

# ABSTRACT OF THESIS

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The reaction of phenylphosphine with alkynes has been studied with a view to establishing a new synthetic route to the phosphorus heterocycles, phosphorin and phosphole. The study included an investigation of a simple thermal reaction of alkynes with phenylphosphine, which proved that with terminal alkynes the phosphorus moiety added preferentially to the terminal carbon atom. Unusual reduction and fragmentation steps were observed during this investigation and a radical mechanism for this and other reactions involved has been proposed. The study was extended to the reaction of phenylphosphine with penta-1,4-diyne and it has been proved that this reaction cannot be used as a route to phosphorins. The phosphorin precursors were prepared but could only be obtained as one component of an inseparable mixture. It has also been proved that although the thermal reaction of phenylphosphine with buta-1,3-diyne is a route to phospholes, these compounds are inseparable from their reduced analogues, phospholenes.

The properties of some phospholes were also investigated and a series of novel derivatives, phospholimines were synthesised. The structure of these derivatives has been examined and a mechanism for their formation proposed. The diene character of these compounds was investigated by their reaction with dimethyl acetylenedicarboxylate. This alkyne was found to "insert" into the imine double bond ( $-P=N-$ ) in a reaction that competed with the Diels-Alder addition. The normal Diels-Alder adducts of these phospholimines could not be isolated because they were found to aromatise by a retro Diels-Alder reaction. An attempt was made to establish the nature of the phosphorus fragment extruded during this step. The effect on these reactions of different substituents on the imine nitrogen was also studied and it was proved that electron withdrawing groups completely inhibited the insertion reaction.

ABSTRACT OF THESIS



ASPECTS OF THE CHEMISTRY OF  
PHOSPHINES AND PHOSPHOLES

A Thesis presented for the degree of  
Doctor of Philosophy in the Faculty of  
Science of the University of Edinburgh

by

Robert Duncan Gee, B.Sc.

September 1971.



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I declare that this thesis is my own composition, that the work described has been carried out by myself and that it has not, previously been submitted for a Higher Degree.

The Thesis describes results of research carried out in the Chemistry Departments of St. Andrews and Edinburgh Universities under the supervision of Professor J.I.G. Cadogan since the 1st. October 1968, the date of my admission as a research student.

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I thank Professor J.I.G.Cadogan for suggesting the research topic and for his continued interest, advice and encouragement throughout the time in which this work was executed.

In addition I thank my laboratory colleagues and the teaching, technical and secretarial staffs of the Chemistry Departments of Edinburgh and St.Andrews Universities for their specialised assistance on many occasions.

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I INTRODUCTION

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## I INTRODUCTION.

### Preamble.

The name phosphorus comes from the Greek and means "light bearer" and it was the property of white phosphorus to glow in the dark that earned the element its name. The material was thought by early alchemists and "chemysts" to be a compound of phlogiston and hydrochloric acid but this idea fell with the phlogiston theory after Lavoisiers "Traite Elementaire de Chemie" in 1789.

The chemical and industrial interest in phosphorus compounds has come in the last thirty years with the widespread use of phosphate fertilisers and detergent additives. Organophosphorus compounds have been investigated industrially as antibiotics, self extinguishing polymers, flameproofers and oil additives. Complexes of phosphines and cyclic phosphines with transition metals have been patented as catalysts in the production of alcohols from alkenes.

Besides the industrial uses, organophosphorus compounds are of particular chemical interest because of the unusual properties phosphorus contributes. This is especially true of the phosphorus heterocyclic analogues of pyrrole and pyridine, which have been reported within the last ten years.

This thesis is concerned with some phosphorus heterocycles, new synthetic routes from phosphines and alkynes and the properties of some phosphole derivatives. The introduction will therefore describe the reactions of phosphines with unsaturated

compounds that are relevant to the synthetic route described later, the present syntheses and properties of known phospholes and phosphorins, and finally the Diels-Alder reaction related to that of some phosphole derivatives.

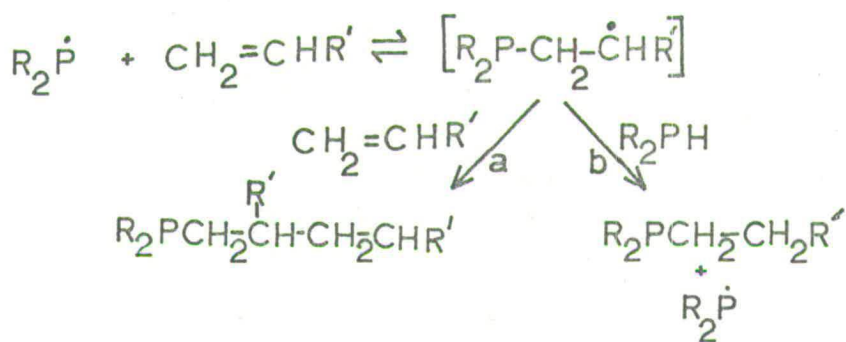


This suggestion is supported by work of Aguir and Daigle<sup>3</sup> who have shown that diphenylphosphinolithium reacts with cis or trans 1,2-dichloroethyl-ene to give cis or trans 1,2-diphosphines stereospecifically, which they believed ruled out an elimination followed by an addition mechanism. A nucleophilic addition of trialkyl and triarylphosphines was observed as the initiation of the polymerisation of 1,1-dicyanoethyl-ene by Horner et al.<sup>4</sup>, which could be terminated by acid. If sufficient acid was present polymerisation was completely inhibited, as with the reaction of triphenylphosphine and prop-2-enoic acid to give  $[\text{Ph}_3\text{PCH}_2\text{CH}_2\text{CO}_2\text{H}]^+\text{Br}^-$ <sup>5</sup>. A similar reaction of phosphine itself with polypropenes and polybutenes in the presence of various acids was reported by Hoff and Hill<sup>6</sup>.

Thus it has been proved that phosphine and substituted phosphines can add to activated alkenes by several ionic mechanisms. Work by Stiles, Rust, and Vaughan<sup>7</sup> in 1952 demonstrated that this was not a limitation. These workers studied the addition of phosphine to alkenes, as a synthetic route to substituted phosphines, by free radical initiation. They showed that under U.V. irradiation at room temperature or with di-t-butylperoxide, phosphine formed a mixture of primary, secondary and tertiary phosphines with a wide variety of alkenes including but-1-ene and cyclohexene. If however they used a large excess of alkene quantitative yields of tertiary phosphines were formed.

The synthetic use of this reaction was extended by Rauhut et al.<sup>8</sup> who preferred to use azo-bis(isobutyl)-nitrile initiator. They investigated the variation caused by different molar ratios and pressure of phosphine on the products and also

how other phosphines react. They found selective formation of secondary phosphines could occur when sterically hindered alkenes, like cyclohexene, were used. Only small amounts of telomer formation were reported even with readily polymerisable alkenes like styrene or ethyl acrylate, which implies an efficient chain transfer to the PH bond. Thus step b) is preferred to step a) in the scheme below.

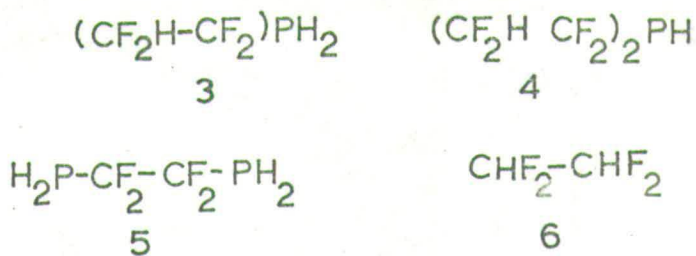


Pellon<sup>10</sup> specifically studied the chain transfer to a variety of phosphines during polymerisation of styrene and concluded that PhPH has unusual stability but that Ph<sub>2</sub>P more so. He suggested that substantial delocalisation of the lone electron contributed to this stability.

Pellon<sup>9</sup> later confirmed this conclusion when studying the reversibility of addition of phenylphosphino radicals to cis-but-2-ene. He observed the isomerisation to trans but-2-ene during the reaction with phenyl, dibutyl, and 2 cyanophosphine and by comparison showed that PhPH was the phosphorus radical most easily added reversibly.

