethyl ether anaesthetic grade) was dried over sodium. Toluene was purified by the procedure described in Vogel. Tetrahydrofuran and dioxan were purified by passage through an alumina column and stored over sodium. Methylene chloride and ethylene dichloride were distilled and stored over molecular sieve. All other solvents and reagents were distilled or recrystallised and stored over molecular sieve where appropriate.
1. Preparation of Azides

(a) 1-Azido-2-nitrobenzene

1-Azido-2-nitrobenzene was prepared by a modification of the azide preparation described by Fitton and Smalley. o-Nitroaniline was diazotised in 5N hydrochloric acid and the diazonium salt solution allowed to react with sodium azide. The product extracted into ether. Column chromatography on alumina with ether gave the product as a cream-coloured crystalline solid, m. p. 48-50° (lit., m. p. 52°).

Other azides prepared in this way are shown below. Yields were 65-95%. All products showed the characteristic 2100 cm⁻¹ band in the i. r.:

2-Azidoacetophenone  m. p. 18-20° (lit., m. p. 23°)
4-Azidoazobenzene  m. p. 84-86° (lit., m. p. 90°)

The precursor 4-aminoazobenzene was prepared by the method described in Vogel.

2-Azidobenzophenone oil  (lit., m. p. 34-35°)
2-Azido-3-nitrotoluene  m. p. 44-46° (lit., m. p. 50°)
3-Azido-4-nitrotoluene  m. p. 86-87° (lit., m. p. 87°)
4-Azido-3-nitrotoluene  m. p. 32-33° (lit., m. p. 36°)

(2-Azidophenyl)diphenylphosphine oxide  m. p. 140-142°

This compound was not obtained completely pure due to the difficulty of separating it from the starting amine. m/e; 319

C₁₈H₁₄N₃OP requires m/e; 319.
4-Azidoanisole  m. p. 33-34° (lit., m. p. 36°)
1-Azido-4-iodobenzene  m. p. 35-36° (lit., m. p. 36°)
4-Azido-3-nitroanisole  m. p. 69-70° (lit., m. p. 74°)

4-Azidobenzene sulphonamide  m. p. 105-106°
m/e; 198. C₆H₆N₄O₂S requires m/e 198.

(b) 2,4-Dinitrophenyl Azide

2,4-Dinitrophenyl Azide was prepared by a method based on
that of Lindsay and Allen.\textsuperscript{119} 2,4-Dinitrophenylhydrazine hydrochloride was reacted with sodium nitrite below 5°. Extraction and chromatography on alumina gave 2,4-dinitrophenyl azide m.p. 68-69° (lit.,\textsuperscript{115} m.p. 69°) as yellow needles.

(c) 1,4-Diazidobenzene

1,4-Diazidobenzene was prepared by the method of Herring.\textsuperscript{120} The product was purified by chromatography on alumina with ether. 1,4-Diazidobenzene m.p. 78-79° (lit., m.p. 81-82°) was obtained as orange crystals which gradually turned brown on standing.

(d) 2-Azido-1-nitronaphthalene

2-Azido-1-nitronaphthalene was prepared by the method of Boscher, Dyall and Sadler.\textsuperscript{121} 2-Amino-1-nitronaphthalene was diazotised in a mixture of glacial acetic and concentrated sulphuric acids with sodium nitrite. Reaction with sodium azide, extraction and chromatography on alumina with ether gave 2-azido-1-nitronaphthalene m.p. 117-118° (lit.,\textsuperscript{121} m.p. 118-119°).

The following azides were also prepared in this way.

1-Azido-8-nitronaphthalene m.p. 126-127° (lit.,\textsuperscript{115} m.p. 131-132°). The amine precursor was prepared by the nitration of 1-naphthylamine as described by Hodgson and Davy.\textsuperscript{122}

1-Azido-2-nitro-4-(trifluoromethyl)benzene oil. This required chromatography on alumina with petrol.

(e) 2-Azidobenzoic Acid

Anthranilic acid was diazotised as in (d) above. The solution was extracted with methylene chloride, washed with sodium carbonate and brine and dried over anhydrous magnesium sulphate. The solvent was removed and the product recrystallised from methanol to yield 2-azidobenzoic acid m.p. 141-142° (lit.,\textsuperscript{115} m.p. 145-146°).

(f) Tosyl Azide

Tosyl azide was prepared by the method of Weil and Cais.\textsuperscript{124}
A methanolic solution of tosyl chloride was treated with sodium azide dissolved in a minimum of water. The mixture was then diluted with water the two layers separated, the non-aqueous layer collected, washed with water and dried over calcium chloride to give tosyl azide, which was not further purified.

Also prepared by this procedure were the following.

4-Nitrobenzenesulphonyl Azide m. p. 99-101° (lit., m. p. 103°)
Benzoyl Azide m. p. 30-31° (lit., m. p. 32°)
4-Nitrobenzoyl Azide m. p. 66-68° (lit., m. p. 69°).

2,4-Dinitrobenzoyl Azide m. p. 64-65°

Found: C, 35.4; H, 1.3; N, 29.5%.

C₇N₃N₅O₅ requires C, 35.5; H, 1.3; N, 28.7%.

Picryl Azide m. p. 65-67° (lit., m. p. 70°)

Solids were filtered off and recrystallised rapidly from methanol.

(g) Diphenyolphosphinyl Azide

Diphenyolphosphinyl Azide was prepared by a modification of the procedure described by Baldwin and Washburn.

Diphenyolphosphinyl chloride, prepared either by treating dichlorophenylphosphine with oxygen or by the action of thionyl chloride on diphenyl phosphinic acid, was stirred with sodium azide in acetonitrile under scrupulously dry conditions for 12 h. Filtration and removal of the solvent left diphenyl phosphinyl azide as a pale yellow oil pure enough for use.

(h) Other Azides

Samples of 4-azidobenzonitrile and mesyl azide were supplied by Dr. I. Gosney; 3-Azidobromobenzene, 3-azidotoluene and 3-Azido anisole by Miss H. McWilliam; 4-azidobenzoic acid, 3-azidophthalic anhydrydride and 2-azidobenzimidazole by Messrs. Kodak Ltd.; and benzyl azide by Mr. H. Mackie.
2. Miscellaneous Starting Materials

(a) **N-Aminophthalimide**

N-Aminophthalimide m.p. 198-202° (lit., m.p. 200-205°) which resolidifies and remelts 339-340° (lit., m.p. 338-341°) was prepared by the method of Drew and Hatt from phthalimide and hydrazine hydrate.

(b) **4-Phenylurazole**

This was prepared by the method of Cookson by Mr. B. D. Baigrie.

m.p. 206° (lit., m.p. 206-207°)

(c) **5-Aryl-1, 2, 5-dioxazolidin-2-ones**

5-Phenyl- and 5-(4-nitrophenyl)-1, 2, 5-dioxazolidin-2-one were prepared by Dr. I. Gosney by the method of Sauer.

5-Phenyl- m.p. 60-62° (lit., m.p. 61-62°)
5-(4-Nitrophenyl)- m.p. 144-148(d) (lit., m.p. 146-148° (d))
3. **Preparation of Phospholes and Phosphole Oxides**

(a) **1,4-Diarylbuta-1,3-dienes**

These were prepared by the method of Corson by the condensation of a phenylacetic acid with cinnamaldehyde in the presence of litharge with acetic anhydride as solvent. The following were prepared in this way.

1,4-Diphenylbuta-1,3-diene  
\[ \text{m. p. } 151-152^\circ \text{C} \]  
(lit. m. p. 152-153^\circ)

1-(4-Methoxyphenyl)-4-phenylbuta-1,3-diene  
\[ \text{m. p. } 162-164^\circ \text{C} \]  
(lit. m. p. 163-164^\circ)

Found: C, 86.0; H, 7.0%. m/e; 236.

\[ \text{C}_{17}\text{H}_{16}\text{O} \text{ requires } C, 86.4; H, 6.8%. m/e; 236. \]

N.m.r. \( (\text{CDCl}_3) \tau 2.2-3.8 \) (13H, aromatic and olefinic protons), 6.20 (3H, s, methoxyl protons).

1-Phenyl-4-(p-tolyl)buta-1,3-diene  
\[ \text{m. p. } 155-156^\circ \text{C} \]  
(lit. m. p. 155-156^\circ)

Found: C, 92.3; H, 7.5%. m/e; 220.

\[ \text{C}_{17}\text{H}_{16} \text{ requires } C, 92.5; H, 7.7%. m/e; 220. \]

N.m.r. \( (\text{CDCl}_3) \tau 2.5-3.7 \) (13H, aromatic and olefinic protons) 7.68 (3H, s, methyl protons).

1,4-Ditolylbuta-1,3-diene was prepared by a modification of the method described by McDonald and Campbell. 4-Methyl-cinnamyl bromide was prepared by the method of Bruton and Ingold and the triphenylphosphonium salt subsequently prepared by heating the crude bromide with triphenylphosphine in xylene. The salt was then reacted with tolualdehyde in 0.2M lithium ethoxide in ethanol to give the butadiene which was filtered off and recrystallised from methanol/benzene.  
\[ \text{m. p. } 202-203^\circ \text{C} \]  
(lit. m. p. 198-200^\circ)

Found: C, 92.6; H, 8.0%. m/e; 234.

\[ \text{C}_{18}\text{H}_{18} \text{ requires } C, 92.3; H, 7.7%. m/e; 234. \]

N.m.r. \( (\text{CDCl}_3) \tau 2.5-3.7 \) (12H, aromatic and olefinic protons), 7.7 (6H, methyl protons).
(b) **1, 2, 5-Triphenylphosphole**

The method used was a modification of that described by Campbell et al. \(^\text{21}\) A mixture of 1, 4-diphenylbuta-1, 3-diene (26.5 g., 0.13 mol) and dichlorophenyl phosphine (35 g, 0.2 mol) were heated at 215\(^\circ\)C for 6 h under nitrogen. The cooled mixture was triturated under ether. The solid was filtered off, washed with ether, dissolved in a minimum of hot chloroform and filtered while still hot. Long yellow fluorescent needles of 1, 2, 5-triphenylphosphole formed on cooling (8-12 g, 25-35\%) m.p. 187-179\(^\circ\) (lit., \(^\text{21}\) m.p. 187-189\(^\circ\)).

(c) **Reaction of Dichlorophenylphosphine with 1-(4-Methoxyphenyl)-4-phenylbuta-1, 3-diene.**

The butadiene (12 g, 0.05 mol) was heated with dichlorophenylphosphine (18 g) at 215\(^\circ\)C until no more hydrogen chloride was evolved. On cooling the mixture set as a black tar. Chromatography on alumina gave only 1, 2, 5-triphenylphosphole (0.16 g, 1\%) m.p. 182-183\(^\circ\) (lit., \(^\text{21}\) m.p. 187-189\(^\circ\)), m/e; 312: \(C_{22}H_{17}P\) requires m/e; 312: n.m.r. showed no methyl absorption, ir identical to an authentic sample. The remainder of the reaction mixture, a black tar was not further investigated.

(d) **Reaction of Dichlorophenylphosphine with 1-Tolyl-4-phenylbuta-1, 3-diene.**

The butadiene (21 g, 0.1 mol) was heated at 215\(^\circ\)C with the phosphine as above. The yellow solid which formed on cooling was purified as in (b) to give a fluorescent crystalline solid (7.00 g) m.p. 162-163\(^\circ\).

N.m.r. (CDCl\(_3\)) \(\tau\) 2.3-3.1 (aromatic), 7.76 (methyl). The integration showed a ration of aromatic : methyl protons of 31:3 while the required ratio is 21:3. Low eV mass spectrometry showed two peaks 326 and 312 in the ratio 1.8:1.

The product was oxidised with lead tetraacetate by the procedure described in (h) below.
N.m.r. (CDCl₃) τ 2.0-3.2 (aromatic) 7.76 (methyl).

The integration showed a ratio of 25:3 after several recrystallisations.

A low eV mass spectrum of the initial product showed the peaks 342 and 328 in the ratio 1.6:1.

H.s.l.c. on alumina (Spherisorb A 20Y) with 30% dioxan in n-hexane showed two peaks one of which had the same retention time as 1,2,5-triphenylphosphole-1-oxide in an approximate ratio of 1.8:1.

Thus the product of the reaction appears to be approximately a 3:2 mixture of 1,2-diphenyl-3-tolylphosphole and 1,2,5-triphenylphosphole.

Analysis on both the initial and oxidised products corresponded to a 3:2 mixture.

Initial Product:-

Found: C, 85.1; H, 6.0%.

C₂₂H₁₇P requires C, 84.6; H, 5.5%.
C₂₃H₁₉P requires C, 84.7; H, 5.8%.

Oxidised product:-

Found: C, 80.4; H, 5.5%.

C₂₂H₁₇PO requires C, 80.6; H, 5.2%.
C₂₃H₁₉PO requires C, 80.6; H, 5.6%.

The mass spectrum of the oxidised product also shows a peak m/e; 356 (Intensity 3% of m/e;342) which may correspond to 1-phenyl-2, 5-ditoly1phosphole-1-oxide.

(e) Reaction of Dichlorophenylphosphine with 1,4-Ditoly1buta-1,3-diene

The diene (4.02 g, 0.002 mol) and dichlorophenylphosphine (7.00 g, 0.004 mol) were reacted as above to yield a yellow fluorescent product (0.98 g) after recrystallisation from chloroform/ether. The mother liquor was evaporated and the remaining solid dissolved in methylene chloride and oxidised with
lead tetraacetate as above. Chromatography on alumina with chloroform gave the mixed oxide (0.41 g).

The low eV mass spectrum of the phosphole showed the peaks m/e; 354, 340, 326, 312 in the ratio 1:17:25:6.
N.m.r. (CDCl₃) τ 2.2-3.2 (aromatic), 7.73 (methyl).
The ratio of aromatic:methyl protons of 30:7 corresponds well with mixture composition estimated by mass spectrometry.
(Requires 30:7).

The low eV mass spectrum of the phosphole oxides showed the peaks m/e; 360, 356, 342, 328 in the ratio 1:29:35:7.
Analysis of the oxide mixture by h.s.l.c. showed three major components, two of which corresponded to 1,2,5-triphenylphosphole oxide and 1,2-diphenyl-5-tolylphosphole, the latter being the major component.

Thus the product of the reaction is believed to be a mixture of 1,2,5-tritolylphosphole 1-phenyl-2,5-ditolylphosphole, 1,2-diphenyl-5-tolylphosphole and 1,2,5-triphenylphosphole.

(f) Reaction of 1,4-Ditolylbuta-1,3-diene with Dichlorotolylphosphine.

Dichlorotolylphosphine was prepared by the method of Buchner and Lockhardt by a Friedel-Crafts reaction between toluene and phosphorus trichloride in the presence of aluminium chloride. The dichlorophosphine was distilled b.p. 120° at 14 mm. Hg (lit., 133 b.p. 120° at 13 mm Hg).
N.m.r. (CDCl₃) τ 8.1-8.9 (4H, aromatic) 3.63 (3H, s, methyl protons).

The dichlorotolylphosphine (4.00 g, 0.002 mol) was allowed to react with 1,4-ditolylbuta-1,3-diene (3.00 g, 0.001 mol) under the conditions described for the preparation of 1,2,5-triphenylphosphole to yield a pale-yellow, fluorescent, crystalline solid, m.p. 182-183° (0.58 g, 13%), thought to be 1,3,5-tritolylphosphole.

Found: C, 85.1; H, 6.7%. m/e; 354.

C₂₅H₂₅ requires C, 84.4; H, 7.1%. m/e; 354.
A small quantity of product was oxidised to the phosphole oxide and analysed by h.s.l.c. Only one peak was observed. 

\[
\text{N.m.r. } (\text{CDCl}_3) \; \tau \; 2.5-3.1 \; (12\text{H, } \delta, \text{ aromatic}), \; 7.6-7.8 \; (9\text{H, three overlapping } \delta, \text{ methyl protons}).
\]

The low eV mass spectrum of both the initial and oxidised product showed only peaks corresponding to a single parent.

\[\text{(g) } 1,2,5\text{-Triphenylphosphole Oxide}\]

Two methods for the preparation of this compound were used. 1,2,5-Triphenylphosphole was oxidised either by method of Cookson \(^{21}\) using hydrogen peroxide in ethanol-ethyl acetate or with lead tetraacetate in methylene chloride. The latter reaction was found to be almost instantaneous and quantitative. The pure product m.p. 236-238\(^\circ\) (lit., \(^{21}\) m.p. 237-239\(^\circ\)) was obtained by elution of the reaction mixture through a short alumina column. This method was also considered more convenient for the oxidation of other phosphole mixtures described in (d), (e) and (f) above.
4. Preparation of Phospholimines

(a) Reaction of 1, 2, 5-Triphenylphosphole with Aryl Azides.

1. N-(4-Phenylazophenyl)-1, 2, 5-triphenylphospholimine.

1, 2, 5-Triphenylphosphole (1.00 g, 0.003 mol) was boiled under reflux with 4-azidoazobenzene (0.69 g, 0.003 mol) in toluene (30 ml) under nitrogen. Removal of solvent and re-crystallisation from chloroform/ether and then isopropanol/chloroform yielded red needles of the phospholimine (0.63 g, 38%) m.p. 252-254°.

Found: C, 77.5; H, 5.1; N, 7.9; m/e; 507.

C\text{34}H\text{26}N\text{3}P requires C, 77.5; H, 4.9; N, 7.9%. m/e; 507.

N.m.r. (CDCl\text{3}) \( \delta \) 1.9-2.1 (2H, c, ortho proton PhP), 2.2-2.9 (23H, aromatic), 3.00 and 3.08 (2H, half of the A2B2 complex of the N-phenyl ring protons).

I.r. \( \nu_{max} \) 1300 (P=N) cm\text{\textsuperscript{-1}}

U.V. (methanol) \( \lambda_{max} \) 206 (35,000), 215 (25,400) sh., 393 (39,100) nm.

2. N-(4-Methoxyphenyl)-1, 2, 5-triphenylphospholimine.

The phosphole (4.00 g, 0.013 mol) and 4-azidoanisole (3.00 g, 0.020 mol) were heated in toluene (75 ml) at 100° under nitrogen until no further nitrogen evolution was observed. On cooling blue-black crystals of the phospholimine (3.45 g, 65%) m.p. 196-198° formed which were filtered off and washed with ether.

Found: C, 80.0; H, 5.7; N, 2.8%. m/e; 433.