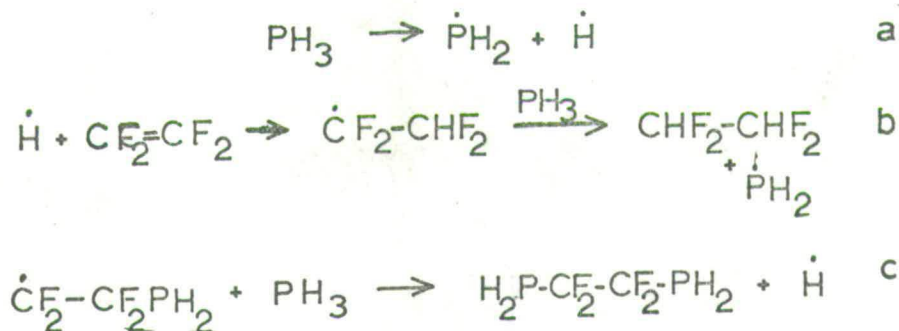
An uninitiated thermal addition of phosphine and phenylphosphine to fluorinated alkenes was reported by Parshall, England and Lindsey<sup>11</sup>. These workers added phosphine to 1,1,2,2-tetrafluoroethyl-1-ene and besides the expected 1,1,2,2,-tetrafluoroethylphosphine (3) and

bis (1,1,2,2-tetrafluoroethyl)phosphine (4) adducts they also isolated a biphosphine (5) and fluorinated alkane (6).



A similar reaction was reported with phenylphosphine but only a 50% accountability was observed.

Burch, Goldwhite and Haszeldine<sup>12</sup> reported a similar reaction, initiated by U.V., of fluorinated alkenes with phosphine. They postulated a complex radical mechanism that included the addition, abstraction steps below b) to account for the ethane produced.



They were doubtful about assigning the formation of a biphosphine to a radical coupling reaction and suggested a displacement step c) could be involved.

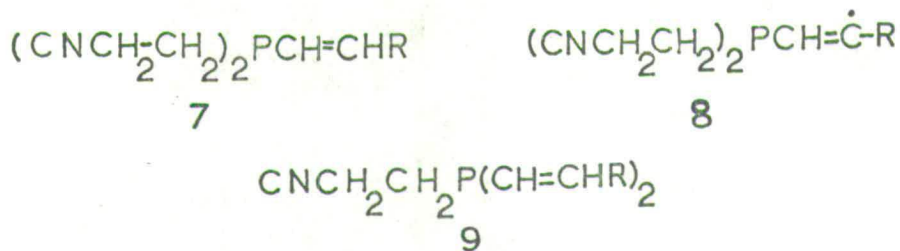
Further studies<sup>13</sup> include the observation, during the reaction of bis(trifluoromethyl)phosphine with a variety of alkenes, that fluoroalkylphosphino radicals add reversibly to trans-but-2-ene; a parallel to Pellon's report<sup>10</sup> mentioned earlier.

The important addition reaction of phosphines with alkenes

is therefore the radical process although other modes of reaction are possible.

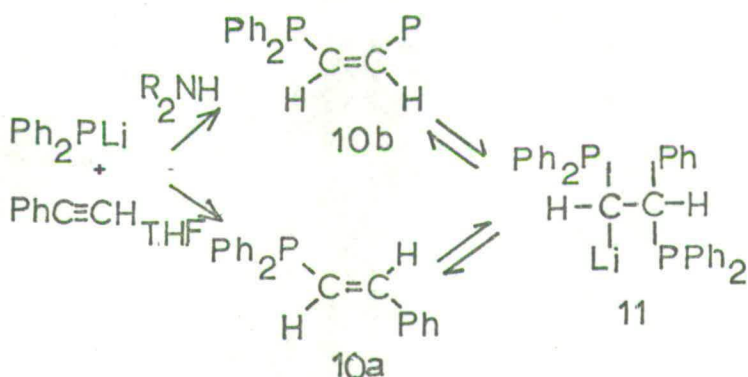
## A 2) Reaction of Phosphines with Alkynes.

The reaction of phosphines with alkynes has not been studied in the same detail as that with alkenes, except in one special case that will be discussed later. Rauhut et al.<sup>8</sup>, as an extension of their synthetic studies with alkenes, reported the reaction of bis(2-cyanoethyl)phosphine with 1-octyne initiated by azo-bis(isobutyl)nitrile. They found that a 1:1 adduct (7) was formed as well as substantial amounts of high boiling material, which they proved were not due to a reaction of the unsaturated phosphine (7) with the alkene, but probably a side reaction of a radical intermediate (8). Hept-1-yne was reacted with 2-cyanoethylphosphine to give a low yield of tertiary phosphine by diaddition (9). None of the secondary phosphine intermediate was observed, which implied that it was either more reactive or very susceptible to side reactions.



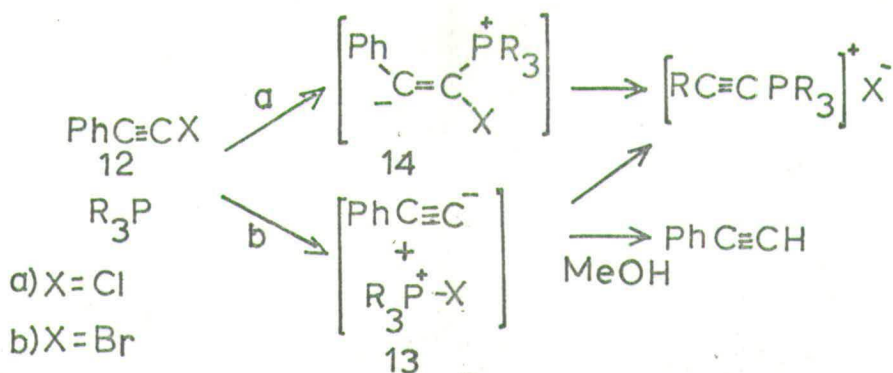
Diphenylphosphinolithium was shown to add to 2-phenyleth-1-yne in tetrahydrofuran to give mostly diphenyl-(2-trans-phenyleth-1-yne)ylphosphine (10a), but the cis isomer (10b) when a primary or secondary amine was added to the reaction mixture<sup>14</sup>. This observation was tentatively explained by the reversible addition of a second molecule of phosphinolithium (11) which, results in formation

of the most sterically favoured isomer. The authors suggested that complex formation with the added amine accounts for the different stereochemistry observed in that reaction. They also clarified the stereochemistry of the product obtained by Hoffmann and Diehr<sup>15</sup> from the slow reaction of diphenylphosphine and 1-phenyleth-1-yne at 100°, but showed that the former was not an intermediate in their reaction, because the conditions were too mild.

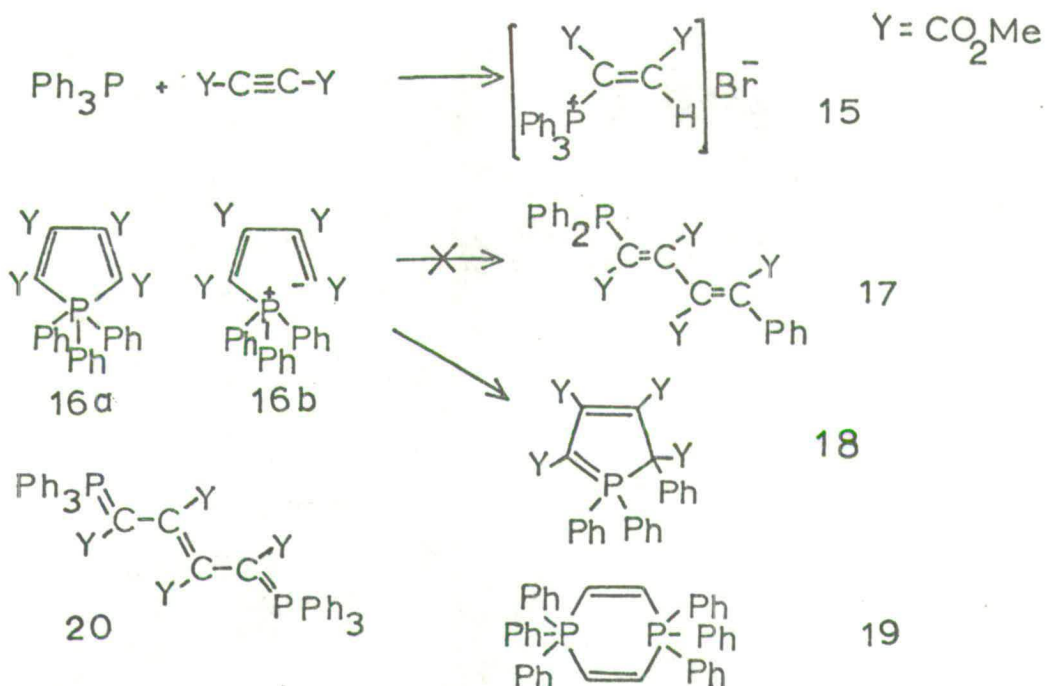


This reversible addition of diphenylphosphinolithium is a parallel to the reversible addition of phenylphosphino radicals to alkenes.

Nucleophilic reactions of phosphines with alkynes was also studied by Fujii, Dickstein and Miller<sup>16</sup> although a special case, 1-halo-2-phenyleth-1-yne (12) was used. This group concluded that with trialkylphosphines and a bromo-alkyne the only reaction path involved abstraction to form trialkylphosphonium bromide and a phenylethyne anion that could be trapped with methanol as 2 phenyleth-1-yne (path (b) below). If however a chloro-alkyne was used nucleophilic attack by the phosphine gave the intermediate phosphonium salt (14).

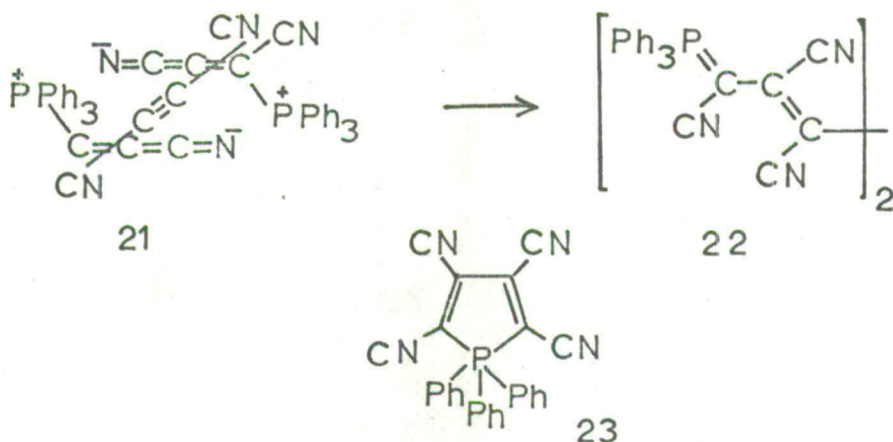


Hoffmann<sup>15</sup> reported a study of proton catalysed reactions of secondary and tertiary phosphines with a variety of alkynes, where phosphonium salts were isolated. These authors mentioned the reaction of triphenylphosphine with dimethyl acetylenedicarboxylate, one that has caused considerable trouble to several workers. In Hoffmann's case proton catalysis led to formation unambiguously of the phosphonium salt (15).

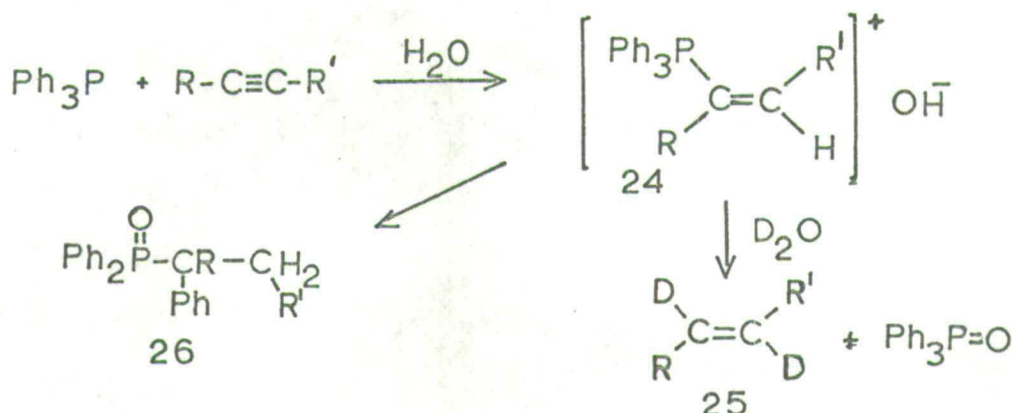


The reaction in ether at  $-50^{\circ}$ , without an acid catalyst, was reported by Johnson and Tebby<sup>17</sup> in 1961 to give a 1:2 adduct. These authors preferred to assign the zwitter ion (16b) structure, rather than the phosphole isomer (16a), to the product which they found readily rearranged to two stable compounds. Hendrickson, Spenger and Sims<sup>18</sup> also reported this reaction but resolutely maintained that the phosphole (16a) form was the only acceptable one by comparison to the arsole analogue they also prepared. Johnson and Tebby<sup>17</sup> investigated one of the rearranged products and proposed an open chain phosphine (17) formed by phenyl migration. Later, Waite, Tebby, Ward and Williams<sup>19</sup> retracted this conclusion in favour of a stable 2H-phosphole (18). A similarly confused account of the reaction of triphenylphosphine with dimethyl acetylenedicarboxylate in varying molar ratios concluded that a 2:2 adduct isolated was not a diphosphorin (19) as originally claimed<sup>17</sup>, but in fact the diphosphorane (20)<sup>20</sup>.

Tebby<sup>24</sup> has followed up another report of a penta-covalent phosphorus phosphole (23) from the reaction of triphenylphosphine with dicyanoacetylene<sup>21</sup>. These authors claimed that an alkylidene-1,6-diphosphorane (22) was in fact formed and prefer the mechanism of coupling two dipolar intermediates with another molecule of alkyne to others proposed (21).



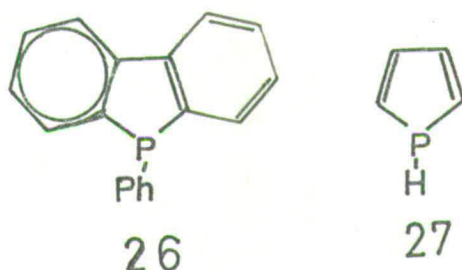
This type of phosphorane structure is one that recurs in the reactions of triphenylphosphine with dimethyl acetylenedicarboxylate<sup>25</sup>. However when, the reaction of triphenylphosphine with a variety of alkynes occurs in the presence of water a phosphonium salt is formed as an intermediate (24), which is hydrolysed to a trans-alkene. This reaction has been utilised to form deuterated alkenes (25) in reasonable yield<sup>26</sup>. Tebby<sup>27</sup> et al. had earlier reported a similar reaction with triarylphosphines and 2-phenyleth-1-yne and later<sup>28</sup> proposed an extraordinary route to the phosphine oxide they isolated (26), although they did exclude a mechanism based on a phosphacyclopropene intermediate.



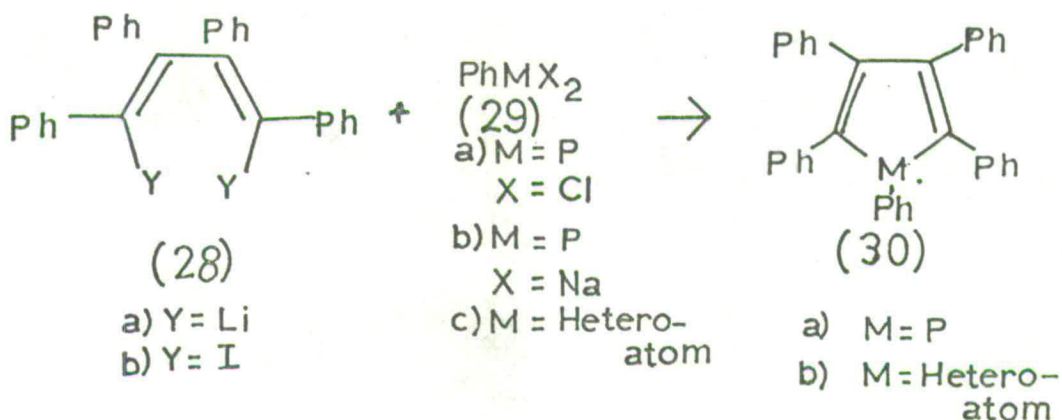
Thus the reactions of phosphines with alkenes and alkynes can involve radical, cationic, anionic or zwitterionic intermediates depending on the conditions chosen. This makes elucidation of mechanisms and identification of products a complex task, as has been shown by the variety of pathways and structures put forward for the reaction of triphenylphosphine and dimethyl acetylenedicarboxylate.