C\text{29}H\text{24}N\text{O}P requires C, 80.0; H, 5.6; N, 3.2%. m/e; 433.

N.m.r. (CDCl\text{3}) \( \delta \) 1.8-2.1 (2H, c, ortho protons PhP), 2.1-2.8 (19H, aromatic), 3.04, 3.12, 3.26 and 3.35 (4H, A2B2 system of N-phenyl ring protons), 6.31 (3H, s, methoxyl protons).

I.r. \( \nu_{max} \) 1300 (P=N) cm\text{\textsuperscript{-1}}

U.V. (methanol) \( \lambda_{max} \) 208 (33,900), 228 (29,400) 240 (21,900),
3. N-(4-Iodophenyl)-1, 2, 5-triphenylphospholimine.

1, 2, 5-Triphenylphosphole (4.00 g, 0.012 mol) was reacted with 4-azidoiodobenzene (4.00 g, 0.018 mol) as in (a)2. Removal of solvent and recrystallisation from chloroform ether gave the phospholimine (3.81 g, 57%) m. p. 218-222\(^\circ\) as salmon-pink crystals.

Found: C, 63.9; H, 4.0; N, 3.0%. \(\text{C}_{28}\text{H}_{21}\text{NIP}\) requires C, 63.5; H, 4.0; N, 2.7%. m/e; 528.

N. m. r. (CDCl\(_3\)) \(\tau\) 1.86-2.12 (2H, \(c\), ortho protons PhP), 2.30-2.86 (17H, \(c\), aromatic), 3.30 and 3.90 (2H, half of \(A_2B_2\) system of the N-phenyl ring protons).

I.r. \(\nu_{\text{max}}\) 1305 (P=N) cm\(^{-1}\).

U.V. (methanol) \(\lambda_{\text{max}}\) 207 (36, 500), 253 (25,000), 375 (14,000) nm.

4. N-(4-Carboxyphenyl)-1, 2, 5-triphenylphospholimine

1, 2, 5-Triphenylphosphole (1.04 g, 0.003 mol) and 4-azido- benzoic acid (0.97 g, 0.006 mol) were reacted as in (a)2. The orange microcrystalline solid which crystallised from the reaction mixture was filtered off and washed with ether to yield the phospholimine (1.31 g, 88%) m. p. 268-269\(^\circ\) (d).

Found: C, 77.6; H, 5.0; N, 3.2%.

\(\text{C}_{29}\text{H}_{22}\text{NO}_2\text{P}\) requires C, 77.6; H, 4.9; N, 3.1%.

The mass spectrum showed a parent ion m/e 447.

Found: 447.137987

\(\text{C}_{29}\text{H}_{22}\text{NO}_2\text{P}\) requires 447.138819

N. m. r. (d\(_6\) - DMSO) \(\tau\) 1.86-2.88 (26H, \(c\), aromatic), 3.19 and 3.29 (2H, part of \(A_2B_2\) system of N-phenyl ring protons).

A scan from -5\(\tau\) failed to locate the carboxyl proton.

I.r. \(\nu_{\text{max}}\) 3100-2500 (OH) 1660 (C=O) 1310 (P=N) cm\(^{-1}\).

5. N-(4-Methoxy-2-nitrophenyl)-1, 2, 5-triphenylphospholimine.

1, 2, 5-Triphenylphosphole (2.02 g, 0.007 mol) and 4-azido-3-nitroanisole (1.51 g, 0.008 mol) were reacted as in (a)2. Evaporation of the solvent and recrystallisation of the residue from
chloroform ether gave blue-black cubes of N-(4-methoxy-2-nitrophenyl)-1,2,5-triphenylphospholimine (1.82 g, 59%) m.p. 172-173\(^\circ\).

Found: C, 72.0; H, 5.0; N, 5.9%.

C\(_{29}H_{23}N_2O_3\) requires C, 72.6; H, 4.8; N, 5.9%.

The mass spectrum showed the correct parent ion m/e; 478.

Found: 478.143676.

C\(_{29}H_{23}N_2O_3\) requires 478.144631.

N.m.r. (CDCl\(_3\)) \(\tau\) 1.84-2.00 (2H, \(\delta\), ortho protons PhP), 2.28-2.80 (16H, \(\delta\), aromatic), 3.34 (2H, \(\delta\), ring protons of N-phenyl), 6.35 (3H, \(\delta\), methoxyl protons).

I.r. \(\nu_{\text{max}}\) 1510 (NO\(_2\)) 1250 (P=N) cm\(^{-1}\)

U.V. \(\lambda_{\text{max}}\) (methanol) 207 (36,000), 230 (34,000), 394 (16,000).

6. N-(4-Methyl-2-nitrophenyl)-1,2,5-triphenylphospholimine

The phosphole (2.02 g, 0.007 mol) was heated with 4-azido-3-nitrotoluene (1.32 g, 0.008 mol) in toluene at 100\(^\circ\) as in (a)2. Removal of solvent and fractional recrystallisation of the residue from chloroform ether gave phosphole oxide (1.00 g, 47%), i.r. identical to an authentic sample and large red cubes of the phospholimine (1.35 g, 42%) m.p. 154-156\(^\circ\).

Found: C, 75.3; H, 5.0; N, 6.1%.

C\(_{29}H_{23}N_2O_2P\) requires C, 75.4; H, 5.0; N, 6.1%.

Found: 462.113288.

C\(_{29}H_{23}N_2O_2P\) requires 462.113331.

N.m.r. (CDCl\(_3\)) \(\tau\) 1.78-2.02 (2H, \(\delta\), ortho protons PhP), 2.30-3.40 (18H, \(\delta\), aromatic), 7.90 (3H, \(\delta\), methyl protons).

I.r. \(\nu_{\text{max}}\) 1495 (NO\(_2\)) 1325 (P=N) cm\(^{-1}\)

7. N-(2,4-Dinitrophenyl)-1,2,5-triphenylphospholimine

1,2,5-Triphenylphosphole (0.98 g, 0.003 mol) and 2,4-dinitrophenyl azide (0.80 g, 0.004 mol) were reacted as in (a)2. Removal of solvent and chromatography on dry column alumina with ether gave recovered phosphole (0.42 g, 43%), the phosphole oxide
(0.24 g, 22%) and the phospholimine (0.26 g, 13%) m.p. 151-152° as golden-yellow needles after recrystallisation from chloroform ether.

Found: C, 67.6; H, 4.4; N, 8.4%.

\[ \text{C}_{28}\text{H}_{20}\text{N}_{3}\text{O}_{4}\text{P} \text{ requires C, 68.3; H, 4.1; N, 8.5%.} \]

The mass spectrum showed the correct parent ion, m/e; 493.

Found: 493.118458.

\[ \text{C}_{28}\text{H}_{20}\text{N}_{3}\text{O}_{4}\text{P} \text{ requires 493.119143.} \]

N.m.r. (CDCl₃) \( \tau \) 1.42 (1H, dd, 3-proton of N-phenyl ring), 1.79-2.10 (2H, c, ortho protons of PPh), 2.10-2.21 (2H, c, 5-proton on N-phenyl overlapped by phosphole ring proton) 2.36-2.84 (14H, c, aromatic) 3.40 (1H, dd, 6-proton on N-phenyl ring).

U.V. \( \lambda_{max} \) (methanol) 207 (36,000), 224 (33,000), 374 (32,000).

8. \text{N-(2-Nitro-4-trifluoromethylphenyl)-1, 2, 5-triphenylphospholimine.}

1-Azido-2-nitro-4-trifluoromethyl benzene (1.00 g, 0.004 mol) and 1, 2, 5-triphenylphosphole (1.04 g, 0.003 mol) were reacted as in (a)2. Removal of solvent and dry column chromatography on alumina with ether gave phosphole (0.23 g, 23%), phosphole oxide (0.13 g, 11%) and the phospholimine (0.62 g, 35%) m.p. 186-187° as yellow cubes after recrystallisation from chloroform/ether.

Found: C, 66.9; H, 3.9; N, 5.4%. m/e; 516.

\[ \text{C}_{29}\text{H}_{20}\text{N}_{2}\text{O}_{2}\text{PF}_{3} \text{ requires C, 67.4; H, 3.9; N, 5.6%. m/e; 516.} \]

9. \text{N-2-(1-Nitronaphthyl)-1, 2, 5-triphenylphospholimine.}

2-Azido-1- nitronaphthalene (1.80 g, 0.008 mol) and 1, 2, 5-triphenylphosphole (2.08 g, 0.007 mol) were reacted as in (a)2. Removal of solvent and recrystallisation from chloroform/ether gave the phospholimine (0.64 g, 18%) m.p. 212-214°.

1, 2, 5-Triphenylphosphole (0.63 g, 30%) was also recovered.
Found: C, 77.9; H, 4.7; N, 5.6%. m/e; 498.
\( \text{C}_{32}\text{H}_{23}\text{N}_2\text{O}_2\text{P} \) requires C, 77.6; H, 4.6; N, 5.6%. m/e; 498.

10. N-(3-Bromophenyl)-1, 2, 5-triphenylphospholimine.

4-Azidobromobenzene (1.01 g, 0.005 mol) and 1, 2, 5-triphenylphosphole (1.04 g, 0.003 mol) were heated in toluene (25 ml) at 100° under nitrogen. Deep red crystals of N-(3-bromophenyl)-1, 2, 5-triphenylphospholimine (1.12 g, 71%) m.p. 210-212° formed on cooling.

Found: C, 69.9; H, 4.4; N, 2.7%. m/e; 482
\( \text{C}_{28}\text{H}_{21}\text{BrNP} \) requires C, 69.6; H, 4.4; N, 2.9%. m/e; 482

11. N-m-Tolyl-1, 2, 5-triphenylphospholimine.

m-Tolyl azide (0.34 g, 0.006 mol) and 1, 2, 5-triphenylphosphole (1.04 g, 0.003 mol) were reacted as in (a)2. The solvent was removed and the residue recrystallised from chloroform/ether to yield brown needles of the phospholimine (0.98 g, 71%) m.p. 196-197°.

Found: C, 83.7; H, 5.7; N, 3.1%. m/e; 417
\( \text{C}_{29}\text{H}_{24}\text{NP} \) requires C, 83.5; H, 5.8; N, 3.4%. m/e; 417
N.m.r. (CDCl₃) \( \tau \) 1.8-3.7 (21H, c, aromatic), 7.81 (3H, s, methyl protons).

12. N-(4-Cyanophenyl)-1, 2, 5-triphenylphospholimine.

This was prepared as in (a)2 from 4-azidobenzonitrile (0.72 g, 0.005 mol) and 1, 2, 5-triphenylphosphole (1.04 g, 0.003 mol). Addition of petrol precipitated the crude product which was recrystallised from chloroform/ether to yield brown crystals of N-(4-cyanophenyl)-1, 2, 5-triphenylphospholimine (0.62 g, 43%) m.p. 209-210°C.

Found: C, 81.0; H, 4.9; N, 6.5%. m/e; 428
\( \text{C}_{29}\text{H}_{21}\text{N}_2\text{P} \) requires C, 81.3; H, 4.9; N, 6.5%. m/e; 428
I.r. \( \nu_{\text{max}} \) 2205 (C N), 1275 (P=N) cm.⁻¹
13. N-2-Benzimidazoly1-1, 2, 5-triphenylphospholimine.

1, 2, 5-Triphenylphosphole (1.01 g, 0.003 mol) and 2-azidobenzimidazole (0.94 g, 0.006 mol) were heated in toluene as in (a)2. Removal of solvent and recrystallisation of the residue from chloroform/ether gave an orange-red amorphous solid which was identified as impure phospholimine (0.62 g, 43%) m.p. 178-180°.

The mass spectrum showed correct parent peak: m/e; 443.

**Found:** 443.154245.

C_{29}H_{22}N_3P \text{ requires } 443.155137.

U.V. (methanol) \( \lambda_{\text{max}} \): 217 (43, 500), 293 (17.800), 390 (9, 100) nm.

14. N-3-(Phthalic anhydrido)-1, 2, 5-triphenylphospholimine.

The phosphole (1.01 g, 0.003 mol) and 3-azidophthalic anhydride (0.61 g, 0.003 mol) were reacted as in (a)2. The solvent was removed and the residue recrystallised from chloroform/ether. Yellow crystals of impure N-(3-phthalic anhydrido)-1, 2, 5-triphenylphospholimine (1.11 g, 73%) m.p. 209-211° were obtained.

The mass spectrum showed the correct parent ion: m/e; 473.

**Found:** 473.116977.

C_{30}H_{20}NO_3P \text{ requires } 473.118083.

N.m.r. (CDCl3) \( \tau \): 1.64-1.88 (2H, ortho protons PhP) 2.26-3.26 (18H, aromatic).

I.r. \( \nu_{\text{max}} \): 1840, 1765 (C=O) 1260 (P= N) cm.\(^{-1}\)

U.V. (methanol) \( \lambda_{\text{max}} \): 206 (32,800), 221 (27,500) sh., 249, (18,600) sh., 294 (13,300), 390 (15,700) nm.

15. N-(2-Diphenylphosphinylphenyl)-1, 2, 5-triphenylphospholimine.

The phosphole (0.55 g, 0.002 mol) was reacted with 2-azidophenyldiphenylphosphine oxide (0.56 g, 0.002 mol) as in (a)2. The solvent was removed and the residue recrystallised from chloroform/ether to give red cubes of the phospholimine (0.22 g, 20%) m.p. 278-279°.
Found: C, 78.5; H, 5.3; N, 2.2%.

\[ \text{C}_{40}\text{H}_{31}\text{NOP}_2 \text{ requires } \text{C}, 79.5; \text{H}, 5.1; \text{N}, 2.3\% . \]

The mass spectrum showed the correct parent peak: m/e; 603.

Found: 603.187077.

\[ \text{C}_{40}\text{H}_{31}\text{NOP}_2 \text{ requires } 603.188098. \]

16. N-(2-Benzoylphenyl)-1, 2, 5-triphenylphospholimine.

2-Azidobenzophenone (4.00 g, 0.017 mol) and 1, 2, 5-triphenylphosphole (2.00 g, 0.006 mol) were heated in toluene as in (a)2. Removal of solvent and recrystallisation from chloroform/ether gave bright red crystals of N-(2-benzoylphenyl)-1, 2, 5-triphenylphospholimine (1.43 g, 45%) m. p. 191-192°.

Found: C, 82.2; H, 5.4; N, 2.9%. m/e; 507.

\[ \text{C}_{35}\text{H}_{26}\text{NOP} \text{ requires } \text{C}, 82.5; \text{H}, 5.1; \text{N}, 2.8\%. \text{ m/e; 507.} \]

I. r. \[ \nu_{\max} \text{ 1650 (C=O) 1285 (P=N) cm}^{-1} \]

17. N-(2-Nitrophenyl)-1, 2, 5-triphenylphospholimine

This was prepared as described in (a)2., from 1, 2, 5-triphenylphosphole (4.00 g, 0.012 mol) and o-azidonitrobenzene (3.21 g, 0.026 mol). The crude product was recrystallised from chloroform/ether to give bright orange cubes of the phospholimine (4.37 g, 77%) m. p. 188-190°.

Found: C, 74.9; H, 4.8; N, 6.0%. m/e; 448.

\[ \text{C}_{28}\text{H}_{21}\text{N}_2\text{O}_2\text{P requires } \text{C}, 75.0; \text{H}, 4.8; \text{N}, 6.2\%. \text{ m/e; 448.} \]

N. m. r. (CDCl3) \[ \tau \text{ 1.86-2.04 (2H, \sigma, ortho protons PhP), 2.26-3.50 (26H, \sigma, aromatic).} \]

I. r. \[ \nu_{\max} \text{ 1505 (NO}_2) \]

U. V. \[ \lambda_{\max} \text{ (methanol) 208 (32,000), 236 (30,000), 390 (17,600).} \]

18. N-(4-Sulphamoylphenyl)-1, 2, 5-triphenylphospholimine.

This was prepared from 4-azidobenzenesulphonamide (1.74 g, 0.006 mol) and 1, 2, 5-triphenylphosphole (0.82 g, 0.003 mol) as described in (a)2. The phospholimine (1.14 g, 90%) m. p. 208-211° was obtained by recrystallisation from chloroform/ether.
Found: C, 68.6; H, 4.9; N, 5.8%.

C$_{28}$H$_{23}$N$_2$SO$_2$P requires C, 69.5; H, 4.8; N, 5.8%.

A mass spectrum showed the correct parent ion: m/e; 482.

Found: 482.122946.

C$_{28}$H$_{23}$N$_2$SO$_2$P requires 482.121779.

N.m.r. (CDCl$_3$) $\tau$ 1.9-2.1 (2H, $s$, ortho protons PhP),
2.2-2.9 (2H, $s$, aromatic) 3.05 and 3.13 (2H, half A$_2$B$_2$
system of N-phenyl ring protons) 5.41 (2H, $s$, amide protons).

U.V. $\lambda_{\text{max}}$ (methanol) 206 (33,000), 268 (19,000), 292
(22,000), 390 (13,500) nm.

19. N-(2-Methyl-6-nitrophenyl)-1, 2, 5-triphenyolphosphol-
imine.

2-Azido-3-nitrotoluene (1.50 g, 0.110 mol) and the
phosphole (2.08 g, 0.078 mol) were reacted together in toluene
as described in (a)2. The crude product was recrystallised first
from chloroform/ether and then isopropanol/chloroform to yield
the phospholimine (2.40 g, 81%) m.p. 195-196$^\circ$.

Found: C, 74.7; H, 5.1; N, 6.0%.

C$_{29}$H$_{28}$N$_2$O$_2$P requires C, 75.4; H, 5.0; N, 6.1%.

The mass spectrum showed the correct parent ion: m/e; 462.

Found: 462.147985.

C$_{29}$H$_{28}$N$_2$O$_2$P requires 462.149707.

N.m.r. (CDCl$_3$) $\tau$ 1.84-2.10 (2H, $s$, ortho protons PhP),
2.30-3.10 (16H, $s$, aromatic), 2.35-2.55 (2H, part of N-phenyl
ring complex), 7.71 (3H, $s$, methyl protons).

I.r. $\nu_{\text{max}}$ 1550 (NO$_2$) 1260 (P=N).

20. N-(5-Methyl-2-nitrophenyl)-1, 2, 5-triphenyolphospholimine.

3-Azido-4-nitrotoluene (1.50 g, 0.011 mol) was heated at
100$^\circ$ in toluene with 1, 2, 5-triphenyolphosphole (2.08 g, 0.008 mol)
as in (a)2. After evolution of nitrogen was complete (3h) a con-
siderable amount of the phosphole remained (t.l.c.). More azide
(1.00 g, 0.007 mol) was added and the reaction continued. Dry
column chromatography on alumina with ether followed by recrystallisation from chloroform/ether gave the phospholimine (1.08 g, 35%) m. p. 195-196°.