I B) PHOSPHORUS HETEROCYCLES.

Furan, thiophenes and pyrroles have been known for decades but the related phosphole system was not reported until the first derivative, 5-phenyl-5H-dibenzophosphole (26), also referred to as 9-phenyl-9-phosphafluorene, was isolated from the thermolysis of pentaphenylphosphorane ( $\text{Ph}_5\text{P}$ ) by Wittig and Geissler<sup>29</sup> in 1953.

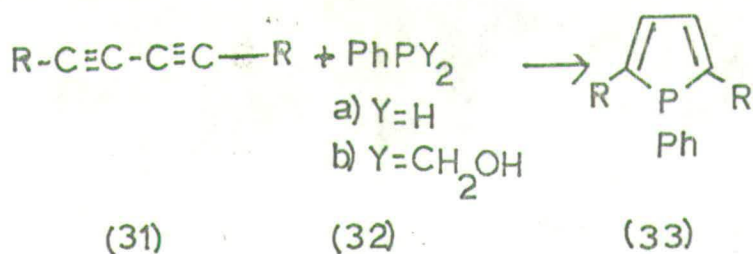
B. 1) Preparation of Phospholes.

The parent phosphole (27) has not been synthesised and the first simple phosphole was only reported in 1959 and then independantly by two groups. Leavitt, Manuel, and Johnson<sup>30</sup> prepared 1,4-dilithiobuta-1,3-diene (28a) from the controlled dimerisation of  $\text{PhC}\equiv\text{CPh}$  with lithium and then reacted it with phenylphosponous dichloride to obtain 1,2,3,4,5-pentaphenylphosphole (30a). They later extended the reaction, with Matternas and Lehmann<sup>31</sup>, to include the cyclopentadiene derivatives of arsenic, antimony, tin and germanium (30b).

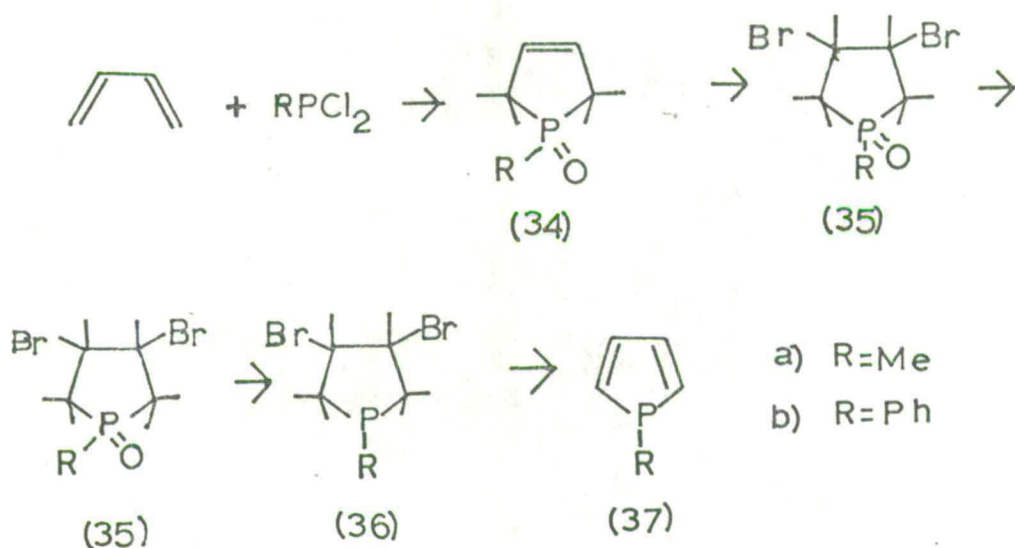


Braye and Hubel<sup>32</sup> simultaneously reported that the reaction of phenylphosphonous dichloride with the iron pentacarbonyl complex  $\text{Fe}_2(\text{CO})_6(\text{PhC}\equiv\text{CPh})_2$  also gave the phosphole (30a). Independently they used the reaction of 1,4-dilithobuta-1,3-diene to confirm the product. Braye, Hubel and Calpier<sup>33</sup> later prepared 1,4-diiodobuta-1,3-diene (28b) by the action of iodine on the lithium compound (28a). They reacted it with phenylphosphinodisodium  $\text{PhPNa}_2$  (29b) and related compounds  $\text{PhMX}_2$  (29c) to extend the synthesis to a wide range of heterocyclic pentadienes (30b). These two methods have now produced the heterocycles of phosphorus, arsenic, antimony, tin, germanium, mercury, gold, boron, silicon, zirconium and tellurium but are however limited to the pentaphenyl derivatives.

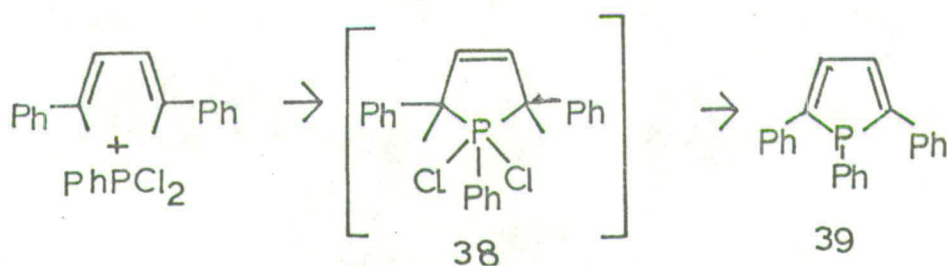
The most general phosphole synthesis reported is that due to Märkl and Potthast<sup>34</sup> and is closely related to those of pyrroles<sup>35</sup> and thiophenes<sup>36</sup>. Phenylphosphine (32a) in benzene, or a benzene tetrahydrofuran mixture, containing catalytic quantities of butyl or phenyl lithium reacts readily with 1,4-dialkylbuta-1,3-dienes (31) and 1,4-diarylbuta-1,3-dienes (31) to give 1-phenyl-2,5-dialkylphospholes (33) and 1-phenyl-2,5-diarylphospholes (33) in good yield. These authors also replaced phenylphosphine by bis(hydroxymethyl)phenylphosphine (32) in pyridine but found lower yields in all cases. 2,5-dimethyl-1-phenylphosphole (33) prepared by these methods was the first with alkyl groups on the ring.



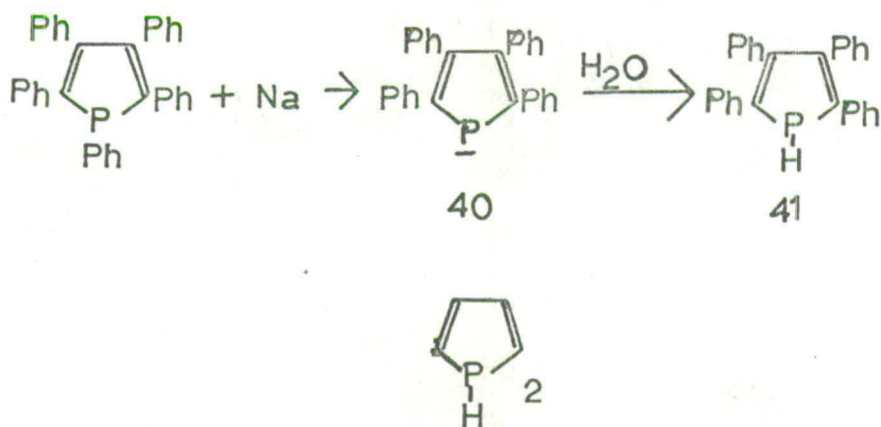
However, the three routes mentioned so far all produce phosphole with ring substituents. The more involved approach of Quinn and Bryson<sup>37</sup> and Märkl and Potthast<sup>38</sup> produced 1-methylphosphole (37a) and 1-phenylphosphole (37b) respectively. Both groups of workers reacted the appropriate phosphonous dichloride with buta-1,3-diene, in a Diels-Alder type of reaction, to produce the phospholene oxides (34a:34b) obtained by McKormack<sup>39</sup>. The phospholene oxides were brominated to 3,4-dibromo-1-methylphospholene-1-oxide (35a) and 3,4-dibromo-1-phenylphospholene-1-oxide (35b) and then reduced with trichlorosilane<sup>37</sup> or phenylsilane<sup>38</sup> to the corresponding dibromophospholanes (36). Dehydrobromination with potassium-*t*-butoxide gave 1-methylphosphole<sup>37</sup> (37a) and 1-phenylphosphole<sup>38</sup> (37b).



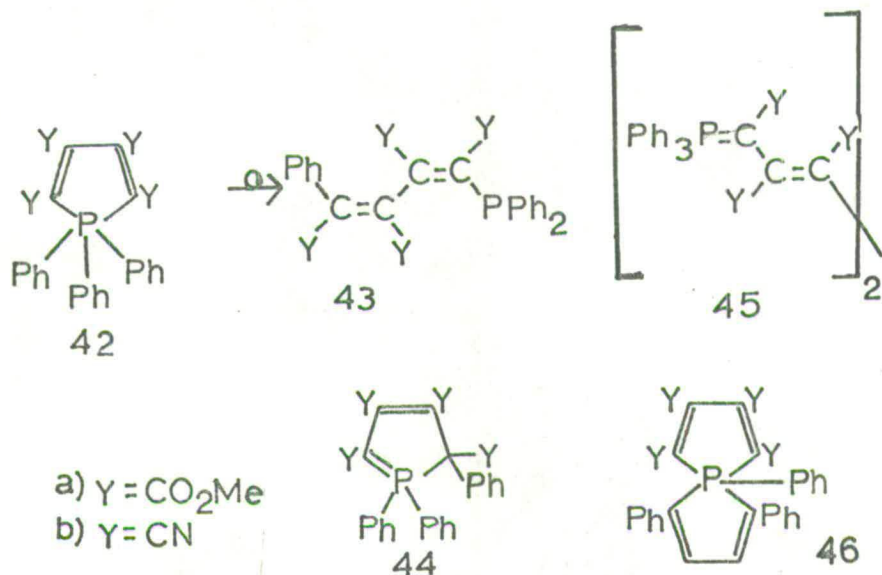
1-Ethoxyphosphole-1-oxide was prepared by a similar route by Usher and Westheimer<sup>40</sup> but could only be isolated as a dimer. A related synthesis, but reputedly more restricted, is that of 1,2,5-triphenylphosphole by Campbell, Cockson, Hocking and Hughes<sup>42</sup>. 1,4-Diphenylbuta-1,3-diene is heated to 220° with phenylphosphonous dichloride. The initial reaction is almost certainly a Diels-Alder type but the phospholene intermediate (38) spontaneously dehydrochlorinates under the reaction conditions to give the corresponding phosphole (39) in reasonable yield.



The only phosphole unsubstituted on phosphorus reported is due to Braye<sup>43</sup>. Reaction of 1,2,3,4,5-pentaphenylphosphole with alkali metals yields the anion (40) which reacts readily with water to form 2,3,4,5-tetraphenylphosphole (41). The work was published as an abstract in 1964<sup>43</sup> and later as a patent<sup>44</sup> but has not been further documented or repeated. Hughes<sup>41</sup> suggested that this reaction is a possible route to the parent phosphole (2).

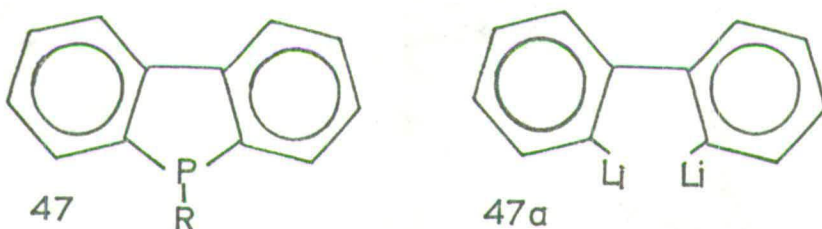


There have been several reports<sup>17,18,21,22</sup> of simple phospholes containing pentavalent phosphorus but only one remains unchallenged. Johnson and Tebby<sup>17</sup> claimed that 2,3,4,5-tetramethyl 1,1,1-triphenylphosphole-2,3,4,5-tetracarboxylate (42) was produced from the reaction of triphenylphosphine in dimethyl acetylenedicarboxylate. Both Johnson<sup>17</sup> and Hendrickson<sup>18</sup> found that the phosphole (42a) is unstable at room temperatures and rearranges to a yellow open chain isomer (43). More recent work by Tebby<sup>21</sup> has shown that another rearranged product is also present, which is claimed to be the 2H-phosphole (44). A similar dispute has occurred with the reaction of triphenylphosphine with dicyanoacetylene. Reddy and Weiss<sup>27</sup> claimed that the phosphole (42b) is formed, but Tebby<sup>24</sup> discounted this and in a more detailed study showed the adduct to be the phosphorane (45).

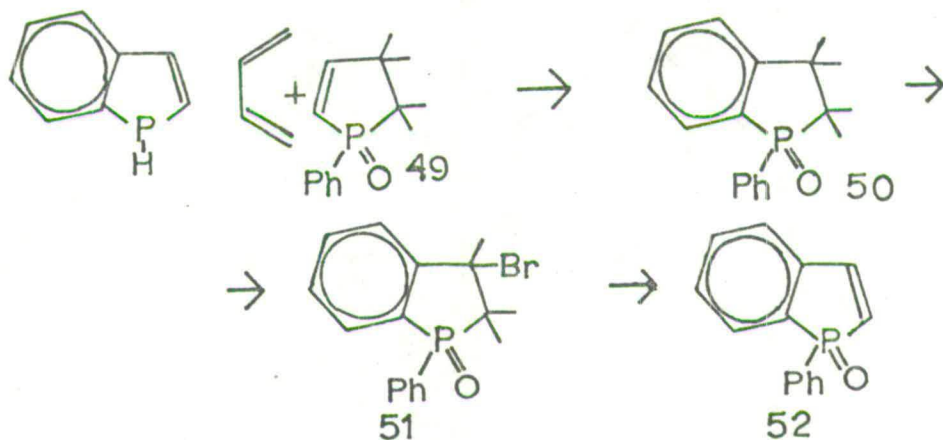


Hughes and Uaboonkul<sup>22</sup> claimed to form the spirophosphole (46) from the reaction of dimethyl acetylenedicarboxylate with 1,2,5-triphenylphosphole but this will be discussed in the section on reactions of phospholes (Ch. I. Sect. B2.).

The isolation of 5-phenyl-5H-dibenzophosphole (47) from the thermolysis of pentaphenylphosphine was mentioned earlier but this limited synthesis was superseded by Wittig<sup>46</sup> and Millar.<sup>47</sup> These workers prepared 2,2-dilithobiphenyl (47a) from phenyl lithium and 2,2-dibromophenyl and reacted it with phenylphosponous dichloride to yield the 5-phenyl-5H-dibenzophosphole (47). A wide variety of other methods have been developed for the preparation of dibenzophosphole which include phosphorane systems containing dibenzophosphole units<sup>45</sup>.