1, 2, 5-Triphenylphosphole oxide (0.35 g, 16%) was also isolated from the column.

The mass spectrum showed the correct parent ion: m/e; 462.

Found: 462.148964.

C_{29}H_{28}N_{2}O_{2}P requires 462.149707.

N. m. r. (CDCl_{3}) \tau 1.84-2.10 (2H, \delta, ortho protons PhP),

2.30-3.10 (16H, \delta, aromatic), 2.35-2.55 (2H, part of N-phenyl ring complex), 7.71 (3H, s, methyl protons).

I. r. \nu_{max} 1610 (NO) 1260 (P=N) cm. \textsuperscript{-1}

21. N-(3-Methoxyphenyl)-1, 2, 5-triphenylphospholimine.

The phosphole (1.04 g, 0.003 mol) was treated with m-azidoanisole (0.96 g, 0.006 mol) at 100° as in (a)2. Recrystallisation of the crude product from chloroform/ether gave N-(3-methoxyphenyl)-1, 2, 5-triphenylphospholimine (0.96 g, 66%) m. p. 187-189° as blue-black cubes.

Found: C, 80.1; H, 5.7; N, 3.3%. m/e; 433.

C_{29}H_{24}NOP requires C, 80.0; H, 5.5; N, 3.2%. m/e; 433.

N. m. r. (CDCl_{3}) \tau 1.8-3.9 (26H, \delta, aromatic), 6.37 (3H, s, methoxy protons).

I. r. \nu_{max} 1335 (P=N) cm. \textsuperscript{-1}

22. N-(2-Carboxyphenyl)-1, 2, 5-triphenylphospholimine.

1, 2, 5-Triphenylphosphole (1.97 g, 0.006 mol) and 2-azido-benzoic acid (1.50 g, 0.009 mol) were heated in toluene as in (a)2. Removal of solvent and recrystallisation from chloroform/ether produced the phospholimine (1.24 g, 44%) m. p. 158-159°, m/e 447. C_{29}H_{22}NO_{2}P requires m/e; 447.

23. N-(4-Tolyl)-1, 2, 5-triphenylphospholimine

N-(4-Tolyl)-1, 2, 5-triphenylphospholimine was prepared from
p-tolyl azide (8.00 g, 0.06 mol) and 1, 2, 5-triphenylphosphole as in (a)2. Brown crystals of the phospholimine (10.02 g, 74%) m.p. 196-199° (Lit.,24 m.p. 195-196°) were collected after recrystallisation from chloroform/ether. I.r. and u.v. identical to an authentic sample.
(b) Preparation of N-(4-Azidophenyl)-1, 2, 5-triphenylphospholimine and Derivatives.

1. N-(4-Azidophenyl)-1, 2, 5-triphenylphospholimine.

1, 2, 5-Triphenylphosphate (5.00 g, 0.016 mol) and 1,4-diazidobenzene (4.12 g, 0.026 mol) were heated in toluene at 80° under nitrogen. When nitrogen evolution was complete, the cooled mixture was treated with petrol and a dark green solid (0.52 g) was precipitated and tentatively identified from the mass spectrum as N,N'-(1,4-phenyl)-bis-1, 2, 5-triphenylphospholimine. (m/e; 728. C_{50}H_{38}N_{2}P_{2} requires 728). The remainder of the reaction mixture was concentrated to small volume and treated with a large excess of petrol. An orange solid was precipitated, filtered off and recrystallised from chloroform/ether to give brown cubes of the phospholimine (2.50 g, 35%) m.p. 120-121° (d).

Found: C, 76.0; H, 4.9; N, 11.9%. m/e; 444.

N_{m.r.} (CDCl_{3}) \tau 2.9-3.2 (2H, \text{ortho protons PhP}), 2.4-3.0 (21H, \text{aromatic}), 3.2-3.4 (2H, \text{half of the A_{2}B_{2} complex of N-phenyl ring}).

I. r. \nu_{max} 2090, 2150 (N_{3}), 1270 (P=N) cm^{-1}

U. V. (methanol) \lambda_{max} 207, 217 sh. (44, 500), 275 (26, 700), 390 (16, 800) nm.

2. N-(4-Trimethylphosphorimidophenyl)-1, 2, 5-triphenylphospholimine.

N-(4-Azidophenyl)-1, 2, 5-triphenylphospholimine (0.42 g, 0.001 mol) was treated in benzene (10 ml) with trimethylphosphite (3 ml). After standing for 24 h at room temperature brown crystals had formed which were filtered off and washed with ether to give the phospholimine (0.50 g, 89%) m.p. 207-210°.

Found: C, 68.7; H, 5.6; N, 5.2%. m/e; 540.

C_{31}H_{30}N_{2}O_{3}P_{2} requires C, 69.0; H, 5.6; N, 5.3%. m/e; 540.

N_{m.r.} 1.86-2.11 (2H, \text{ortho protons PhP}), 2.20-2.86
N-(4-Triphenylphosphiniminophenyl)-1, 2, 5-triphenylphospholimine.

N-(4-Azidophenyl)-1, 2, 5-triphenylphospholimine (0.44 g, 0.001 mol) and triphenylphosphine (0.31 g, 0.001 mol) were mixed in dry tetrahydrofuran and warmed to 50°C for 15 min. On cooling green crystals of N-(4-triphenylphosphiniminophenyl)-1, 2, 5-triphenylphospholimine (0.52 g, 78%) m. p. 222-224°C formed in the reaction mixture.

The mass spectrum showed the correct parent ion: m/e; 678.

Found: 678.234013.

C_{46}H_{36}N_{2}P_{2} requires 678.235382.
(c) **N-(Phenyl carboxylate)-1, 2, 5-triphenylphospholimine**

1, 2, 5-Triphenylphosphole (2.03 g, 0.006 mol) and phenyl azidoformate (1.96 g, 0.012 mol) were heated at 100° in toluene as in (a)2. Evaporation to dryness and recrystallisation of the residue from chloroform/ether gave the phospholimine (1.04 g, 30%) m.p. 185-187° as a yellow microcrystalline solid.

Found: C, 76.9; H, 5.0; N, 2.9%. m/e; 447. C\textsubscript{29}H\textsubscript{22}NO requires C, 76.9; H, 4.9; N, 3.1%. m/e; 447.

N.m.r. (CDCl\textsubscript{3}) τ 1.88-2.13 (2H, \text{ortho protons PhP}), 2.24-3.10 (20H, \text{aromatic}).

I.r. ν\text{max} 1640 (C=O) 1270 (P=N) cm\textsuperscript{-1}

U.V. (methanol) λ\text{max} 208 (31,900), 221 (29,300), 394 (12,600) nm.
(d) Reaction of 1, 2, 5-Triphenylphosphole with Sulphonyl, Phosphinyl and Benzyl Azides.

1. N-Mesyl-1, 2, 5-triphenylphospholimine.

Mesyl azide (1.42 g, 0.016 mol) was reacted with 1, 2, 5-triphenylphospholimine (3.72 g, 0.012 mol) in refluxing toluene (60 ml) for 1.5 h. On cooling yellow crystals formed which were filtered off and washed with ether to give the phospholimine (4.11 g, 92%), m.p. 242-243°.

Found: C, 68.1; H, 5.1; N, 3.4%. m/e; 405.

\[
C_{23}H_{20}NO_2 \quad \text{requires} \quad C, 68.2; H, 5.0; N, 3.5%. m/e; 405.
\]

N.m.r. 1.9-2.9 (3H, aromatic), 7.4 and 7.3 (3H, methyl protons). Decoupling on phosphorus did not collapse this latter pair of peaks to a singlet.

i.r. \( \nu_{\max} \) 1275 (P=N) cm.\(^{-1}\)

2. N-(4-Nitrobenzene)sulphonyl-1, 2, 5-triphenylphospholimine.

The phosphole (4.12 g, 0.013 mol) and 4-nitrobenzenesulphonyl azide (3.07 g, 0.013 mol) were reacted as in (d)\(^1\) to yield the phospholimine (5.04 g, 72%) m.p. 222-223°.

Found: C, 65.5; H, 4.1; N, 5.5%. m/e; 492.

\[
C_{28}H_{21}N_2O_4PS \quad \text{requires} \quad C, 65.5; H, 4.1; N, 5.4%. m/e; 492.
\]

N.m.r. (CDCl\(_3\)) \( \tau \) 1.92-2.92 (c, aromatic).

i.r. \( \nu_{\max} \) 1270(P=N) cm.\(^{-1}\)

3. N-Tosyl-1, 2, 5-triphenylphospholimine.

1, 2, 5-Triphenylphosphole (6.00 g, 0.019 mol) and tosyl azide (5.00 g, 0.025 mol) were allowed to react as in (d)\(^1\). N-Tosyl-1, 2, 5-triphenylphospholimine (7.01 g, 78%) m.p. 249-252° (245-247°) was filtered off and washed with ether. I.r. and u.v. identical to an authentic sample.

4. N-Diphenylphosphinyl-1, 2, 5-triphenylphospholimine.

1, 2, 5-Triphenylphosphole (0.91 g, 0.003 mol) was boiled
under reflux with diphenylphosphinyl azide (1.20 g, 0.005 mol) in toluene (100 ml). After 6 h the reaction was not complete (t. l. c.) and a further addition of azide (1.00 g, 0.004 mol) was made. The mixture was concentrated to one third its volume and added to excess ether and left at 0°C. Bright yellow crystals of the phospholimine (0.46 g, 32%) m. p. 218-222°C were collected after recrystallisation from chloroform/ether.

Found: C, 76.6; H, 5.2; N, 2.6%.
\[ \text{C}_{34}\text{H}_{27}\text{NOP}_2 \] requires C, 77.3; H, 5.1; N, 2.6%.
The mass spectrum showed the correct parent ion: m/e; 527.

Found: 527.157074.
\[ \text{C}_{34}\text{H}_{27}\text{NOP}_2 \] requires 527.156789.

N. m. r. (CDCl₃) \( \tau \) 1.82-2.08 (2H, \( \delta \), ortho protons PhP), 2.29-3.01 (25H, \( \delta \), aromatic).
I. r. \( \nu_{\text{max}} \) 1165 (P=N) 1209 (P=O) cm\(^{-1}\)
U. V. (methanol) \( \lambda_{\text{max}} \) 209 (33,800), 223 (32,700), 396 (10,000) nm.

5. **Reaction of 1,2,5-Triphenylphosphole with Benzyl Azide.**

1, 2, 5-Triphenylphosphole (3.00 g, 0.01 mol) and benzyl azide (2.64 g, 0.02 mol) were heated in toluene at 100°C. On removal of solvent a red gum was obtained which would not crystallise. Prolonged trituration under ether produced a yellow solid which was recrystallised from chloroform/ether to give yellow crystals identified as 1, 2, 5-triphenylphosphole-1-oxide, m. p. 233-234°C (Lit.\(^{21}\) m. p. 237-239°C), ir identical to an authentic sample.
Preparation of N-Benzoyl-1, 2, 5-triphenylphospholimines.

1. N-Benzoyl-1, 2, 5-triphenylphospholimine.
   a) The phosphole (1.04 g, 0.003 mol) and 5-phenyl-1, 2, 5-dioxazalidin-2-one (0.51 g, 0.003 mol) were ground to an intimate mixture with a catalytic quantity of copper bronze and heated in a melt at 120° in a stream of nitrogen for 10 min. The mixture was then dissolved in chloroform, filtered, adsorbed on dry column alumina and chromatographed with ether to give crude phospholimine (0.68 g, 54%). Recrystallisation from chloroform/ether gave yellow crystals of N-benzoyl-1, 2, 5-triphenylphospholimine (0.30 g, 24%) m. p. 210° (d) residue melts 225°.

   Found: C, 80.2; H, 5.2; N, 3.2%. m/e; 431.

   C<sub>29</sub>H<sub>22</sub>NOP requires C, 80.6; H, 5.1; N, 3.3%. m/e; 431.

   I. r. max 1600 (C=N) 1565 (C=O) 1320 (P=N) cm.⁻¹

   1, 2, 5-Triphenyl phosphole (0.20 g, 19%) and 1, 2, 5-triphenyl phosphole oxide (0.08 g, 7%) were also recovered from the column.

   b) Reaction (e) 1. a. was repeated at 150°. A white smoke smelling strongly of benzonitrile was evolved. 1, 2, 5-Triphenylphosphole oxide (96%), i. r. identical to an authentic sample, was isolated by dry column chromatography.

   c) Attempted Reactions of 1, 2, 5-Triphenylphosphole with Benzoyl Azide.

   Benzoyl azide was heated with 1, 2, 5-triphenyl phosphole both in equimolar amounts and with the azide in large excess in toluene at 100°, 80° and 70° and in acetonitrile at 70°. At temperatures above 80° nitrogen was evolved but each attempt resulted in a recovery of phosphole greater than 80%. Diphenylurea was isolated as a product by dry column chromatography. When the azide was present in large (10 m) excess the recovery of phosphole oxide suggested about 3% reaction based on phosphole. The mass spectrum of the crude isolated phosphole oxide showed a small peak m/e; 431 (0.1% of base peak, m/e; 328). This
is the only evidence for phospholimine formation. Below 70° no nitrogen evolution was observed.

2. N-(4-Nitrobenzoyl)-1, 2, 5-triphenylphospholimine.

a) 1, 2, 5-Triphenylphosphole (0.93 g, 0.003 mol) and 5-(4-nitrophenyl)-1, 2, 5-dioxazalidin-2-one (0.62 g, 0.003 mol) were reacted as in e.1.a.). The crude product (0.92 g) was chromatographed on dry column alumina with ether to give the phospholimine (0.42 g, 36%) m.p. 192-193° after recrystallisation from chloroform/ether.

Found: 73.2; H, 4.6; N, 6.0%. m/e; 476. 
C_{29}H_{21}N_{2}O_{3}P requires 73.1; H, 4.4; N, 5.9%. m/e; 476. 
I. r. \( \gamma_{\text{max}} \) 1612 (C=N), 1582 (C=O), 1330 (P=N) cm\(^{-1}\) 
A sample heated to its m.p. showed two spots on t. l. c. corresponding to phosphole oxide and p-nitrobenzonitrile.

b) The above reaction was repeated at 150°. Dry column chromatography gave three products: recovered phosphole (33%); 1, 2, 5-triphenyl phosphole oxide (50%), i. r. identical to an authentic sample; and p-nitrobenzonitrile (24%) m.p. 145-146° (Lit. 115 m.p. 149°) i. r. identical to an authentic sample.

c) Preparation from 4-Nitrobenzoyl Azide.

4-Nitrobenzoyl azide (0.61 g, 0.007 mol) and 1, 2, 5-triphenyl phosphole (1.04 g, 0.003 mol) were heated in toluene (25 ml) at 85°, the minimum temperature at which nitrogen was seen to be evolved. On cooling the phosphole (0.64 g, 62%) crystallised from the mixture. The remainder of the reaction mixture was chromatographed on dry column alumina with ether to give crude product (0.09 g, 6%) which on recrystallisation from chloroform/ether gave yellow crystals of the phospholimine (0.04 g, 3%) m.p. 179-181°. I. r. identical to the authentic sample from (e) 2. a).

T.LC. of the product showed one spot; t.l.c. of a sample heated to its melting point showed two spots corresponding to p-nitrobenzonitrile and 1, 2, 5-triphenylphosphole oxide.
3. N-(2,4-Dinitrobenzoyl)-1,2,5-triphenylphospholimine.

1, 2, 5-Triphenylphosphole (1.04 g, 0.003 mol) and 2,4-dinitrobenzoyl azide (2.00 g, 0.008 mol) were stirred in toluene (50 ml) at 50\(^\circ\). As the reaction proceeded a crystalline solid was deposited. When nitrogen evolution was complete the solid (1.54 g, 92\%) was filtered off and recrystallised from chloroform/ether to give lemon-yellow crystals of the phospholimine (1.32 g, 55\%) m.p. 222-223\(^\circ\).

Found: C, 66.5; H, 3.8; N, 7.9\%. m/e; 521.

C\(_{29}\)H\(_{20}\)N\(_3\)O\(_5\)P requires C, 66.6; H, 3.8; N, 8.1\%. m/e; 521.

I.r. \(\gamma\)\(_{\text{max}}\) 1610 (C=N), 1587 (C=O), 1539, 1530 (NO\(_2\)), 1325 (P=N) cm\(^{-1}\).
Preparations and Attempted Preparations from Nitrene and Nitrenoid Sources

1. **The Reaction of 1, 2, 5-Triphenylphosphole with Ethyl N-(p-Nitrobenzene sulphonyloxy)carbamate.**

   The phosphole (2.02 g, 0.007 mol) was stirred vigorously with the carbamate (1.85 g, 0.007 mol) in methylene chloride (150 ml). Triethylamine (1.0 ml) was added dropwise over 0.5 h and the stirring continued for a further hour. The solvent was removed and the residue recrystallised from ethanol. The product was washed with a little ethylene dichloride to remove the last traces of unreacted phosphole. A further recrystallisation from chloroform/ether gave N-(ethyl carboxylate)-1, 2, 5-triphenylphospholimine (0.91 g, 36%) m. p. 219-221°C (lit. m. p. 220-221°C), i.r. identical with an authentic sample.

   No reaction occurred in the absence of triethylamine.

2. **Oxidation of N-Amino phthalimide with Lead Tetraacetate in the presence of 1, 2, 5-Triphenylphosphole.**

   N-Amino phthalimide (0.65 g, 0.004 mol) and 1, 2, 5-triphenylphosphole (1.04 g, 0.003 mol) were stirred in dry methylene chloride at room temperature. Solid, dried lead tetraacetate (1.24 g, 0.004 mol) was added and the solution turned deep red. Gradually (over 15-30 min) the solution turned fluorescent yellow-green. The mixture was filtered through celite and the solvent evaporated. The residue was chromatographed on dry column alumina with ether to give phosphole oxide (1.18 g, 87%) m. p. 228-230°C (lit. m. p. 237-239°C), i.r. identical to authentic sample. The other component of the mixture, N-aminophthalimide was identified by t.l.c. only.

3. **Reaction of 1, 2, 5-Triphenylphosphole with N-Phthalimido-(2-acetylbenzofuro)[2, 3-b]aziridine.**

   The aziridine (1.00 g, 0.003 mol) was boiled under reflux with the phosphole (0.90 g, 0.003 mol) for 4 h. The resultant red
solution was evaporated to dryness and the residue, a red gum, triturated under ether. The orange solid thus obtained was re-crystallised from chloroform/ether to yield deep red cubes (0.29 g) m.p. 231-235 °. Two parent peaks were found on the mass spectrum: m/e; 472.

Found: 472.13391

C_{30}H_{21}N_2O_2P requires 472.134058.

and m/e; 488.

Found: 488.127884.

C_{30}H_{21}N_2O_2P requires 488.128972.

i.r. \( \nu_{\text{max}} \) 1760, 1740, 1720, 1690 (C=O) 1365 (P=N) cm\(^{-1}\)

U.V. \( \lambda_{\text{max}} \) (ethanol) 212 (24,000), 392 (8,000) nm.

The mother liquor was concentrated to yield phosphole oxide (0.41 g, 24%) m.p. 232-233 ° (lit., m.p. 237-239 °), i.r. identical to an authentic sample. The remaining mother liquor contained a mixture of products including unreacted phosphole, phosphole oxide and N-aminophthalimide (t. l. c.).

4. Reaction of 1, 2, 5-Triphenylphosphole with Tetrazolo-[1, 2-a][4, 6-dimethylpyrimidine.

The phosphole (1.04 g, 0.003 mol) and the tetrazole (0.45 g, 0.003 mol) were boiled under reflux in toluene (50 ml) for 2 h. No reaction occurred (t. l. c.). A catalytic quantity of copper bronze was added and the solution maintained at 80°. Nitrogen was evolved and the reaction was complete in 30 min. The solvent was removed and the residue chromatographed on dry column alumina with ether to give yellow crystals of impure N-2-(4, 6-dimethylpyrimidyl)-1, 2, 5-triphenylphospholimine (0.51 g, 35%) m.p. Decomposition from 160° residue melts 236-240°.

The mass spectrum showed the correct parent ion: m/e; 433.

Found: 433.170992.

C_{28}H_{24}N_3P requires 433.170777.

N.m.r. 1.68-2.10 (2H, ortho protons PhP), 2.20-2.92
(15H, c, aromatic) 3.73 (1H, s, pyrimidyl ring proton), 7.88 (6H, s, methyl protons).
I. r. \( \nu_{\text{max}} \) 1338 (P=N) cm\(^{-1}\)

5. **Reaction of 1, 2, 5-Triphenylphosphole with p-Nitro-nitrosobenzene.**

p-Nitronitrosobenzene (0.50 g, 0.003 mol) in ethylene dichloride (10 ml) was added dropwise to a solution of 1, 2, 5-triphenyl phosphole (1.04 g, 0.003 mol) and triethyl phosphite (0.55 g, 0.003 mol) in ethylene dichloride (30 ml). The resultant dark brown solution was evaporated to dryness and the residue chromatographed on dry column alumina with ether. Recrystallisation from chloroform/ether gave N-(p-nitro)-1, 2, 5-triphenyl phospholimine (0.12 g, 8%) m. p. 207-210° (lit. m. p. 212-214°), i. r. identical to an authentic sample.
5. **Preparation of Phosphinimines**

1. **N-(o-Nitrophenyl)iminotriphenylphosphorane**

Triphenylphosphine (3.22 g, 0.012 mol) in ether (20 ml) was mixed with o-azidonitrobenzene in ether (20 ml). No nitrogen evolution was observed. After 30 min a yellow crystalline solid formed which was filtered off and washed with ether. Warming this compound released nitrogen and thus it assumed to be the intermediate triazine (2.92 g, 42%). The triazine was boiled under reflux in chloroform (10 ml) until nitrogen evolution ceased (ca. 15 min). Addition of excess ether to the hot solution gave yellow crystals of the phosphinimine (1.41 g, 34%) m.p. 141-142° (lit. 67° m.p. 151-152°)

**Found:** C, 72.1; H, 4.8; N, 7.0%.  
**C\textsubscript{24}H\textsubscript{19}N\textsubscript{2}O\textsubscript{2}P** requires C, 72.3; H, 5.0; N, 7.0%.  
The mass spectrum showed the correct parent ion: m/e; 398.

2. **N-(4-Methyl-2-nitrophenyl)iminotriphenylphosphorane.**

Triphenylphosphine (2.20 g, 0.010 mol) and 4-azido-3-nitrotoluene were reacted as in 1. to yield the triazine (2.40 g, 80%) which was decomposed as above to give the phosphinimine (0.86 g, 30%).

**Found:** C, 72.4; H, 5.2; N, 6.8%. m/e; 412.  
**C\textsubscript{25}H\textsubscript{21}N\textsubscript{2}O\textsubscript{2}P** requires C, 72.8; H, 5.1; N, 6.8%. m/e; 412.

3. **N-(2-Carboxyphenyl)iminotriphenylphosphorane.**

Triphenylphosphine (2.00 g, 0.008 mol) and 2-azidobenzoic acid (1.03 g, 0.007 mol) were reacted as in 1. The triazine\textsuperscript{58} was isolated (2.74 g, 92%). D.T.A. showed violent decomposition from
125°.

Found: C, 70.2; H, 4.9; N, 9.8%.

\( C_{25}H_{20}N_3O_2P \) requires C, 70.5; H, 4.7; N, 9.9%.
The triazine (0.42 g, 0.001 mol) was decomposed in toluene at 100°. Removal of solvent and recrystallisation from chloroform/ether gave brownish crystals of the phosphinimine (0.37 g, 100%) m. p. 205-209° (lit. 58 m. p. 212°).

Found: C, 75.4; H, 5.3; N, 3.6%.

\( C_{25}H_{20}NO_2P \) requires C, 75.6; H, 5.1; N, 3.6%.
The compound can be decolorised by boiling in triethylamine under reflux for several hours.

4. **N-(2, 4-Dinitrophenyl)iminotriphenylphosphorane.**
The phosphine (2.40 g, 0.009 mol) and 2, 4-dinitrophenyl azide (1.50 g, 0.007 mol) were reacted as in 1. above. The isolated triazine (3.02 g, 89%) was decomposed in chloroform and treated with ether to give the phosphinimine (2.42 g, 77%) m. p. 190-192° (lit. 67 m. p. 201-202°).

Found: C, 64.8; H, 4.2; N, 9.4%. m/e; 443.

\( C_{24}H_{18}N_3O_4P \) requires C, 64.9; H, 4.1; N, 9.5%. m/e; 443.

5. **N-Picryliminotriphenylphosphorane.**
Picryl azide (1.52 g, 0.006 mol) and triphenylphosphine (2.07 g, 0.008 mol) were reacted as in 1. above to yield a deep red crystalline triazene (3.02 g, 100%). D. T. A. shows rapid decomposition above 90°.

Found: C, 55.1; H, 3.3; N, 16.3%.

\( C_{24}H_{17}N_6O_6P \) requires C, 55.7; H, 3.3; N, 16.2%.
The triazine (2.23 g, 0.005 mol) was allowed to decompose in boiling chloroform and when nitrogen evolution had ceased ether was added to give the crystalline phosphinimine (0.96 g, 45%) m. p. 183-184° (lit. 67 m. p. 183-184°).

Found: C, 58.9; H, 3.7; N, 11.7%.

\( C_{24}H_{17}N_4O_6P \) requires C, 59.0; H, 3.5; N, 11.5%.
6. **N-2-(8-Nitronaphthyl)iminotriphenylphosphorane.**

Triphenylphosphine (0.60 g, 0.002 mol) and 2-azido-8-nitronaphthalene (0.40 g, 0.002 mol) were mixed in ether. Triazine formation was not observed and brown crystals of the phosphinimine (0.61 g, 70%) m.p. 210-212° were filtered off and washed with ether.

Found: C, 74.9; H, 4.8; N, 6.3%. m/e; 448. 
C_{28}H_{21}N_{2}O_{2}P requires C, 75.0; H, 4.7; N, 6.2%. m/e; 448.

7. **N-(2-Acetylphenyl)iminotriphenylphosphorane.**

2-Azidoacetophenone (1.00 g, 0.006 mol) and triphenylphosphine (1.86 g, 0.007 mol) were reacted as in 1. A pale yellow triazine (2.43 g, 96%) was isolated and decomposed as above to give white prisms of N-(2-acetylphenyl)iminotriphenylphosphorane (2.21 g, 90%) m.p. 125-126°.

Found: C, 78.3; H, 5.7; N, 3.4%. m/e; 395. 
C_{26}H_{22}NOP requires C, 79.0; H, 5.6; N, 3.4%. m/e; 395.

N.m.r. (CDCl₃) δ 2.20-3.78 (19H, c, aromatic), 7.39 (3H, s, methyl protons).

I.r. ν max. 1690 (C=O) 1340 (P=N) cm⁻¹

8. **N-(2-Benzoylphenyl)iminotriphenylphosphorane.**

2-Azidobenzophenone (2.23 g, 0.010 mol) and triphenylphosphine (2.70 g, 0.010 mol) were mixed in ether, the triazine filtered off and decomposed as above to give pale yellow crystals of N-(2-benzoylphenyl)iminotriphenylphosphorane (4.21 g, 88%) m.p. 188-190°.

Found: C, 81.2; H, 5.3; N, 3.1%. m/e; 457. 
C_{31}H_{24}NOP requires C, 81.1; H, 5.3; N, 3.1%. m/e; 457.

I.r. ν max. 1697 (C=O) 1325 (P=N) cm⁻¹

9. **N-(p-Tolyl)iminotriphenylphosphorane.**

Triphenylphosphine (4.50 g, 0.017 mol) and p-tolyl azide were mixed in ether at room temperature. Nitrogen was released
and after 30 min the product was precipitated with petrol and recrystallised from chloroform /ether to give the phosphinimine (3.72 g, 67%) m. p. 130-131\(^\circ\) (lit.\(^6\) m. p. 131-132\(^\circ\))

Found: C, 82.1; H, 6.1; N, 3.8%. m/e; 367.

\(\text{C}_{25}\text{H}_{22}\text{NP}\) requires C, 82.0; H, 6.0; N, 3.8%. m/e; 367.

10. \(N-\text{(o-Nitrophenyl)iminotrichlorophosphorane.}\)

This was prepared by a modification of the procedure described by Kirsanov.\(^7\)

\(\text{o-Nitroaniline hydrochloride (2.12 g, 0.012 mol) and phosphorus pentachloride (4.20 g, 0.020 mol) were boiled under reflux in toluene (50 ml) until evolution of hydrogen chloride ceased. Dry petrol (100 ml) was added to the reaction mixture and the precipitated material discarded. The filtered solution was tightly sealed and stored at 0\(^\circ\) for 2 days. Brown crystals of } \text{N-(o-nitrophenyl)-iminotrichlorophosphorane (3.40 g, 99%) m. p. 110-112\(^\circ\) (lit.,}\(^7\) m. p. 109-111\(^\circ\)) \text{were filtered off in a dry box and washed thoroughly with anhydrous ether.}

Found: C, 26.8; H, 1.6; N, 10.0%.

\(\text{C}_{6}\text{H}_4\text{N}_2\text{O}_2\text{PCl}_3\) requires C, 26.4; H, 1.4; N, 10.2%.

The mass spectrum showed the correct parent ions expected for the trichloro compound: m/e; 278 \(\text{(}^{37}\text{Cl}_3\text{)}\) 276 \(\text{(}^{37}\text{Cl}_2, ^{35}\text{Cl}\text{)}\) 274 \(\text{(}^{37}\text{Cl, }^{35}\text{Cl}_2\text{)}\) 272 \(\text{(}^{35}\text{Cl}_3\text{)}\).
6. **Preparation of Phosphorimidates**

1. **Triethyl-N-(o-acetylphenyl)phosphorimidate.**

2-Azidoacetophenone (2.00 g, 0.012 mol) and triethyl phosphite (2.00 g, 0.012 mol) were mixed in benzene (20 ml). After the initial reaction had subsided the mixture was boiled under reflux for 1 h. The benzene was evaporated to leave a yellow oil which was distilled at reduced pressure to give the phosphorimidate (3.41 g, 90%) b.p. 121/0.2 mm. Hg.

The mass spectrum showed the correct parent ion: m/e; 299.

N.m.r. (CDCl₃) δ 2.4-3.6 (4H, s, aromatic), 5.6-6.2 (6H, s, ethoxy methylene protons split by phosphorus), 7.43 (3H, s, acetyl methyl protons), 8.7 (9H, t, ethoxy methyl protons).

2. **Triethyl-N-(o-nitrophenyl)phosphorimidate.**

o-Azidonitrobenzene (2.00 g, 0.012 mol) and triethyl phosphite (2.00 g, 0.012 mol) were reacted as in 1. above. Chromatography on alumina with ether gave the phosphorimidate (3.04 g, 82%) as a yellow oil which was not further purified.

The mass spectrum showed the correct parent ion: m/e; 302.

N.m.r. (CCl₄) δ 2.4-3.6 (4H, s, aromatic), 5.6-6.2 (6H, s, ethoxy methylene protons), 8.65 (9H, t, ethoxy methyl protons).

1. Thermolysis of N-(o-Nitrophenyl)-1, 2, 5-triphenylphospholimine in Mesitylene

The phospholimine (1.04 g, 0.002 mol) was boiled under reflux in mesitylene (25 ml) for 48 h under nitrogen. Buff crystals of impure phosphole oxide (0.48 g, 64%) m.p. 212-213° (lit. m.p. 237-239°), i.r. identical to an authentic sample, formed on cooling. Chromatography of the mother liquor on alumina provided further phosphole oxide (0.18 g, 24%. Overall yield 88%).

2. Thermolysis of N-(o-Nitrophenyl)-1, 2, 5-triphenylphospholimine in Sealed Tubes at 160°.

Sealed tubes containing the phospholimine (0.02-0.03 g) in mesitylene (1 ml) were heated in an oil bath at 160° for 48 h.

G.l.c. analysis (10% FFAP, 150°; 5% Carbowax, 160°) showed a peak corresponding to benzofurazan; m.s./g.l.c. (5% Carbowax, 160°) gave the correct parent ion: m/e 120. Preparative g.l.c. was performed on the D.6. gas density balance (10% Carbowax) to give a sample of benzofurazan (50-65%) estimated using biphenyl as internal standard.

Found: 120.032666.

\[ \text{C}_6\text{H}_4\text{N}_2\text{O} \] requires 120.032360.

3. Thermolysis of Various N-(Nitroaryl)iminophosphoranes in Mesitylene at 160°.

a. N-(o-Nitroaryl)-1, 2, 5-triphenylphospholimines.

The procedure was as for 2. above. The reactions were quantified, using bibenzyl as internal standard, and the products isolated on the D.6 instrument. The results are summarised on Table I.
<table>
<thead>
<tr>
<th>Aryl Group</th>
<th>m.s./g.l.c. (m/e)</th>
<th>Exact Mass</th>
<th>Formula</th>
<th>Requires</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-NO₂-6-Me-phenyl</td>
<td>134</td>
<td>134.047791</td>
<td>C₇H₆N₂O</td>
<td>134.048010</td>
<td>50</td>
</tr>
<tr>
<td>2-NO₂-5-Me-phenyl</td>
<td>134</td>
<td>134.048054</td>
<td>C₇H₁₆N₂O</td>
<td>134.048010</td>
<td>32</td>
</tr>
<tr>
<td>2-NO₂-4-Me-phenyl</td>
<td>134</td>
<td>134.048053</td>
<td>C₇H₁₆N₂O</td>
<td>134.048010</td>
<td>46[1]</td>
</tr>
<tr>
<td>2-NO₂-4-MeO-phenyl</td>
<td>150</td>
<td>150.042803</td>
<td>C₇H₆N₂O₂</td>
<td>150.042924</td>
<td>44[2]</td>
</tr>
<tr>
<td>2-(1-NO₂-naphthyl)</td>
<td>170</td>
<td></td>
<td>C₁₀H₆N₂O</td>
<td>170</td>
<td>6-8%</td>
</tr>
<tr>
<td>2,4-(NO₂)₂-phenyl</td>
<td>-</td>
<td></td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2-NO₂-4-CF₃-phenyl</td>
<td>-</td>
<td></td>
<td></td>
<td>-</td>
<td>[3]</td>
</tr>
</tbody>
</table>
Notes on Table I.

[1] 5-Methylbenzofurazan m. p. 33-35° (lit. 34° m. p. 37°)
[2] 5-Methoxybenzofurazan m. p. 95-98° (lit. 99° m. p. 99°)
N. m. r. 2.17-3.20 (4H, c, aromatic) 6.09 (3H, s, methoxyl protons).
[3] 4-Amino-3-nitrobenzotrifluoride (10% estimated by g. l. c.)
m/e; 206 was isolated by preparative g. l. c.
Found: 206.030771.

C₇H₅N₂O₂F₃ requires 206.030306.

b. N-(o-Nitroaryl)iminotriphenylphosphoranes.
The N-(2-nitroaryl)iminotriphenylphosphoranes (aryl = phenyl, 4Me-phenyl and 4-NO₂-phenyl) all proved stable under the conditions for thermolysis described in 2. above.

c. Triethyl-N-(o-nitrophenyl)phosphorimidate.
The phosphorimidate proved stable under the thermolytic conditions described in 2. above.

d. N-(o-Nitrophenyl)iminotrichloroiminophosphorane.
The iminophosphorane (0.76 g) in mesitylene (5 ml) was thermolysed as in 2. above. G. l. c. analysis (5% Carbowax, 150°) showed two peaks of similar magnitude. G. l. c. /m. s. analysis gave m/e; 151±1 and m/e; 120. The peak m/e; 120 had the same retention time as an authentic sample of benzofurazan. Black tar accounted for up to 50% of the aminophosphorane.

e. N-1-(8-Nitronaphthyl)iminotriphenylphosphorane.
Thermolysis for 3 weeks in mesitylene under nitrogen gave recovery of the phosphinimine (90-95%) and a small quantity of tarry residue which was not further investigated.

N-(o-Nitrophenyl)-1,2,5-triphenylphospholimine (0.38 g) was dissolved in bromobenzene (10 ml) with biphenyl (0.15 g) as internal standard. The solution was divided into two parts, to one of which was added 1,2,5-triphenylphosphole (0.18 g). A third
solution was prepared of the phospholimine (0.18 g) biphenyl (0.07 g) in bromobenzene (10 ml). Aliquots (0.25 ml) of the solution were placed in sealed tubes and heated at 149° in an oil bath.