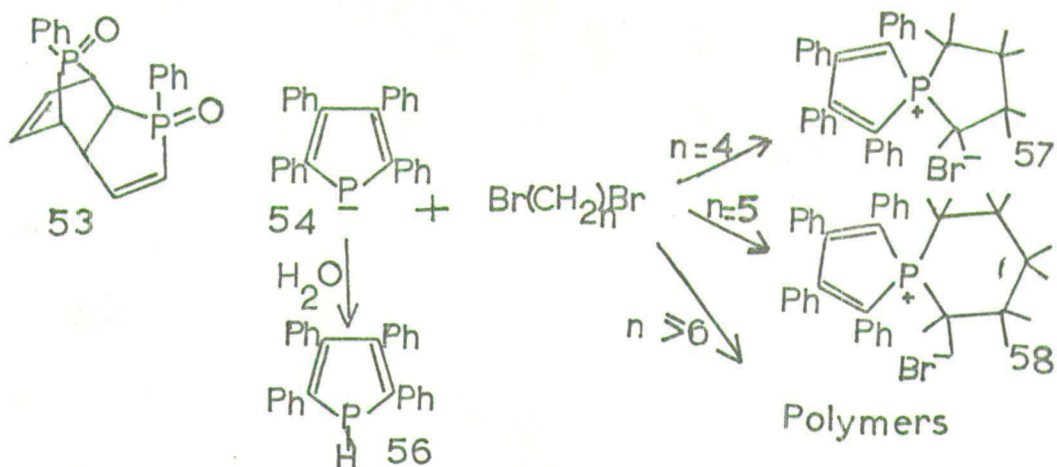
The other fused ring compound in the phosphole series is phosphindole (48) and the only derivative was reported by Chang and Tong<sup>48</sup>. 1-Phenylphosphol-2-ene-1-oxide (49) was reacted with 1,4-diacetylbuta-1,3-diene to give 1-phenylphosphindoline-1-oxide (50). This was then brominated with N bromosuccinamide to the 3-bromo derivative (51). Dehydrobromination then gives 1-phenylphosphindole-1-oxide (52).



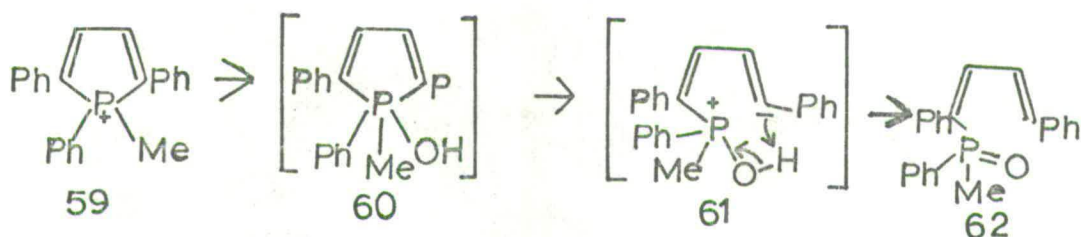
B 2) Reactions of phospholes.

The chemistry of the simple phosphole ring naturally varies with different substituents on phosphorus and the ring. However all phospholes prepared to date readily form oxides, either by exposure to air, in the case of 1-methylphosphole<sup>37</sup>, 1-arylphosphole<sup>38</sup> and phospholes with alkyl ring substituents, or by the action of dilute hydrogen peroxide in the case of aryl phospholes such as 1,2,5-triphenylphosphole<sup>42</sup>. Except in the case of the highly hindered 1,2,3,4,5-pentaphenylphosphole-1-oxide, phosphole oxides readily dimerise in a Diels-Alder type reaction. Thus 1-phenyl-1-oxide gave the multiple ring system (53). 1-Ethoxyphosphole-1-oxide could only be isolated as this type of dimer. This property demonstrates the increased diene character of the oxides. The sulphides and selenides of 1,2,5-triphenylphosphole were also readily prepared but do not show the green fluorescence characteristic of the oxide.

An important synthetic reaction of aryl-phospholes is that with potassium or lithium metal<sup>43</sup>. The anion (54) is formed following cleavage of the P-Ar bond and reacts with alkyl halides to give the corresponding phosphole<sup>44</sup>. When dibromoalkanes (55) were used<sup>49</sup> self-quaternisation gave the bicyclo systems almost quantitatively (57, n=4), or (58, n=5), but then in low yield with much polymeric material. This result implies the greater preference of phosphorus for five membered rings. Larger rings (55, n=6) are not formed and only polymeric material was observed. The reaction of the anion (54) with water is claimed as a route to 2,3,4,5-triphenylphosphole (56) as mentioned earlier (Ch.I Sect.B1).

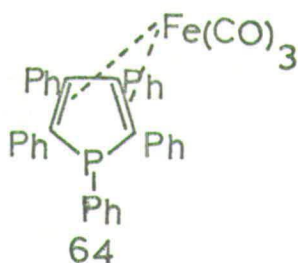
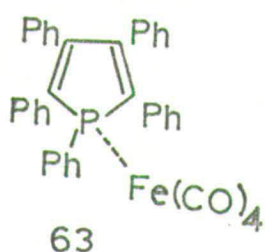


Work by Bergesen<sup>50</sup> has shown that 1,2,5-triphenylphosphole is readily quaternised with methyl iodide and he has studied the reaction of the salt formed (59) with sodium hydroxide. No cyclic products were formed and these workers attribute this to conjugation between the phosphole ring system and the phenyl groups giving a more stable anion on C-Ph than the alternative on P-Ph. Thus the initially unstable phosphorane (60) gave the zwitterion (61) and proton migration then produced the stable phosphine oxide.

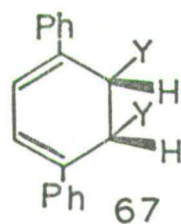
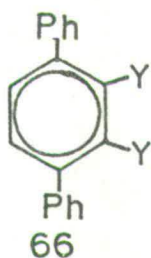
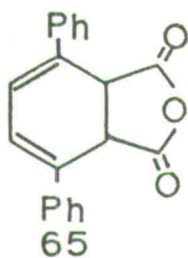


These reactions show that the lone pair on phosphorus is readily available, a property that Mann<sup>45</sup> considers is supported by the formation<sup>51</sup> of a pentacarbonyl complex (63) that has similar spectral data to  $\text{R}_3\text{P}-\text{Fe}(\text{CO})_4$ <sup>52</sup>. The phosphole-tricarbonyl complex (64) was also prepared and Mann considers this to be a parallel to other non-aromatic conjugated dienes. However 1,2,3,4,5-pentaphenylphosphole-1-oxide reacts even more readily with pentacarbonyl

iron to give analogous complexes.

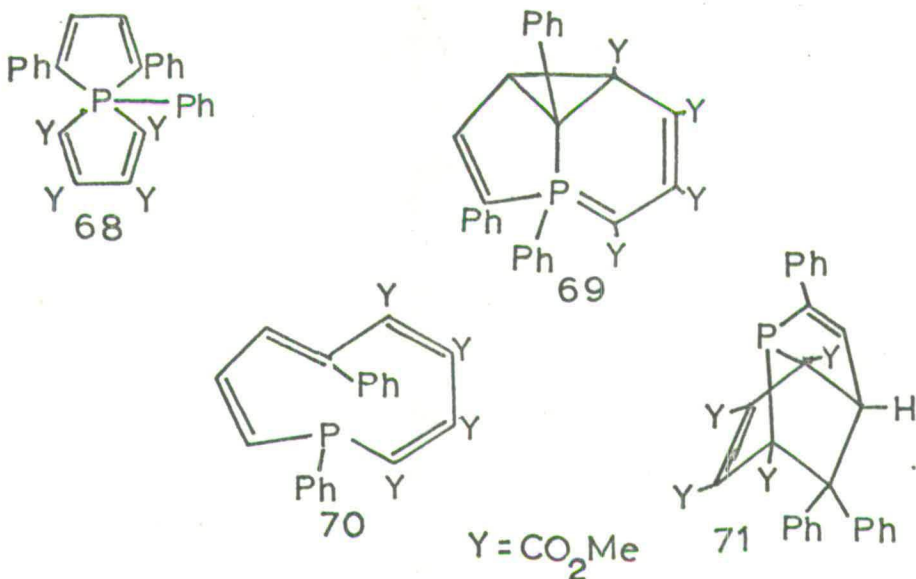


The diene reactivity of 1,2,5-triphenylphosphole has been studied in some detail, initially by Campbell et al.<sup>42</sup> and then later by Hughes and Uaboonkul<sup>22</sup>. Campbell found that elevated temperatures of 150° were needed to obtain a reaction of the phosphole with maleic anhydride and dimethyl acetylenedicarboxylate. These reactions were followed by observing the [PhP] extrusion products 3,6-diphenylphthalic anhydride (65) and 1,2-dimethyl 3,6-diphenylphthalate (66) respectively. A similar extrusion reaction was observed with 1,2,3,4,5-pentaphenylphosphole and Mann<sup>45</sup> assumes the phosphorus fragment has formed a polyphenyl-substituted cyclic polyphosphine. Phosphole oxides however react under normal conditions with maleic anhydride and acrylonitrile to yield the normal Diels-Alder adducts. With dimethyl acetylenedicarboxylate at 150°, however, the oxide rapidly gave the phthalate (66) and with dimethyl fumarate, 3,6-diphenyl 3,5-cyclohexadiene-trans-1,2-dicarboxylate (67) thus extruding the [POPh] fragment.



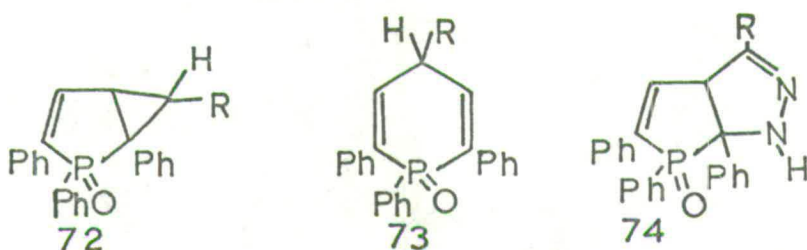
The reaction of 1,2,5-triphenylphosphole received more attention from Hughes<sup>22</sup>, who confirmed the reaction with dimethyl acetylenedicarboxylate, but also found that a reaction in neat alkyne over several days gave several products. One of these was shown to be the phthalate (66) and another a 4:1 adduct in low yield (2.5%), which was not investigated further. The main product was a 2:1 adduct that received a detailed physical and chemical investigation. The authors' involved argument concludes that the product is a spiro-biphosphole (68) which readily rearranges to a bicyclophosphine (71).

It was the original suggestions<sup>17,18</sup> of pentacovalent phosphorus phospholes that induced Hughes<sup>22</sup> to postulate the spirophosphole (68) as a product of this reaction. In a later study Tebby<sup>23</sup> disputed this suggestion and claimed that phenyl migration and rearrangement had occurred to give a complicated tricyclo-allylidene phosphorane (69). Tebby et al.<sup>23</sup> repeated the rearrangement reported by Hughes and confirmed the proposed structure (71) by <sup>31</sup>P n.m.r. unavailable to the other workers. They explained this rearrangement to (71) by a ring-chain tautomerism involving an intermediate nine-membered ring (70).



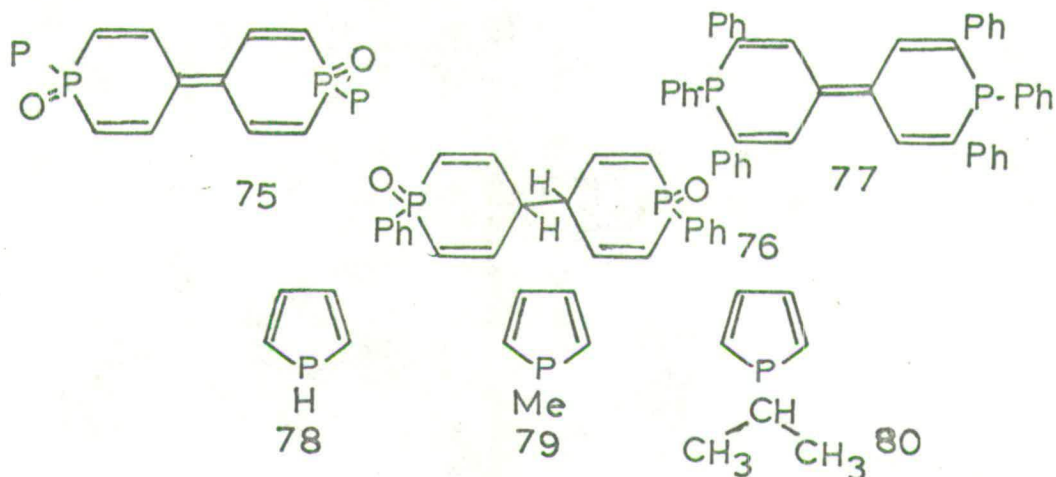
The work by Hughes and Uaboonkul does however highlight the diene and tertiary phosphine character of 1,2,5-triphenylphosphole and is evidence against the aromatic nature of aryl-phospholes.

Since pyrrole is known to undergo ring expansion to pyridines the potential formation of phosphorins from phospholes is of considerable interest. The reaction of 1,2,5-triphenylphosphole with methyl diazoacetate gave various products under different conditions <sup>42</sup>. The phosphole in boiling dioxan containing copper powder gave the dimethyl ester (67), presumably from intermediate decomposition of the diazoacetate to dimethyl fumarate followed by the extrusion reaction mentioned above. Without a copper catalyst present a colourless methyl ester  $C_{25}H_{21}O_3P$  was obtained. The ester could have several structures but a combination of physical and chemical evidence eliminated all but a bicyclopopholene oxide (72) or a 1,4-dihydrophosphorin oxide (73). By a similar reaction under mild conditions the pyrazoline (74) was obtained which decomposed to either of the products (72:73).



The reaction of diazomethane to give (72 R=H) was studied by Hughes and Srivnavit <sup>54</sup> specifically as a possible route to phosphorins. The authors' detailed report of the thermolysis and photolysis of the cyclopropane (72) and pyrazoline (74) derivative concluded that 4,4'-diphosphabi(cyclohexa-1,5-dienyl) (75) and 4,4'-diphosphabi(cyclohexa-2,5-dienylidene) (76) systems

were produced. This was confirmed by reduction to the compound (77) prepared by Märkl<sup>34</sup>. Thus although these particular ring expansion reactions failed to form the simple phosphorin, these results are encouraging and suggest that a possible route does exist.



Quinn, Bryson and Moreland<sup>37</sup>, have prepared the closest relative of phosphole (78) namely 1-methylphosphole (79) by a route described earlier. These workers<sup>56</sup> consider it the most suitable example available to study the possible aromaticity of the phosphole ring, since there is no distracting conjugative effect of an aryl substituent. This phosphole is easily oxidised and decomposes on distillation unless special precautions are taken. Methyl iodide readily forms the 1,1-dimethylphospholium iodide but some doubt exists concerning the monomeric nature of the product.

The proton n.m.r. spectra of 1-methylphosphole shows a complex,  $\tau$  2.5-3.5, which was reproduced theoretically by computer to obtain coupling constants which were in the normal range expected for this arrangement. The authors suggested that the deshielding of the ring protons results from a ring current effect which also

influences the methyl protons. This opinion was supported by observations by Märkl on 1-phenylphosphole<sup>36</sup>. More significant evidence of donation of the phosphorus lone pair to the  $\pi$  electron system and decrease of diene character comes from the <sup>31</sup>P n.m.r.<sup>56</sup> spectra of the neat liquid at +8.7 p.p.m., relative to 85% phosphoric acid, when compared with that of 1-methyl-3-phospholene (+41.8), ethyldivinylphosphine (+20.8) and trivinylphosphine (+20.7). Further support comes from the U.V. spectra of 1-methylphosphole,  $\lambda_{\text{max}}$  286 nm, which resembles that of N-methylpyrrole,  $\lambda_{\text{max}}$  280 nm, and not that of ethyldivinylphosphine,  $\lambda_{\text{max}}$  236 nm.

1-Methylphosphole is not extracted from solution by 2N Hydrochloric acid like its precursor 1-methyl-3-phospholene and is therefore less basic, although the ease of oxidation and quaternisation shows the lone pair of electrons to be fairly available. With stronger acid, 6N Hydrochloric, the phosphole decomposes and thus resembles simple pyrroles, which are notoriously sensitive to strong acids. It has been established that carbon protonation, not nitrogen, occurs in pyrrole<sup>57</sup> but this point was not investigated in the phosphole.