The progress of the reaction was followed by g.l.c. (5% Carbowax, 150°), the benzofurazan concentration being measured as a fraction of the internal standard. The results in all cases were found to follow first order kinetics. The best lines were found by the least squares technique. The results are shown in graphs 1, 2 and 3.
Explanatory Note

$B_T$ is the ratio of product (benzofurazan) to standard (biphenyl) at time $T$. $B_\infty$ is this ratio at $T_\infty$ which was 48 h.

Graph 1. - Thermolysis of phospholimine (0.3814 g) in bromobenzene (5 ml).

Graph 2. - Thermolysis of phospholimine (0.1787 g) in bromobenzene (5 ml).

Graph 3. - Thermolysis of phospholimine (0.3814 g) in bromobenzene (5 ml) in the presence of 1, 2, 5-triphenylphosphole (0.18 g).
Graph 1

\[ \log \frac{B_\infty}{B_\infty - B_T} \]

Gradient = \( k = 2.8 \times 10^{-3} \text{ min}^{-1} \)
\[ \text{Gradient } = k = 3 \times 10^{-3} \text{ min}^{-1} \]
Graph 3

\[ \log \frac{B_\infty}{B_\infty - B_T} \]

Gradient \( k = 2.7 \times 10^{-3} \text{ min}^{-1} \)
Decomposition of N-(o-Nitrophenyl)-1, 2, 5-triphenylphosphole in the presence of 1, 2-Diphenyl-5-tolylphosphole.

The phospholimine (2.23 g, 0.005 mol) and a mixture of 1, 2, 5-triphenylphosphole and 1, 2-diphenyl-5-tolylphosphole (1:2.8, 1.63 g, 0.005 mol) were heated in mesitylene (100 ml) for 72 h. The phosphole oxide fraction (1.58 g, 95-100%) was separated by chromatography on alumina. N.m.r. and low eV. mass spectrometry both showed a mixture of 1, 2, 5-triphenylphosphole-1-oxide and 1, 2-diphenyl-5-tolylphosphole-1-oxide in the ratio 7.5:1. After correcting for 1, 2, 5-triphenylphosphole added it was found that the ratio of oxide originating from the phospholimine to that formed from the phosphole was 7:1.

Competitive Deoxygenation of Benzofuroxan by 1, 2, 5-Triphenylphosphole and 1, 2-Diphenyl-5-tolylphosphole.

1, 2, 5-Triphenylphosphole (0.52 g, 0.0017 mol) and a mixture of 1, 2, 5-triphenylphosphole and 1, 2-diphenyl-5-tolylphosphole (0.54 g 1:1.8) and benzofuroxan (0.20 g, 0.0015 mol) were boiled under reflux in benzene for 4 h. The solvent was removed and chromatography on alumina gave the mixed oxides. Low eV. mass spectrometry and n.m.r. showed the ratio of 1, 2, 5-triphenylphosphole-1-oxide to 1, 2-diphenyl-5-tolylphosphole-1-oxide to be 1.4:1 which after correction for the mixed phosphole shows the rates of deoxygenation of benzofuroxan to be almost equal.

Reaction of 1, 2, 5-Triphenylphosphole with N-(o-nitrophenyl)-iminotriphenylphosphorane.

The phosphinimine (1.00 g, 0.003 mol) and 1, 2, 5-triphenylphosphole (1.00 g, 0.003 mol) were heated in mesitylene at 150° for 72 h. 1, 2, 5-Triphenylphosphole-1-oxide (0.12 g, 8%) was isolated from the reaction mixture.
A vigorously stirred mixture of 1, 2, 5-triphenylphosphole (3.12 g, 0.010 mol) and o-nitrobenzyl bromide (8.00 g, 0.03 mol) in benzene (100 ml) was boiled under reflux for 20 h. The solid which formed in the cooled mixture was filtered off and recrystallised from isopropanol to give orange crystals of 1-(o-nitrophenyl)-1, 2, 5-triphenylphospholium bromide (3.92 g, 74%) m. p. 130-138°. N. m. r. \( \delta^{6} \) DMSO \( \tau \) 1.2-3.0 (c, aromatic) 1.13 (d, methylene protons, \( J_{PH} \) 14Hz).

The phosphonium bromide was treated in the following deoxygenated solvents with various bases: dimethoxyethane and potassium \( t \)-butoxide; dimethoxyethane and sodium hydride; ethanol and sodium ethoxide; and mesitylene and sodium hydride. In each case a deep purple solution was formed which was assumed to be the ylid. The solutions were boiled under reflux for several days. In no case was there any evidence for a reaction of the type described for the N-(a-nitroaryl)-1, 2, 5-phospholimines (i.e. 1, 2, 5-triphenylphosphole oxide was not detected). However, the ylid solution was found to give 1, 2, 5-triphenylphosphole oxide in the presence of air or moisture.

1. N-(o-Acetylphenyl)iminotriphenylphosphorane.

Freshly prepared and recrystallised phosphinimine (0.50 g, 0.001 mol) was heated in o-dichlorobenzene (4 ml) at 160°C for 48 h. G.l.c. analysis (5% Carbowax, 5% S.E. 30) showed no volatiles. Chromatography on alumina of the entire reaction mixture gave triphenylphosphine oxide (0.10 g, 33%), i.r. identical to an authentic sample and a fluorescent solid which was recrystallised from petrol to give non-fluorescent white crystals of 2-(o-amino-phenyl)-4-methylquinoline (0.08 g, 50%) m.p. 79-80°C (lit., m.p. 82-83°C).

Found: C, 82.1; H, 6.0; N, 11.7%. m/e; 234. C₁₆H₁₄N₂ requires C, 82.0; H, 6.0; N, 12.0%. m/e; 234.
N.m.r. (CDCl₃) 7.1.4-3.1 (9H, s, aromatic), 3.27 (2H, s, [broad], NH₂), 3.92 (3H, s, methyl).

The mass spectrum also showed a small peak m/e; 495±1.

2. Triethyl-N-(o-acetylphenyl)phosphorimidate.

The phosphorimidate was passed through a hot tube packed with glass wool at 450°C at 0.2 mm Hg. The collected oil proved to be mainly starting material. G.l.c./m.s. analysis (5% Carbowax, 200°C) showed three peaks: m/e; 299, 299 and 271±1. Chromatography on dry column alumina gave three components: m/e; 299, 299 and 271. The difficulty in achieving pure products and their presence in minute amounts led to very poor n.m.r. spectra which could not be interpreted.

Direct pyrolysis at atmospheric pressure in a test tube at 450°C under nitrogen gave red tars.


The phosphinimine was heated in o-dichlorobenzene for 14 days alone and in the presence of copper-bronze. No reaction was observed and the phosphinimine was recovered (95%).
4. N-(2-Benzoylphenyl)-1, 2, 5-triphenylphospholimine.

The phospholimine (0.65 g, 0.0013 mol) was heated in mesitylene for 21 days at 160°. Chromatography on alumina gave 1, 2, 5-triphenylphosphole oxide (0.24 g, 58%), m. p. 231-232° (lit., m. p. 237-239°), i. r. identical to an authentic sample, recovered phospholimine (0.13 g, 22%), m. p. 180-182° (m. p. 191-192°), a brown tarry material (0.04 g, 18%) and a white crystalline compound, m. p. 184-185° suspected to be dibenzo[b:f]-4,8-diphenyl-1,5-diazocine (lit., m. p. 190°).

Found: C, 87.2; H, 5.2; N, 7.7%. m/e; 358.

5. N-(2-Carboxyphenyl)iminotriphenylphosphorane.

The phosphinimine (0.24 g, 0.0006 mol) was thermolysed for 48 h in o-dichlorobenzene (4 ml). G. I. c. analysis showed no volatiles. The mixture was chromatographed on alumina. A bright yellow fluorescence was noted on introduction of the sample on the column which faded through various shades of green and eventually disappeared. Irradiation with long U. V. light showed a pale blue fluorescence. Triphenyl phosphine oxide (0.08 g, 50%) was isolated, i. r. identical to an authentic sample. An off-white solid was washed off with methanol which proved to be a mixture of polymeric materials some too high melting to come off the m. s. probe.

Further attempts to isolate the original fluorescent material (dry column chromatography, rapid chromatography on short columns on both alumina and silica and distillation) met with no success.

6. N-(2-Carboxyphenyl)-1, 2, 5-triphenylphospholimine.

Thermolysis of the phospholimine gave an almost quantitative yield of phosphole oxide and similar polymeric materials as in 5. above. No volatiles were found (g. l. c.).
10. **Reaction of 1, 2, 5-Triphenylphosphole Derivatives with Dienophiles.**

1. **Reaction of Dimethyl Acetylenedicarboxylate with N-Mesyl-1, 2, 5-triphenylphospholimine.**

   a. The N-mesylphospholimine (0.50 g, 0.0012 mol) and the acetylene (1.5 g, 0.013 mol) in mesitylene (50 ml) were boiled under reflux for 12 h. Removal of the solvent by distillation and dry column chromatography on alumina with ether gave dimethyl 3,6-diphenylphthalate (0.33 g, 77%) m.p. 192-193°C (lit., 24 m.p. 189-191°C, i.r. identical to an authentic sample. A second fraction (0.10 g) was seen (t.l.c.) to be a mixture of the phthalate and unreacted phospholimine. A brown gummy solid was isolated from the head of the column. I.r. gave only a series of broad characterless peaks.

   b. The phospholimine (0.41 g, 0.001 mol) and the acetylene (0.42 g, 0.003 mol) were boiled under reflux in chloroform for 10 days. The mixture was chromatographed on dry column alumina with ethyl acetate. The fraction which did not elute was cut out and washed from the alumina with methanol and the solvent removed a white crystalline solid was isolated which was identified as the phthalate (0.04 g, 11%) m.p. 189-190°C (lit., 24 m.p. 189-191°C), i.r. identical to an authentic sample. A small quantity of brown gum was also found in this fraction. T.l.c. showed that the characteristics of this fraction had now changed and that the phthalate now ran near the solvent front. The phospholimine (0.13 g, 32%) was also isolated from the column, i.r. identical to an authentic sample.

2. **Reactions of Phospholimines with Benzyne.**

   The benzyne was generated by the thermolysis of benzene-diazonium-2-carboxylate as described by Friedman. 135

   a. N-Phenyl-1, 2, 5-triphenylphospholimine (1.00 g, 0.002 mol) was boiled under reflux in benzene (100 ml) with benzene-diazonium-2-carboxylate (0.6 g moist with benzene) for 3 days.
The solution was concentrated and chromatographed on alumina to yield a white crystalline solid (80 mg) m.p. 132-135°, m/e; 280, tentatively identified as 1,4-diphenylnaphthalene (1%) (lit. m.p. 135-138°), $C_{22}H_{16}$ requires m/e; 280. A peak in the mass spectrum at m/e; 230 suggests that it is a mixture with some other hydrocarbon. 1,2,5-Triphenylphosphole oxide (0.61 g, 74%) m.p. 224-229, i.r. identical to an authentic sample; m/e; 328. $C_{22}H_{17}PO$ requires 328.

b. N-(p-Nitrophenyl)-1,2,5-triphenylphospholimine was treated as in a. above. The solids were precipitated with petrol and the mass spectrum showed a peak m/e; 524 corresponding to a 1:1 adduct. $C_{34}H_{25}N_2O_2P$ requires 524. Attempts by fractional crystallisation and chromatography to obtain a pure sample failed and the mass spectrum is the only evidence for adduct formation.


a. Reaction of N-MesyI-1,2,5-triphenylphospholimine with Diethyl Azodiformate.

(i) The phospholimine (0.58 g, 0.0014 mol) and the dienophile (0.85 g, 0.005 mol) were boiled under reflux in mesitylene for 3 days. No reaction occurred and the phospholimine (95%), identified by i.r. and t.l.c. was recovered unchanged.

(ii) The phospholimine (0.58 g, 0.0014 mol) was heated on a Woods metal bath at 170° for 10 min. The phospholimine (80%), i.r. identical to an authentic sample, was recovered unchanged. The other products were polar tars which would not chromatograph except with methanol and were not further investigated.

b. Reaction of 1,2,5-Triphenylphosphole Oxides with Diethyl Azodiformate.

The phosphole oxide (0.50 g, 0.0015 mol) and the dienophile (0.87 g, 0.005 mol) were boiled under reflux in benzene (20 ml) for 8 days. Removal of solvent and dry column chromatography
on alumina with ether yielded a yellow solid (0.32 g) and a white crystalline solid (0.02 g) identified as diethyl hydrazodiformate. M p. 128-129° (lit. m. p. 130°); m/e; 176. C₄H₁₂N₂O₄ requires m/e; 176.

The yellow material was chromatographed on a wet column to yield four distinct fractions: (0.08 g), m/e; 502: (0.07 g), m/e; 678: (0.04 g), m/e; 678: (0.11 g), m/e; 676.

4. **Reaction of N-Mesyl-1, 2, 5-triphenylphospholimine with 4-Phenyl-1, 2, 4-triazoline-2, 5-dione.**

4-Phenyl-1, 2, 4-triazoline-2, 5-dione was prepared in situ by the oxidation of 4-phenylurazole with t-butyl hypochlorite as described by Cookson.

To a stirred solution of N-mesyl-1, 2, 5-triphenylphospholimine (0.50 g, 0.001 mol) and 4-phenylurazole (0.22 g, 0.001 mol) was added t-butyl hypochlorite (0.16 g, 0.001 mol) dropwise in the dark. After stirring for 12 h the red solution was chromatographed on dry column alumina with ether to yield recovered phospholimine (0.28 g, 56%) i.r. and t. l. c. identical to an authentic sample. A purple solid (0.04 g), m/e; 615 and a red solid (0.03 g) which remained at the head of the column, were also isolated. The mass spectrum of the latter suggested polymeric material.

4. **Attempted Trapping of the Extruded Phosphorus Fragment in the Reactions between Phosphole Derivatives and Dimethyl Acetylenedicarboxylate.**

a. **With Propyl-Disulphide**

N-p-Tosyl-1, 2, 5-triphenylphospholimine (0.50 g, 0.001 mol) and dimethyl acetylenedicarboxylate (0.94 g, 0.006 mol) were heated at 150° in propyl disulphide (4 ml) in a sealed tube for 2 days. On standing dimethyl 3, 6-diphenylphthalate (0.02 g) crystallised from the mixture. Chromatography on alumina yielded a mixture of products (0.61 g), the remainder of the reaction mixture being tars and were held on the column. Thin layer chromatography on alumina enabled separation of further phthalate (0.03 g, total
yield 14\%). A fluorescent yellow oil (0.20 g), m/e; 285+1.
I.r. \( \text{max} \ 1740 \ \text{(C=O)} \ \text{cm}^{-1} \)
N.M.R. (CC\(_4\)) \( \tau \ 6.1-6.4 \ \text{(c)} \)

The remaining material appeared as a brown gum and was not further investigated.

When the reaction was done in mesitylene using equimolar quantities of the disulphide, phospholimine and acetylene the phthalate yield rose to 70\% and phosphinimine (25\%) was recovered. No evidence for trapping was found however.

b. With p-Dimethoxybenzene.

p-Dimethoxybenzene (10 g) was melted on an oil bath at 150\°. Phosphole oxide (1.08 g, 0.0033 mol) was dissolved in the melt and dimethyl acetylenedicarboxylate (0.47 g, 0.0034 mol) was added dropwise. The mixture was maintained at 150\° for two days. Wet column chromatography on alumina gave the phthalate (0.73 g, 92\%) m.p. 190-191\° (lit. m.p. 189-191\°), i.r. identical to an authentic sample. A small quantity of polymeric tar was also isolated.
DISCUSSION

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DISCUSSION

1. Formation of Phospholimines.

As has been mentioned above the first 1, 2, 5-triphenyl-
phospholimines were made by Gee\textsuperscript{24} from the reaction of 1, 2, 5-
triphenylphosphole with azides and with chloramine T. The
purpose in preparing these compounds was to 'extend the available
phosphole derivatives' so that a more intensive study of Diels-
Alder reactions of the diene system might be made and that
perhaps the extruded phosphorus fragment might be more readily
trapped and identified. Both Gee's\textsuperscript{24} and this present study have
failed to detect the phosphorus fragment although investigation of
these compounds in their own right has led to some interesting
and sometimes unexpected chemistry.

a. Reactions of 1, 2, 5-Triphenylphosphole with Azides.

The reaction of tertiary phosphines with aryl azides has
already been discussed at some length in the Introduction and it
seems likely that the reaction between the phosphole and azides
follows a similar course. However, there is a marked reduction
in nucleophilicity of the phosphole compared to triphenylphosphine,
and, in general it does not react with aryl azides below 70-80\degree.
9-Phenyl-9-phosphafluorene reacts readily with tosyl azide and
\(\alpha\)-nitrophenyl azide at room temperature with evolution of nitrogen.
The buttressing effect of the \(\alpha\)-nitro-group in the reaction of \(\alpha\)-
nitrophenyl azide with triphenylphosphine resulting in triazene
formation was not observed in the reaction with the phospha-
fluorene. This is in agreement with Mislow's\textsuperscript{27} observations
concerning the inversion barriers about phosphorus in simple and
annulated phospholes which he correlated with aromaticity and
hence with the availability of the phosphorus lone pair.

While there is no direct evidence for triazine formation, the
conditions necessary for reaction between an azide and 1, 2, 5-
triphenylphosphole are sufficiently severe to decompose all triphenylphosphine triazenes handled by the author. Hence it is likely that the triazine, if formed, is present only as a transient intermediate. All attempts to obtain a triazine by reacting the phosphole with azides below the minimum temperature of nitrogen evolution failed.

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

\[
\text{ArN}_3
\]

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

\[
\text{Ph}' \quad \text{N-N=N-Ar}
\]

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

\[
\text{N-Ar}
\]

Scheme 1

The reaction of 1, 2, 5-triphenylphosphole with azides is fairly general. In the experimental section are described the preparation of phosphorimines by reaction with aryl azides, sulphonyl azides, azido formates and diphenylphosphinyl azide. The lower nucleophilicity of the phosphole compared to triphenylphosphine, however, reduces the scope of the reaction if there is an alternative facile thermal intramolecular reaction which the azide can undergo. For example, it was found that the phosphole would not react with 2-azidoacetophenone which decomposed, presumably to the anthranil, \(^{136}\) (Scheme 2) without reacting with

\[
\begin{align*}
\text{COMe} & \quad \text{Me} \\
\text{N}_3 & \quad \text{Me}
\end{align*}
\]

\[
\text{Me}
\]

\[
\text{N}
\]

\[
\text{O}
\]

Scheme 2
the phosphole. Similarly, benzoyl azide preferred to undergo a Curtius rearrangement to phenyl isocyanate (Scheme 3)

\[
\text{PhCON}_3 \rightarrow \text{PhNCO} \rightarrow \text{PhNHCONHPh}
\]

\[
\ast \text{N}_2 \quad \text{Scheme 3}
\]

subsequently converted to diphenylurea which was isolated. A small peak is the mass spectrum was the only evidence for phospholimine formation. If the electrophilicity of the benzoyl azide group was increased by substitution of the phenyl ring with nitro-groups a more significant reaction was noted: 4-nitrobenzoyl azide gave 3% and 2,4-dinitrobenzoyl azide gave 55% respectively of the desired phospholimine when allowed to react in equimolar quantities. There was also a significant drop in the minimum temperature required for nitrogen evolution, from 85° in the case of the benzoyl and 4-nitrobenzoyl azides to 50° with 2,4-dinitrobenzoyl azide. Thus the azide route to benzoyl phospholimines is not general, but another route to these compounds will be described below.

From the reaction of 1, 2, 5-triphenyl phosphole with benzyl azide was obtained 1, 2, 5-triphenylphosphole oxide. This is best explained by assuming phospholimine formation followed by hydrolysis, despite the use of dry solvents. That the phospholimine would be readily hydrolysed is expected as there is no possibility of delocalising the negative charge on nitrogen in the benzene ring as conjugation is precluded by the intervening methylene group. The compound is, indeed, similar to triphenylphosphinimine, itself, which hydrolyses on exposure to air. Hence it is expected that the nitrogen will be basic and as stated in the Introduction the ease of hydrolysis is correlated to basicity as the first step is protonation on nitrogen (Scheme 4).
Scheme 4

TABLE I

1, 2, 5-Triphenylphospholimines Prepared from Azides

a. N-Phenyl-1, 2, 5-triphenylphospholimines.

<table>
<thead>
<tr>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>R⁵</th>
<th>R⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>H</td>
<td>-N₂Ph</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>-I</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>CO₂H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>CN</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>SO₂NH₂</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>CH₃</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>R²</td>
<td>R³</td>
<td>R⁴</td>
<td>R⁵</td>
<td>R⁶</td>
</tr>
<tr>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
<td>N₃</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>H</td>
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<td>H</td>
<td>H</td>
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<tr>
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<td>H</td>
<td>N=PPh₃</td>
<td>H</td>
<td>H</td>
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<td>H</td>
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<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>NO₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
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<td>H</td>
<td>Me</td>
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<td>Me</td>
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<td>OMe</td>
<td>H</td>
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<tr>
<td>NO₂</td>
<td>H</td>
<td>NO₂</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>CO₂H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>P(O)Ph₂</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
<tr>
<td>C(O)Ph</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
</tr>
</tbody>
</table>

b. **Other N-Aryl Compounds.**

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

\[
X = \begin{array}{c}
\text{NO₂} \\
\text{O} & \quad \text{O} \\
\text{N} & \quad \text{H} \\
\text{Ph} & \quad \text{Ph} \\
\end{array}
\]
c. **Sulphonyl Derivatives**

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\quad X = \begin{cases} 
\text{Methyl} \\
\text{Tolyl} \\
p\text{-Nitrophenyl}
\end{cases}
\]

---

d. **Phosphinyl Derivatives**

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\quad \text{X} = \begin{cases} 
\text{Ph} \\
\text{Ph}
\end{cases}
\]

---

e. **Carbonyl Derivatives**

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph}
\end{array}
\quad X = \begin{cases} 
\text{Ph} \\
\text{Ph}
\end{cases}
\]

---

114
b. Reactions of 1, 2, 5-Triphenylphosphole with Nitrene and Nitrenoid Species.

Iminophosphoranes can be considered as nitrene adducts of trivalent phosphorus and it has already been mentioned that phosphorimidates have been isolated in phosphite deoxygenation of nitro- and nitroso-compounds. In the reverse of this, nitrenes have been obtained by the photolysis of iminophosphoranes. Thus, Zimmer and Yayawant found, among other products, triphenylphosphine and butylamine on photolysis of N-t-butyliminotriphenylphosphorane (Scheme 5).

\[
\text{Ph}_3\text{PN-CMe}_3 \xrightarrow{\text{hv}} \text{Ph}_3\text{P} + \text{N-CMe}_3 \quad \text{Solvent} \quad \text{H}_2\text{N-CMe}_3
\]

Although the interrelationship of iminophosphorane, nitrene and trivalent phosphorus compound is obvious, little work involving the trapping of nitrenes as iminophosphoranes has been carried out, possibly because the most general route to nitrenes involves decomposition of azides which are known to react with phosphines and phosphites via the intermediacy of a triazene. However there are some known routes to nitrenes which do not involve azides and these have been used in this investigation to produce phospholimines.

Lwowski has described an α-elimination route to ethoxy-carbonyl nitrene by treatment of ethyl N-(p-nitrobenzenesulphonyloxy)-carbamate with base. In the present study the same reaction in the presence of 1, 2, 5-triphenylphosphole gave the phospholimine (2) in 36% yield. No detectable reaction took place in the absence of base, indicating that the reaction proceeds by route 1. rather than route 2. (Scheme 6).
It has been shown by Gosney\textsuperscript{140} that when triphenylphosphine is used in this reaction the reaction proceeds by route 2. This is yet another example of the lower nucleophilicity of the phosphorus atom of the phosphole ring.

The preparation of N-benzoylphospholimines has also been achieved in this investigation by a route involving a nitrene
intermediate. Sauer and Mayer\textsuperscript{128} have reported the thermal decomposition of 5-aryl-1,3,4-dioxazalidin-2-ones to give carbonylnitrenes and carbon dioxide. The temperature required for decomposition ($150^\circ$) proved too high in the case of reaction with triphenylphosphole, however, and the resulting phospholimine decomposed to a benzonitrile and 1,2,5-triphenylphosphole oxide. It was found that modification of this technique by the addition of a catalytic quantity of copper bronze enabled the reaction to take place at $120^\circ$ at which temperature only limited decomposition took place and the product was isolable. (Scheme 7).

This internal Wittig-type reaction has already been discussed in the Introduction (p. 41). The dramatic lowering of the decomposition temperature makes it appear that probably a nitrenoid species is involved rather than a free nitrene. The term 'nitrenoid' is used here to describe a metal complex which reacts to give the products which might be expected from the free nitrene. For example, Kwart and Khan\textsuperscript{141} have reported the copper catalysed decomposition of sulphonyl azides and postulated as an intermediate the copper azide complex (3) which then decomposes to the copper...
nitrene complex (4).

\[
\begin{align*}
\text{Cu} & \quad \overset{\text{N}}{\text{N}} \quad \overset{\text{SO}_2\text{R}}{\text{N}} \\
\text{SO}_2\text{R} & \quad \rightarrow \\
\text{Cu} & \quad \overset{\text{N}}{\text{S}} \quad \overset{\text{O}_2\text{R}}{\text{N}} \\
\text{Cu} & \quad \overset{\text{N}}{\text{S}} \quad \overset{\text{O}_2\text{R}}{\text{N}} \\
\text{Cu} & \quad \overset{\text{N}}{\text{S}} \quad \overset{\text{O}_2\text{R}}{\text{N}} \\
\end{align*}
\]

A similar intermediate (5) may be postulated in the reaction between 1, 2, 5-triphenylphosphole and the dioxazalidinone.

\[
\text{Cu} \quad \overset{\text{NCOAr}}{\text{N}}
\]

5

Although only two examples of this reaction were attempted, (Scheme 7, Ar = phenyl and p-nitrophenyl) it seems likely that the technique may be fairly general in its application. Sauer and Mayer, \textsuperscript{128} however, using dimethyl sulphoxide as trap, report that the presence of electron donating groups causes some isocyanate formation via a Curtius rearrangement resulting in a drop in the yield of sulphonimine.

There have been some examples of phosphinimine formation by reaction of tetrazoles with triphenylphosphine and, as discussed in the Introduction, in some cases at least, the reaction is thought to proceed via the same type of intermediate as in the reaction between phosphines and azides.

However, no reaction was found when the tetrazole (6) was heated with 1, 2, 5-triphenylphosphole in toluene for several hours. Huisgen \textsuperscript{142} has shown that the tetrazole (6) in the presence of copper, \textsuperscript{142} and products were found, typical of a nitrene intermediate. It, therefore, seems likely that the facile formation of the phospholimine (7) in the presence or copper bronze
is due to the intermediacy of a nitrenoid species. (Scheme 8).

The trapping of phthalimidonitrene with 1, 2, 5-triphenylphosphole was also attempted. The first method employed was that of Rees et al. \(^{143}\) N-Aminophthalimide was oxidised by lead tetraacetate in the presence of the phosphole. The solution was observed to turn a deep red colour which gradually faded to yellow. 1, 2, 5-Triphenylphosphole oxide was isolated in high yield from the reaction. A blank reaction showed that 1, 2, 5-triphenylphosphole was readily oxidised by lead tetraacetate in almost quantitative yield and has proved a most satisfactory procedure in our hands for the preparation of phosphole oxides. Dimroth and Lerch\(^{144}\) have described a similar, high yield conversion of phosphites to phosphates with this reagent.

Cadogan and Gosney\(^{145}\) have recently shown that formation of arsinimines from triphenylarsine and amino-compounds in the presence of lead tetraacetate does not involve oxidation of the amine to a nitrene followed by trapping with the arsine. Instead the lead tetraacetate reacts with the arsine to form a diacetate (8) which then
reacts with the amino-group (Scheme 9). The reaction is analogous to the preparation of iminophosphoranes by reaction of phosphine dibromides with amines reported by Horner and Oediger. The diacetate in the triphenylarsine case was stable enough to be isolated. While it is suspected that a similar diacetate is formed in the reaction between the phosphole and lead tetraacetate all attempts to isolate it have failed.

\[
\text{Ph}_3\text{As} \xrightarrow{\text{LTA}} \text{Ph}_3\text{As(OAc)}_2 \xrightarrow{X\text{NH}_2} \text{Ph}_3\text{As}=\text{NX}
\]

Scheme 9

A second method for generation of phthalimidonitrene has recently appeared in the literature. Jones has used the method of Rees described above to generate phthalimidonitrene in the presence of 2-acetylbenzofuran to form the aziridine (9) which dissociates slowly at 80° to regenerate the nitrene and 2-acetylbenzofuran. Using this method, phthalimidonitrene was found to react with 1, 2, 5-triphenylphosphole to give a deep red solid which was identified tentatively by mass spectrometry, ultraviolet and infrared spectroscopy a N-phthalimido-1, 2, 5-triphenylphospholimine. This compound was found to hydrolyse readily in a dilute solution of acetic acid in dry dichloroethylene to 1, 2, 5-triphenylphosphole oxide and N-aminophthalimide. This compound like the N-benzylphospholimine discussed earlier has little opportunity of delocalising the charge on nitrogen and hence would be expected to show high basicity and hence hydrolyse readily. This fact could also explain the transient red colour observed in attempt involving the lead tetraacetate oxidation of N-aminophthalimide. (Scheme 10).

Jones has shown that phthalimidonitrene generated by these two methods above are non-equivalent in their reactions with activated benzenoid compounds. Cadogan and Gosney
have suggested that the species generated by the oxidative route may be a nitrenium ion rather than a nitrene.

It was mentioned in the Introduction that iminophosphoranes had been obtained by deoxygenation of nitro- and nitroso-compounds with phosphorus reagents.

N-(p-Nitrophenyl)-1,2,5-triphenylphospholimine was prepared by the reaction of 1,2,5-triphenylphosphole with p-nitro-nitrosobenzene. The initial experiment was performed using triethyl phosphite in the presence of the phosphole with the hope that the less nucleophilic phosphole might exist in the reaction mixture only as a nitrene trap. Blank tests, however, showed that the phosphole reacted rapidly with the nitroso-compound even
The major product from the reaction was 4,4'-dinitrozoxo-benzene.

There is strong evidence that in certain cases nitrenes are formed in the reaction of nitro- and nitroso-compounds with trivalent phosphorus reagents. Cadogan has suggested initial nucleophilic attack takes place at the oxygen of the nitroso-compound forming the dipolar species (10). Loss of the phosphorus oxide yields the nitrene which can then attack either the nitroso-compound or an available trivalent phosphorus molecule (Scheme 11).

\[
\text{Scheme 11}
\]

Smolenski and Feuer have suggested that the intermediate may have the cyclic structure (11).

It is possible to suggest a mechanism which does not involve nitrenes, however. Iminophosphorane formation may result from initial attack on the nitrogen atom followed by deoxygenation of the intermediate (12) (Scheme 12) or by deoxygenation of an intermediate of structure (11).

\[
\text{Scheme 12}
\]
Recently Holliman has produced evidence which suggests that carbazole formation by deoxygenation of 2-nitro- and 2-nitrosobiphenyls with triethyl phosphite proceed \textit{via} the dipolar species (10). It was found that product distributions were only comparable with those obtained by decomposition of the corresponding azide when the latter were done in triethyl phosphate as solvent. Hence it is concluded that only in this case is a common intermediate formed.

A list of phospholimines prepared from nitrene and nitrenoid sources appears in Table 2.

\textbf{TABLE 2}

<table>
<thead>
<tr>
<th>Phospholimines Prepared from Nitrene and Nitrenoid Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Phospholimines" /></td>
</tr>
<tr>
<td>X = -CO$_2$Et</td>
</tr>
<tr>
<td><img src="image" alt="Chemical Structures" /></td>
</tr>
</tbody>
</table>
2. Thermolytic Reactions of 1, 2, 5-Triphenylphospholimines and Related Compounds.

(a) N-(o-Nitroaryl)-1, 2, 5-triphenylphospholimines.

The original idea that some phospholimines might undergo thermolytic rearrangements arose when 1, 2, 5-triphenylphosphole oxide was obtained as a product from an attempted deoxygenation of N-(o-nitrophenyl)-1, 2, 5-triphenylphospholimine (13) with triethyl phosphite in boiling cumene (152°) for 2 days. Benzofurazan (14) seemed a possible product from the other fragment of the molecule but g.l.c. analysis of the reaction mixture failed to show its presence.

However, when heated in mesitylene at 150-160°, in the absence of triethyl phosphite, the phospholimine (12) was indeed shown to produce benzofurazan in 50-60% yield and 1, 2, 5-triphenylphosphole oxide in 88% yield. (Scheme 13).

![Scheme 13](image)

Substitution of the N-phenyl ring with electron releasing substituents (e.g. methoxy-, methyl-) had little or no effect on the course of the reaction and the benzofurazan yields were of the same order as the unsubstituted compound. Electron withdrawing substituents (e.g. nitro-, trifluoromethyl-), however, appear to suppress the reaction and no benzofurazans were detected. The effect of substituents on the yields of benzofurazan are shown in Table 3.
<table>
<thead>
<tr>
<th>N-Aryl Group</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-NO$_2$-phenyl</td>
<td>50-60</td>
</tr>
<tr>
<td>2-NO$_2$-6-Me-phenyl</td>
<td>50</td>
</tr>
<tr>
<td>2-NO$_2$-5-Me-phenyl</td>
<td>32</td>
</tr>
<tr>
<td>2-NO$_2$-4-Me-phenyl</td>
<td>46</td>
</tr>
<tr>
<td>2-NO$_2$-4-MeO-phenyl</td>
<td>44</td>
</tr>
<tr>
<td>2-(1-NO$_2$-naphthyl)</td>
<td>6-8</td>
</tr>
<tr>
<td>2,4-(NO$_2$)$_2$-phenyl</td>
<td>-</td>
</tr>
<tr>
<td>2-NO$_2$-4-CF$_3$-phenyl</td>
<td>-</td>
</tr>
</tbody>
</table>

Benzofurazans have previously been prepared in a similar reaction by the thermal rearrangement of methyl (2-nitrophenyl)-carbamates(15) with loss of methanol and carbon dioxide.\(^{130}\) (Scheme 14).

\[
\text{NHCO}_2\text{Me} \quad \xrightarrow{\text{N}} \quad [\text{phenyl}][\text{N}]
\]

\[
\text{+MeOH} \quad \text{+CO}_2
\]

Scheme 14

Rearrangement did not occur when the corresponding phosphorimidate (16) or phosphinimine (17) were treated under
the same conditions. However benzofurazan was found as a product in the thermolysis of \( N-(\alpha\text{-nitrophenyl}) \)iminotrichlorophosphorane (18).

\[
\begin{array}{cc}
(\text{EtO})_3\text{P}=\text{N}&\text{Ph}_3\text{P}=\text{N} \\
\text{O}_2\text{N}&\text{O}_2\text{N} \\
\end{array}
\]

16 17

These compounds differ only in the substituents on phosphorus. The ability to undergo the rearrangement appears to correlate with low nucleophilicity in the trivalent phosphorus moiety from which the iminophosphoranes are derived, \( \text{Ph}_3\text{P} > (\text{EtO})_3\text{P} > \text{PCl}_3 \). Considerations of the inductive effects of the substituents around phosphorus in (16) and (18) it would appear that the positive charge on phosphorus is stabilised by electron donation of the ethoxy-groups in (16) and destabilised in (18) by electron withdrawal by the chlorine atoms. This, in turn, may be taken to indicate high electrophilicity in structure (18).

(i) The effect of the ring.

There are at least two roles which the phosphole ring may

* This series is derived from the ability of these compounds to react with azides. As mentioned above while often triphenylphosphine reacts with azide at room temperature, 1, 2, 5-triphenylphosphole require temperatures between 60 and 100°. Phosphorus trichloride has been reported not to react with azides. Nucleophilic attack on azides has been reviewed by L'Abbe.
play in this reaction. It may, as already stated, be merely an electrophilic centre by analogy with \( N-(\alpha\text{-nitrophenyl})\text{iminotri-}
\text{chlorophosphorane.} \) The other possibility is that the reaction owes some of its facility to a 'small ring effect.' These ring effects have been attributed to ring strain but there appears to be no direct evidence for this, and it has been suggested that it is an entropy effect due to a 'loosening of the pseudorotational motion.'

Westheimer\(^{153}\) has attributed the high rate of acid hydrolysis of the cyclic ester (19) to relief of ring strain by the formation of the pentavalent phosphorus intermediate (20), in which the ring can adopt the favourable apical-equatorial form with an OPO angle of 90\(^{\circ}\).

![Diagram 19 and 20](image1)

Hydrolysis is completed by pseudorotation to bring the departing ethoxy group to an apical position which can occur, still maintaining the apical-equatorial orientation of the phosphite ring.

Aksnes and Bergesen\(^{156}\) have investigated nucleophilic displacements on phosphorus in phospholanium salts. Again the five membered ring showed a considerable tendency to accelerate the reaction. The phospholanium salt (21) undergoing reaction 1300 times more quickly than the phosphorinanium salt (22). This has been attributed to the fact that while a six membered ring can span two equatorial positions, ring strain demands that a five membered ring must adopt a position such that it occupies one axial and one equatorial position. Good evidence for this form of mechanism has come from Marsi\(^{157}\) who has shown that phospholanium salts normally hydrolyse with retention of configuration.
and not with inversion as is usually found in phosphonium salts.

Thus it may be that relief of "ring strain" is an important factor in the thermolytic rearrangement of N-(o-nitrophenyl)-1,2,5-triphenyolphospholimines. By increasing the ligands on phosphorus from four to five by coordination with the nitro group, pseudorotation could then occur, hence greatly increasing the entropy of the system and thus would favour the reaction. The angle in the ring would also decrease from the tetrahedral to 90° which again would be favourable and release strain.

If ring effects are, indeed, important in the reactions of phosphole then this would provide an alternative explanation to its reduced nucleophilicity with respect to triphenylphosphine. The C2PC5 bond angle has not been measured in 1,2,5-triphenylphosphole but in 1-benzylphosphole the angle is 90.7°. In reacting with an azide the ring is required to assume tetrahedral geometry which in turn will require the C2PC5 bond angle to enlarge towards 109°. Thus the ring strain in such a system will be large. A similar argument might be used to explain the PO bond energy noted by Millar in 1,2,3,4,5-pentaphenylphosphole.

However, the validation of such explanations will require crystallographic measurement of the C2PC5 bond angle both in
phosphole oxides and in the phospholimines. Recent work by Katz \(^ {178}\) has shown that ring strain has a profound effect on ylid stability and that when the strain becomes very great as in the homocubyl system (23) stable phosphoranes (24) are formed in preference to the ylids.

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

The alternative is to accept Millar's \(^ {26}\) argument about the non-availability of electrons due to conjugation within the ring. When these electrons are utilised in bonding in the PO or PN bond then destabilisation of the aromatic system would cause a large formal positive charge to occur on phosphorus in much the same way as chlorine atoms were seen to do in the case of the iminotrichlorophosphorane.

(ii) **Mechanistic Studies**

There are at least two possible mechanisms for this reaction. The first is an intramolecular mechanism, (Route 1, Scheme 15), involving either the direct ejection of benzofurazan or its precursor \(\alpha\)-nitrenonitrosobenzene, while the second is a two-step process (Route 2, Scheme 15) in which the benzofuroxan is first formed and then deoxygenation by triphenylphosphole also produced in the reaction.
Kinetic studies at 160° in bromobenzene at two concentrations, one half the other, showed the reaction to be first order in phospholimine and yielded virtually the same rate constant \( K = 3 \times 10^{-3} \) min\(^{-1}\). The half life of the phospholimine at this temperature was calculated to be 4 h. In each case the infinity reading was 48 h. While route 1 would be expected to show first order kinetics, route 2 would also show first order kinetics if the second deoxygenation step was very facile. The same rate constant was again obtained
when measurements were made in the presence of added 1, 2, 5-
triphenylphosphole. However, a blank experiment with benzo-
furoxan and 1, 2, 5-triphenylphosphole showed that the reaction took
place readily in boiling benzene and was complete in 1-2 h. Hence
little assistance is obtained from kinetic data in elucidation of the
mechanism except to verify the initial assumption that the reaction
involves a single phospholimine molecule rather than, for example,
a dimeric species.

The other evidence available, however, suggests that the
intramolecular reaction is the more likely mechanism. No
phosphole or benzofuroxan has ever been detected in the reaction
mixture and thermolyses of the o-nitrophenylphospholimines in the
presence of various azides failed to indicate that any phosphole had
been competitively trapped as the phospholimine, although the half
life of the azide was considerably shorter than the half-life of the
N-(o-nitrophenyl)phospholimine. When the decomposition was
carried out in the presence of a 2:1 mixture of 1, 2-diphenyl-5-
tolylphosphole* the ratio of 1, 2, 5-triphenylphosphole oxide to 1, 2-
diphenyl-5-tolylphosphole was found to be (87.5:12.5). Thus most
of the oxide formed came from the phospholimine. The formation
of the 1, 2-diphenyl-5-tolylphosphole oxide can be explained by slow
attack on the nitro-group. This is supported by two facts: namely
that in the presence of 1, 2, 5-triphenylphosphole the overall yield
of benzofurazan decreases, and that the heating of N-(o-nitrophenyl)-
iminotriphenylphosphorane with 1, 2, 5-triphenylphosphole under the
same conditions gives rise to some phosphole oxide formation even
though this ylid does not undergo the rearrangement. (Scheme 16).

* Competitive deoxygenation of benzofuroxan with 1, 2, 5-triphenyl-
phosphole and 1, 2-diphenyl-5-tolylphosphole, both in molar excess
gave a 1:1 distribution of the oxides indicating that their rates of
deoxygenation are equal.
Failure to identify the benzofurazan in the presence of triethyl phosphite may have been due to one or more of three factors. The phosphole oxide isolated was a minor product in a complex mixture and hence the benzofurazan concentration may have been insufficient for g.l.c. analysis. The retention times of benzofurazan and triethylphosphate were very similar on all columns and under all conditions tried, and hence the benzofurazan peak may have been completely overlapped by the large triethylphosphate peak. The third possibility is that there is some reaction between triethylphosphite and the benzofurazan formed. While there is no direct proof for the latter, it would explain certain discrepancies in the literature. Cadogan et al.\textsuperscript{147} claimed that forcing conditions (150° for 5 h) were required for deoxygenation of benzofuroxan to benzofurazan. The yield was 19%. Bailey and Evans\textsuperscript{148} however, find that the reaction is complete in 30 min in boiling benzene in 85% yield. In the present study it has been observed that a reaction takes place between benzofuroxan and triethyl
phosphite at room temperature. Triethylphosphate was identified as a product by g. l. c. after 1 h. Under the conditions used in the present reaction (150° for 3 days) and in view of large yield difference mentioned above between the reaction at 150° and the reaction at 80° it seems possible that the benzofurazan may have been destroyed by phosphite.

In order to test this hypothesis 5′-methoxybenzofurazan was heated at 150° in mesitylene in the presence of triethyl phosphite. G. l. c. gradually showed a new peak appearing at longer retention time than the benzofurazan. However, the product has not yet been identified.

(b) Related Reactions of C and N Ylids Containing Oxygenated Ortho Substituents.

Clearly, the above reaction, in theory, is capable of extension as outlined in Scheme 17.

[PYPh]

\[ \text{Scheme 17} \]

Preliminary investigations have been carried out along these lines.

The observed failure of the corresponding phospholium ylid (25) to undergo a similar rearrangement to the anthranil (26) can be explained in several ways. The electrophilicity of the phosphorus atom may be reduced compared with the phospholimine. A second possibility is that substitution of nitrogen with carbon makes the 6-membered transition state sterically less favourable.
Trippet and Walker have reported such a rearrangement via a four-membered transition state. An attempt to prepare the ylid (27) from the salt (28) resulted in the formation of triphenylphosphine oxide and fulminate ion. (Scheme 18).

\[
\text{Ph}_3\text{PCH}_2\text{NO}_2 \xrightarrow{28 \text{ Br}^-} \left[ \begin{array}{c} \text{Ph}_3\overset{+}{\text{P}-\text{CH}} \\ \text{O}\text{-NO} \end{array} \right] \xrightarrow{\text{Scheme 18}} \text{Ph}_3\text{PO} + \text{CNO}^- \]

A third possibility is that the correct base/solvent system for the reaction has yet to be found.

Some interest has recently been shown in \(\alpha\)-nitrenosarylcarbene, the species (29), and several attempts were made to generate it from phosphorus precursors. The species, itself, is of some theoretical interest since the \(\alpha\)-phenyl dinitrene (30) rearranges to give the dinitrile (31) while Sondheimer has shown that the diacetylene (32), which would be the product from a similar arrangement from \(\alpha\)-phenyl dicarbene (33), spontaneously rearranges to give benzocyclobutene (34) which is isolated as its dimer (35).
The intermediate (29), prepared by the vacuum pyrolysis of 4-phenylbenzotriazine (36), has recently been shown by Rees to give the benzazete (37) which has been isolated at low temperatures. At room temperature it forms a dimer, similar to that of benzocyclobutene and has also been trapped by 'benzyne traps' such as tetracyclone, cyclopentadiene and 1,3-diphenylisobenzofuran.

135
Similarly Gompper has shown that vacuum phase pyrolysis of the 1, 2, 3-triazine (38) gives the azacyclobutadiene (39)

\[
\begin{align*}
38 & \quad \xrightarrow{R = \text{NMe}_2} \quad 39 \\
\end{align*}
\]

The potential routes investigated from phosphorus reagents have involved compounds of the general structure (40).

The vacuum pyrolysis of triethyl-(a-acetylphenyl)phosphorimidate (40; \(R^1 = \text{OEt}, R^2 = \text{CH}_3\)) at 450° produced a mixture of three compounds, the main component of which was unreacted phosphorimidate. The other compounds were found by mass spectrometry to have m/e; 299, an isomer of the starting material and m/e; 271. It is suggested that the compounds are the corresponding phosphoramidate (41) and its N-ethyl derivative (42), but identification is tentative and based only on mass spectral evidence.
Thermolysis of N-(o-acetylphenyl)iminotriphenylphosphorane (40, \(R^1=\text{Ph}, \ R^2=\text{CH}_3\)) in mesitylene gave 2-(o-aminophenyl)-4-methylquinoline (43) in 50% yield. The proposed mechanism involves a Wittig-type reaction between two molecules of the phosphinimine followed by an intramolecular condensation to give the phosphinimine (44). A small peak m/e; 495+1 in the mass spectrum suggests that the final product is the result of hydrolysis of (44) probably during the course of chromatographic separation (Scheme 19).

As already stated the corresponding phospholimine could not be prepared.

\[
\begin{align*}
2 \text{PhCOMe} & \xrightarrow{\text{Me}} \text{PhCN} \\
\text{Ph}_3\text{P} & \xrightarrow{\text{Ph}_{3}\text{P}} \text{Me} \\
\text{Ph}_3\text{P} & \xrightarrow{\text{Ph}_{3}\text{P}} \text{Me} \\
\text{Ph}_3\text{P} & \xrightarrow{\text{Ph}_{3}\text{P}} \text{Me} \\
\text{NH}_2 & \xrightarrow{\text{NH}_2} \text{Ph}_{3}\text{P}
\end{align*}
\]

Scheme 19

\(N-(2\text{-Benzoylphenyl})\text{iminotriphenylphosphorane (40,} \ R^1=R^2=\text{Ph})\text{ proved stable to thermolysis at 160° in mesitylene.} \ N-(2\text{-Benzoylphenyl})-1,2,5\text{-triphenylphospholimine (45) decomposed at the same temperature in mesitylene to give dibenzo[b,f]-4,8-diphenyl-1,5-diazocine (46) in 18% yield.} \ 1,2,5\text{-Triphenylphosphole oxide was recovered in 58% yield.} \ The product is thought to arise by a Wittig-like reaction followed by a second
intramolecular reaction of the same type. (Scheme 20).

The thermolysis of N-(2-carboxyphenyl)iminotriphenylphosphorane (47a) and N-(2-carboxyphenyl)-1, 2, 5-triphenylphospholimine (47b) gives high yields of the corresponding oxides but no other identified products were isolated other than polymeric material. Anthranil, a product which might have been expected by analogy with the formation of benzofurazans from the o-nitrophenylphospholimines, was not detected. The initial product from (47a) was a bright yellow fluorescent material which runs well in non polar solvents on t.l.c. but on exposure to the atmosphere the characteristics of the t.l.c. spot change. It remains on the base line and consists of several polar components. Attempts to isolate the compound by column chromatography, distillation and precipitation were unsuccessful. Hence the compound is high boiling (it could still be detected in the mother liquor when triphenylphosphine oxide
began to distil over) sensitive to hydrolysis and very difficult
to separate from triphenylphosphine oxide, which may suggest that
this is a hydrolysis product although there is no direct proof of
this. The t.l.c. characteristics are consistent with P, N, O
heterocycles handled in this laboratory and hence although no
further evidence is available it is thought the structure might be
(48) or an isomer.

\[ \text{R} = \text{N} \]
\[ \text{HO}_2\text{C} \]
\[ \text{Ph} \]

\[ \text{R} = (a) \]
\[ \text{Ph}_3\text{P} \]

\[ \text{R} = (b) \]
\[ \text{Ph}<\text{P}>\text{Ph} \]

\[ \text{H} \]
\[ \text{PPh}_3 \]

\[ \text{O} \]

\[ \text{O} \]
3. Reactions of 1, 2, 5-Triphenylphospholimines, and other Derivatives of 1, 2, 5-Triphenylphosphole with Dienophiles.

The Diels-Alder reactions of phospholes and derivatives have already been discussed in the Introduction. It was seen that decomposition of the intermediate adduct resulted in the extrusion of the bridgehead phosphorus atom. Although this fragment has never been trapped, it is clear that such reactions may be a potential source of phosphorus analogues of nitrene.

Simple pyroles undergo Diels-Alder reaction with dimethyl acetylenedicarboxylate but do not extrude the bridgehead nitrogen. Methyl pyrrole-1-carboxylate reacts with acetylene to give trimethyl pyrrole-1,3,4-tricarboxylate by extrusion of acetylene. (Scheme 21).\textsuperscript{161}

\[
\begin{align*}
\text{Y} = \text{CO}_2\text{Et} & \quad + \text{C}_2\text{H}_2 \\
\text{Scheme 21}
\end{align*}
\]

While stable adducts with the acetylene are difficult to obtain in the pyrrole series, the furans form readily isolable adducts. Alder and Rickert\textsuperscript{162} have used extrusion of ethylene from the reduced adduct (162) to prepare 3,4-disubstituted furans whose preparation is otherwise difficult. (Scheme 22).

\[
\begin{align*}
\text{RC}\equiv\text{CR} & \quad \rightarrow \quad \text{Scheme 22}
\end{align*}
\]
Bridgehead extrusion occurs in the reaction of isoindoles with acetylenes although the nitrogen fragment has never been detected. (Scheme 23).

\[
\text{Me} \quad \text{Ph} \\
\downarrow \quad \downarrow \\
\text{Me} \quad \text{Ph}
\]

\[
+ \text{YC} \equiv \text{CY} \\
Y = \text{CO}_2\text{Et} \\
\quad \text{Scheme 23}
\]

Similarly the action of benzyne on various heterocyclopentadienes seems to result in the extrusion of bridgehead fragments. Naphthalene has been isolated from the reaction of benzyne with N-methylpyrrole. 2, 3, 4, 5-Tetraphenylcyclopentadienone (tetracyclone) reacts with benzyne with the extrusion of carbon monoxide which may be considered as a stable carbene.

The adduct of benzyne with the silicon heterocycle (49) decomposes at 300\(^\circ\) to give 1, 2, 3, 4-tetraphenylnaphthalene and dimethylpolysilane (Me\(_2\)Si)\(_n\). In the presence of diphenylacetylene compound (50) was obtained.

\[
\text{Ph} \quad \text{Si} \\
\downarrow \quad \downarrow \\
\text{Me} \quad \text{Me}
\]

49

\[
\text{Me} \quad \text{Si} \quad \text{Me} \\
\downarrow \quad \downarrow \\
\text{Ph} \quad \text{Ph}
\]

50

In the present study attempts have been made to prepare stable adducts of phospholimines with dienophiles. Gee\(^{24}\) has shown that N-phenyl phospholimines also undergo an alternative reaction with dimethyl acetylenedicarboxylate in which the acetylene reacts with the phosphorus nitrogen bond rather than
with the diene system (page 24). The phospholimines used in these reactions were therefore those containing the \(-N-\text{SO}_2-\) group which Gee\(^{24}\) has reported do not undergo any reaction other than attack on the diene system.

The \(N\)-sulphonylphospholimines (51 a, b, c) were all found to react in mesitylene to give dimethyl 3, 6-diphenylphthalate (52). Only on one occasion does it appear that a stable adduct may have been isolated. In the reaction between dimethyl acetylene-dicarboxylate and \(N\)-mesyl-1, 2, 5-triphenylphospholimine in chloroform a chromatographic fraction was obtained whose t.l.c. characteristics changed on attempting to remove the solvent. The phthalate (52) was isolated from the residue. The remainder of the fraction was a brown gum.

![Chemical Structure](image)

\[X = (a) \text{Me}\qquad (b) \text{Tolyl}\qquad (c) \text{p-NO}_2\text{-phenyl}\]

In the reaction of \(N\)-phenyl-1, 2, 5-triphenylphospholimine with benzyne produced from benzene diazonium-2-carboxylate. Extrusion took place and 1, 4-diphenynaphthalene was obtained, but only in 1% yield. The principle product of the reaction was identified as 1, 2, 5-triphenylphosphole oxide (74%) but its genesis remains uncertain. In the reaction of \(N-(p\)-nitrophenyl)-1, 2, 5-triphenylphospholimine and benzyne the crude reaction product showed a mass spectral peak corresponding to a 1:1 adduct. It was shown by h.s.l.c. that the product was a mixture of starting material and another compound but separation difficulties foiled
attempts to obtain a sample of the pure material.

Reaction of N-mesylphospholimine (51a) was also attempted with diethyl azodiformate (53). No reaction occurred except at high temperature (180°) when red polymeric gums were obtained. This dienophile did however react with 1, 2, 5-triphenylphosphole oxide. However the reaction mixture was found to be complex. Chromatography on alumina followed by mass spectrometric examination of the fractions showed the following peaks: m/e; 176 which was identified as diethyl hydrazodiformate, (54) m/e; 502 corresponding to a 1:1 adduct, m/e; 676 corresponding to a 2:1 adduct and m/e; 678 corresponding to a 2:1 adduct plus two hydrogen atoms which were found in two fractions.

Apart from (54) the nature of these products is as yet unclear. The 1:1 adduct may, indeed, be the Diels-Alder adduct (55).
However, the presence of a 2:1 adduct may mean that the reaction is a Michael-Type addition of that found in the addition of dimethyl acetylenedicarboxylate to pyrroles. (Scheme 24).

In this case a 2:1 adduct is explicable by further reaction at the 4-position. Alternatively the acquisition of extra hydrogen atoms may indicate that a radical process is also in operation. However it is difficult to speculate as to the structures without further evidence.

A similar situation exists in the reaction of 4-phenyl-1, 2, 4-triazoline-2, 5-dione (56) prepared 'in situ' in the presence of N-mesyl-1, 2, 5-triphenylphospholimine by oxidation of 4-phenylurazole (57) with t-butyl hypochlorite. The isolated product showed a mass spectrum which corresponded to a 1:1 adduct plus a chlorine atom. Again the structure of this compound is not known but the inclusion of a chlorine atom makes the Diels-Alder adduct structure most unlikely. The presence of the hypochlorite again suggests that a radical process may be involved.
Two attempts were made to trap the extruded phosphorus fragment from the reactions of N-sulphonylphospholimines and dimethyl acetylenedicarboxylate. The reagents used were dipropyl disulphide (58) and p-dimethoxybenzene (59). In both cases dimethyl 3,6-diphenylphthalate was isolated but no evidence of successful trapping of the fragment was found.
4. The Spectra of Phospholimines.

1. Infrared

The $P=N$ stretching frequency is reported to be found in the range 1260-1420 cm$^{-1}$ \cite{167}. Definite assignments in this region are difficult. The 1, 2, 5-triphenylphospholimines often showed several bands which might be attributed to this vibration in which case the value quoted has been the peak of strongest intensity. However, it is fair to say that some absorption was found in this region in each case. The assignment of this band has been used as evidence for $\sigma\pi$ - $\pi\pi$ bonding \cite{110,168} as the $P-N$ single bond stretching absorption has been shown to appear in the region 820-680 cm$^{-1}$.

2. Proton Magnetic Resonance

The assignments of the various features of the p.m.r. spectra of phospholimines were elucidated by Gee \cite{24}. It was shown that the phosphole ring protons absorbed completely within the aromatic region appearing as a doublet at approximately $2.6\tau$ ($J_{PH} \approx 30-40\text{Hz}$).

The spectra of N-aryl-1, 2, 5-triphenyl phospholimines also show characteristic bands between 3 and 4\tau. These were shown, by Gee \cite{24} to be assignable to the $o$-protons of the N-aryl ring, which in the case of $p$-substituents is a $A_2B_2$ system, usually half of which appears above 3\tau. This deshielding of the $o$-protons is good evidence for high electron density on the nitrogen atom. In the case of a $p$-methyl substituent all four protons of the N-phenyl ring absorb as a singlet \cite{24} at 3.16\tau and this has been taken as an indication that the electron donating properties of the methyl and $P=N$ are equivalent. When the substituent is $p$-methoxy then again all four protons are found above 3\tau but the system shows four peaks assignable once more to an $A_2B_2$ system.
A feature which has been of some interest since the first preparation of 1, 2, 5-tripheny1phospholimines has been the wide variation in colour found in the crystalline state. N-Methoxyphenyl-compounds are blue-black while the N-phenyl compound is red, N-sulphonyl and N-carbonyl, yellow and N-tolyl, brown. However the U. V. spectra showed very similar envelopes, transitions occurring at c. 210 nm (30,000-45,000) and in the range 380-405 nm (9,000-34,000). Hence it seems possible that the colour difference is due to a crystal effect since the light absorption properties appear to change on dissolving.

Whether or not there is conjugation between the imine part of the molecule and the $\pi$ system in the phosphole ring is a more difficult question. It is still a matter of some controversy whether $\pi$-conjugation can be propagated through orbitals because of the node which occurs on the phosphorus atom.

Dewar noted that the U. V. spectra of cyclic phosphazines (e.g. 59) showed increasing extinction coefficient with ring size but no bathochromic shift was observed. It was concluded that these data were more consistent with an increase in the number of chromophores than an increase in conjugation. A simplified diagram of the type of orbitals envisaged is shown in Fig. 1.
Similarly Bock\textsuperscript{170} in studies of phosphorus-containing azo dyes has found no evidence for conjugation through phosphorus. The structures and colours of some of these compounds are shown in Fig. 2.

\[
\begin{align*}
\text{\text{\text{-P-N=N-P=}} & \quad \text{Violet} \\
\text{N-P-N=N-} & \quad \text{Deep Red} \\
\text{-P=N-N=N-} & \quad \text{Golden Yellow} \\
\text{-P=N-P=N-} & \quad \text{Colourless}
\end{align*}
\]

Fig. 2

Of particular interest to this discussion is the phosphimido chain molecules (Fig. 2, 60) which do not absorb in the visible no matter how far the chain length is extended. This is in contrast to the diphenylpolyenes which absorb in the visible when there are more than three double bonds. This implies that a \(\Pi\)-system of the polyene-type is not established and hence the Dewar model is applicable in this case also.

Goetz,\textsuperscript{171} in a study of \(\text{N-p-nitrophenylphosphinimines}\), has come to much the same conclusion. These phosphinimines exhibit a high intensity absorption at 380 nm (23,000). This is attributed to extended conjugation of the imine part of the molecule. (Scheme 25).
Only small changes in the position of this $\pi_d \rightarrow \pi_d^*$ PNR transition were noted with changes in the nature of the substituents on phosphorus. Goetz has interpreted his results in terms of interaction between the antibonding orbitals of the P=N bond and of a P-phenyl ring, thus lowering $\pi_d \rightarrow \pi_d^*$ transition.

A progressive bathochromic shift was observed as electron releasing groups were substituted on phosphorus. However the largest shift of the series was found when all phenyl groups had been substituted by alkyls. Wiegräbe and Bock have shown that P=N bond order increases as electron withdrawing substituents are placed on phosphorus and hence it would appear that this shift may be associated with charge separation in the PN bond. Lloyd\(^{173}\) has noted that colour in ylids is associated with charge separated rather than covalent forms.

Apart from the nitro-compounds N-aryl phosphinimines do not appear to absorb in this region (380-400 nm). 1,2,5-Tri-phenylphospholimines all absorb strongly in this region. The variation of intensity and position with the substituents on nitrogen makes it appear that the absorption is due to the imine part of the molecule. The p-nitrophenyl compound although showing much higher intensity of absorption, shows no significant bathochromic shift with respect to the N-phenyl compound. It is thus possible that the colour of these compounds is indicative of charge separation in the P-N bond which would fit well with the behaviour found in the intramolecular deoxygenation reactions discussed previously.
Although some authors use direct conjugation through phosphorus to explain spectra of phosphorus compounds it would appear that the bulk of evidence available suggests that it does not happen. The colour of these compounds can, however, be explained by other types of conjugation. Holland and Jones have pointed out that the spectra of phosphole oxides are consistent with spiro-conjugation. This is overlap by orbitals at right angles due to the presence of a spiro atom. (Fig. 3).

![Diagram](image)

\[ S = \text{Spiro-atom} \]

**Fig. 3**

In the case of phosphole oxides it is proposed that overlap occurs between the oxygen lone pair and the \( \pi \)-system within the ring.

A similar 'through space' effect is known to occur in bicyclic ketones such as (61). The spectrum of this compound shows a low intensity pseudo-conjugation band and an intensified \( n \rightarrow \pi^* \) transition.

![Diagram](image)

61
Thus we may explain the colour by spiro conjugation between the $\pi$-system and the nitrogen lone pair or some other such 'through space' interaction, or alternatively that the covalent form of the bond is less favoured than a charge separated form.

Gee\textsuperscript{24} has noted that $N$-phenyl-2,5-di-$t$-butylphospholimine does not absorb in the region 370-400 nm and attributed this to the fact that the band found in the triphenylphospholimines was due to conjugation of some form between the PN bond and the phenyl group. It is possible, of course, that the large $t$-butyl groups force the N-phenyl ring in to such a position that it cannot conjugate effectively with the nitrogen lone pair.

This problem will not be completely resolved until crystal structure determinations have been performed on some phospholimines. At present there is very little data concerning the geometry of iminophosphoranes.\textsuperscript{175, 176}

The visible absorption and crystal colour of some phospholimines are recorded on Table 4.
<table>
<thead>
<tr>
<th>N-Substituent</th>
<th>Colour</th>
<th>max</th>
<th>max</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 4-Phenylazophenyl</td>
<td>Red-orange</td>
<td>393</td>
<td>39,000</td>
</tr>
<tr>
<td>2. Phenyl carboxylate</td>
<td>Yellow</td>
<td>394</td>
<td>12,500</td>
</tr>
<tr>
<td>3. 4-Trimethylphosphorimidatophenyl</td>
<td>Brown</td>
<td>388</td>
<td>13,000</td>
</tr>
<tr>
<td>4. 4-Triphenylphosphiniminophenyl</td>
<td>Green</td>
<td>384</td>
<td></td>
</tr>
<tr>
<td>5. Phenyl</td>
<td>Red</td>
<td>385</td>
<td>14,500</td>
</tr>
<tr>
<td>6. p-Tolyl</td>
<td>Brown</td>
<td>388</td>
<td>12,000</td>
</tr>
<tr>
<td>7. p-Nitrophenyl</td>
<td>Red-orange</td>
<td>384</td>
<td>33,500</td>
</tr>
<tr>
<td>8. Ethyl carboxylate</td>
<td>Yellow</td>
<td>398</td>
<td></td>
</tr>
<tr>
<td>9. 2-Diphenylphosphinylphenyl</td>
<td>Red</td>
<td>390</td>
<td>10,500</td>
</tr>
<tr>
<td>10. p-Methoxyphenyl</td>
<td>Blue-black</td>
<td>386</td>
<td>12,800</td>
</tr>
<tr>
<td>11. p-Iodophenyl</td>
<td>Orange-pink</td>
<td>375</td>
<td>14,000</td>
</tr>
<tr>
<td>12. p-Azidophenyl</td>
<td>Brown</td>
<td>390</td>
<td>16,800</td>
</tr>
<tr>
<td>13. 4-Sulphamoylphenyl</td>
<td>Yellow</td>
<td>388</td>
<td></td>
</tr>
<tr>
<td>14. o-Nitrophenyl</td>
<td>Orange</td>
<td>390</td>
<td>17,600</td>
</tr>
<tr>
<td>15. 3-Phthalic anhydrido-</td>
<td>Yellow</td>
<td>390</td>
<td>15,700</td>
</tr>
<tr>
<td>16. Diphenylphosphinyl</td>
<td>Yellow</td>
<td>396</td>
<td>10,000</td>
</tr>
<tr>
<td>17. 2-Benzimidazolyl</td>
<td></td>
<td>390</td>
<td>9,100</td>
</tr>
<tr>
<td>18. Tosyl</td>
<td>Yellow</td>
<td>403</td>
<td>13,500</td>
</tr>
<tr>
<td>19. 4-Methyl-2-nitrophenyl</td>
<td>Orange</td>
<td>392</td>
<td></td>
</tr>
<tr>
<td>20. 4-Methoxy-2-nitrophenyl</td>
<td>Blue-black</td>
<td>394</td>
<td>16,000</td>
</tr>
<tr>
<td>21. 2,4-Dinitrophenyl</td>
<td>Golden-yellow</td>
<td>374</td>
<td>32,000</td>
</tr>
<tr>
<td>22. 4-Carboxyphenyl</td>
<td>Orange</td>
<td>387</td>
<td></td>
</tr>
<tr>
<td>23. 2-Carboxyphenyl</td>
<td>Orange</td>
<td>394</td>
<td></td>
</tr>
</tbody>
</table>
Table 4 (cont.)

**U. V. Spectra of other phosphole derivatives.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorbance</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, 2, 5-Triphenyl phosphole</td>
<td>222</td>
<td>(24,000)</td>
</tr>
<tr>
<td></td>
<td>369</td>
<td>(18,000)</td>
</tr>
<tr>
<td>Oxide</td>
<td>221</td>
<td>(21,000)</td>
</tr>
<tr>
<td></td>
<td>243</td>
<td>(17,000)</td>
</tr>
<tr>
<td></td>
<td>394</td>
<td>(14,000)</td>
</tr>
<tr>
<td>Selenide</td>
<td>222</td>
<td>(36,000)</td>
</tr>
<tr>
<td></td>
<td>380</td>
<td>(14,000)</td>
</tr>
<tr>
<td>Methiodide</td>
<td>222</td>
<td>(36,000)</td>
</tr>
<tr>
<td></td>
<td>405</td>
<td>(12,000)</td>
</tr>
<tr>
<td>Ethoxycarbonyl-1, 2, 5-triphenyl-phosphole methylene</td>
<td>223</td>
<td>(31,000)</td>
</tr>
<tr>
<td></td>
<td>239</td>
<td>(19,500)</td>
</tr>
<tr>
<td></td>
<td>385</td>
<td>(15,000)</td>
</tr>
<tr>
<td>Triphenylphosphine (α-band)</td>
<td>263</td>
<td>(10,400)</td>
</tr>
<tr>
<td>Oxide</td>
<td>223</td>
<td>(24,000)</td>
</tr>
<tr>
<td></td>
<td>254</td>
<td>(1,000)</td>
</tr>
<tr>
<td></td>
<td>259</td>
<td>(1,400)</td>
</tr>
<tr>
<td></td>
<td>265</td>
<td>(1,900)</td>
</tr>
<tr>
<td></td>
<td>271</td>
<td>(1,600)</td>
</tr>
<tr>
<td>Sulphide</td>
<td>220</td>
<td>(13,000)</td>
</tr>
<tr>
<td></td>
<td>249</td>
<td>(3,600)</td>
</tr>
<tr>
<td>Selenide</td>
<td>220</td>
<td>(34,500)</td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>(5,500)</td>
</tr>
</tbody>
</table>
Appendix I

The Reaction of Diarylbutadienes with Dichloroaryl Phosphines

The reaction of 1,4-diphenylbutadiene with dichlorophenylphosphine to prepare 1,2,5-triphenylphosphole has already been described (page 5). Cookson et al. have proposed that the mechanism involves an initial McCormack reaction followed by dehydrochlorination. To support this assertion they have shown that no reaction occurs when dichlorophenylphosphine oxide is used in place of the phosphine. On these grounds they have argued that the initial step in the reaction is a Diels-Alder type 1,4-addition to the butadiene by the lone pair on phosphorus. It is reported by Hughes that the reaction is general but the results have not been published.

In the course of the present study it was found necessary to prepare a tolyldiphenylphosphole. When the above reaction was employed using 1-phenyl-4-tolylbuta-1,3-diene a mixture of 1,2-diphenyl-5-tolylphosphole and 1,2,5-triphenylphosphole were found in the ratio 2:1. When 1,4-ditolylbuta-1,3-diene was used a mixture of at least three phospholes was obtained: 1,2,5-triphenylphosphole, 1,2-diphenyl-5-tolylphosphole and 1-phenyl-2,5-ditolylphosphole in the ratio 1:5:4. The reaction of 1,4-di-p-tolylbutadiene and dichloro-p-tolylphosphine showed only one peak in analysis by h.s.i.c. Similarly low eV mass spectral analysis showed no other peaks other than the correct parent. However the n.m.r. while indicating the correct ratio of methyl to aromatic protons, showed three methyl resonances while only two would be expected, perhaps indicative of positional scrambling.

At this stage in the study the mechanism producing these strange results is not clear. However, since the reaction is performed at over 200° it is very likely that thermally produced radicals are involved, the dichlorophosphine which is present in large excess acting as a source of aryl radicals.
There seem two possibilities at this stage. The first is that the initial reaction does, indeed, involve a 1,4-addition producing a McCormack adduct which then forms the phosphole. Cleavage of the PPh bond produces a 1-phospholyl radical which then rearranges via a 1,2-aryl shift to a 2-phospholyl radical with the electron on carbon. This radical then attacks a dichloroaryl-phosphine molecule. Several repetitions of this process would produce exchanged products. (Scheme 1).

Alternatively homolytic fission of the C₂Ar bond may occur to produce a radical but this would seem less likely. Such a hypothesis would be easily testable by heating preformed 1,2-diphenyl-5-tolylyphosphole with dichlorophenylphosphine.

The alternative explanation is that the phosphole is not formed by 1,4-addition and that some precursor undergoes rearrangement prior to ring closure. At this stage of the study, however, speculation on these lines is difficult without further evidence.

The reaction between 1-(4-methoxyphenyl)-4-phenylbuta-1,3-diene and dichlorophenylphosphine to yield only demethoxylated product (1%) and tar is less unexpected. There is at least one
precedent for phosphine attack on ethers under strongly acidic conditions. Mann has used this reaction as a route to benzo-phospholonium salts. While Mann attributes ether cleavage of the ether to attack by hydrobromic acid more recent authors have claimed that it is the result of nucleophilic displacement by the phosphine.

![Scheme 2](image-url)
Attempted Preparations of Diphenylphosphinyl Nitrene

A facile route to phosphorus containing nitrenes would be of some commercial importance. Since it is known that incorporation of phosphorus atoms in polymers confers flame-proof properties on the material, the insertion reaction of such a nitrene in the CH bonds of a polymer might provide a convenient route to this end. Fig. 1.

\[
\text{CH} \quad \xrightarrow{\text{\:N-P(0)Ph}_{2}} \quad \text{CNHPPh}_{2}
\]

Fig 1

Decompositions of diphenylphosphinyl azide were performed on various aromatic hydrocarbon solvents. The azide was photolyzed in benzene and diphenylphosphinanilide (1) was isolated in about 1% yield, identified by comparison with an authentic sample. Thermal decompositions were performed in diphenyl ether, 4,4'-dimethylbibenzyl, biphenyl and t-butylbenzene. In no case was definite evidence for any insertion found but diphenylphosphinanilide was found in each case, identified by t.l.c. Diphenylphosphinamide (2), another possible nitrene product was never found. Since the only source of phenyl groups is the azide itself the results suggest the azide prefers to react with itself rather than with the substrate provided.
The azide was remarkably thermally stable. Temperatures of over 200° were required for rapid decomposition. Thus in any flame proofing process azide thermolysis would be of doubtful use. The question of whether the photochemical process involves the nitrene has not been resolved.

Another potential route to the nitrene was thought to be the cleavage of the P=N bond in diphenylphosphinylimino triphenylphosphorane. However this compound appeared stable under all thermolytic and photochemical conditions used.

\[
\text{Ph}_3\text{P} = \text{N-}\overset{\equiv}{\text{P}}\text{Ph}_2
\]
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