Some interesting work on the pyramidal inversion barrier of 1-isopropyl-2-methyl-5-phenylphosphole (80) was reported by Egan, Tang and Mislow<sup>58</sup>. They calculated the barrier with a computer from temperature dependant n.m.r. spectra of the isopropyl region. The very low value of 16 Kcal/mole compared with 29-36 Kcal/mole for dialkylaryl, alkyl diaryl, and triarylphosphines is more surprising since cyclisation normally increases the strain of the transition state and thus increases the barrier height.

These authors also pointed out that the chemical evidence and some of the spectroscopic evidence used in the argument against aromatic character is not relevant to the ground state, which their work considered.

X-ray crystallographic studies have been made on 1-benzylphosphole by Coggan et al.<sup>72</sup>, who have shown the P-C bond to be  $1.78\text{\AA}$ , less than the sum of the radii  $1.84\text{\AA}$ , and a similar contraction to that of other hetero-aromatics and these authors believe this indicates some d-orbital character in the bonds. These workers also studied the micro-wave spectra and showed the ring to be slightly puckered, unlike furan, pyrrole or thiophene, and retention of the pyramidal configuration at phosphorus.

These results summarize the important properties of simple phospholes and shows some conflicting evidence on the possible aromaticity of the phosphole ring. The strong evidence for aromatic character is the n.m.r. and U.V. studies on 1-methylphosphole, which shows that it cannot be considered as a cyclic divinylphosphine, but is more similar to N-methylpyrrole. 1,2,5-Triphenylphosphole has, however, been shown to undergo a Diels-Alder reaction in mild conditions, a diene reaction, and that the phosphorus lone pair of electrons is also attacked. The availability of the lone pair is also demonstrated by the ease of quaternisation and the formation of iron carbonyl complexes, which implies reduced phosphine character<sup>56</sup>. The relative ease of reaction with dienophiles of phosphole oxides when compared with the corresponding phosphole, indicates decreased diene character in the phosphole.

The fierce assertion of Egan et al.<sup>58</sup> that "phospholes have increased delocalisation" following their studies on the pyramidal inversion barrier at phosphorus, conflicts with the comment of Hughes<sup>54</sup> that phospholes have "little or no aromatic character". The most realistic attitude is to consider that the dominant chemistry of phosphorus is superimposed upon an undefinable degree of aromatic character of the phosphole ring, which varies with the substituents.

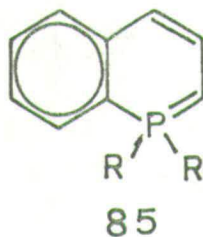
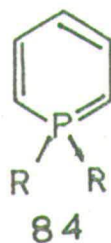
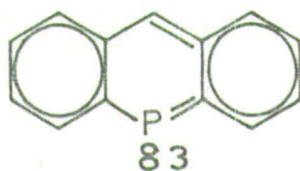
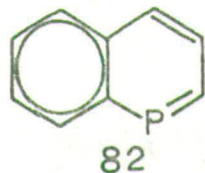
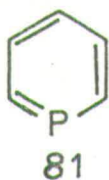
This summary has been deliberately limited to the synthesis and reactions of simple phospholes and the closely related phosphindole and dibenzophosphole systems. It has not included a review of many saturated or partially unsaturated phosphorus ring systems or the exotic compounds produced by Hellwinkel et al.<sup>59</sup>.

An attempt has been made to link the phosphorus five-membered rings with the six-membered ring analogues and to show that the phosphole ring may have considerable aromatic character.

### B: 3) Preparation of Phosphorins.

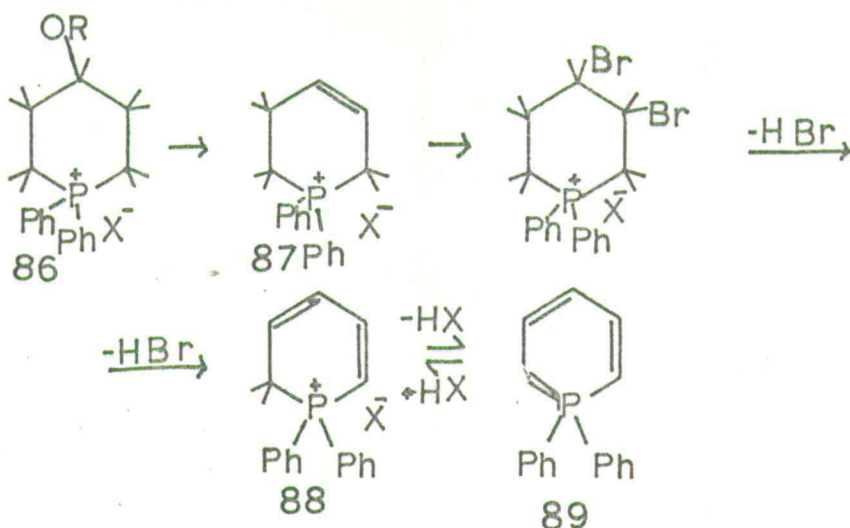
The phosphorus analogues of pyridine, quinoline, acridine and their derivatives have proved even more elusive than their five-membered ring counterparts described earlier. None of the parent compounds, phosphorin<sup>\*</sup> (81), phosphindoline (82), or dibenzophosphorin (83) have been isolated although there is a recent report of dibenzophosphorin<sup>60</sup> in solution. The first successful approach to a fully unsubstituted six-membered phosphorus ring was made in 1963 (84) to the non-classical phosphabenzene systems with 5-covalent phosphorus.

\* See Appendix I page 135.

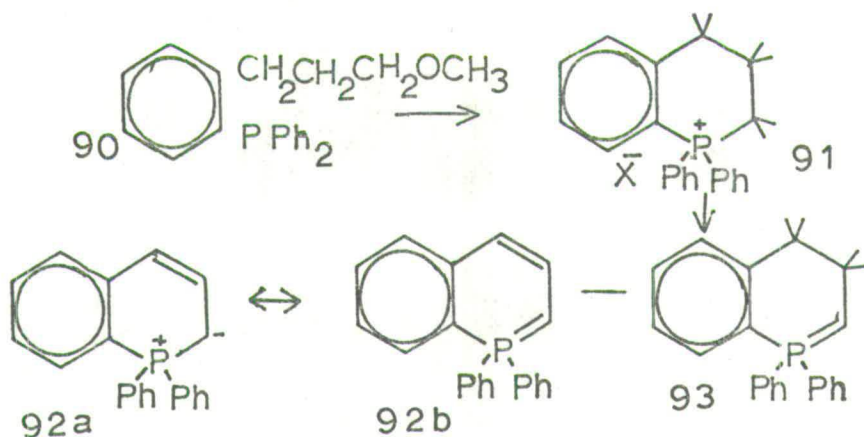


Märkl<sup>61</sup> treated 1,5-dibromo-3-methoxypentane ( $\text{CH}_3\text{OCH}(\text{CH}_2\text{CH}_2\text{Br})_2$ ) with diphenylpotassiophosphine to obtain 4-methoxy-1,5-diphenylphosphorinium bromide (86) which was demethylated to the 4-hydroxy analogue. This secondary alcohol was dehydrated with potassium hydrogen sulphate to 1,2,3,6-tetrahydro-1,1-diphenylphosphorinium cation, isolated as the perchlorate (87). Addition of bromine followed by a two-stage dehydrobromination formed 1,2-dihydro-1,1-diphenylphosphorinium perchlorate (88). Addition of dilute sodium hydroxide to the solution precipitated 1,1-diphenylphosphorin (89) as an amorphous powder. This phosphorin was found to be stable in water but autoxidised readily in organic solvents to coloured phosphoranes of unknown structure.

The compound (89), which Märkl calls "phosphabenzene", readily reacted with acids to reform the cation (88). This work showed the interrelationship of various substituted phosphorins, dihydrophosphorins, tetrahydrophosphorins and phosphoranes involving five covalent phosphorus.



By a related synthesis Märkl<sup>62</sup> also obtained 1,1-diphenyl phosphinoline, sometimes referred to as phosphanaphthalene. An intramolecular quaternisation during cleavage of (O-(3-methoxypropyl)phenyl)diphenylphosphine (90) by hydrobromic acid gave 1,2,3,4-tetrahydro-1,1-diphenylphosphinolium cation (91) from which the phosphinoline (92) was obtained.

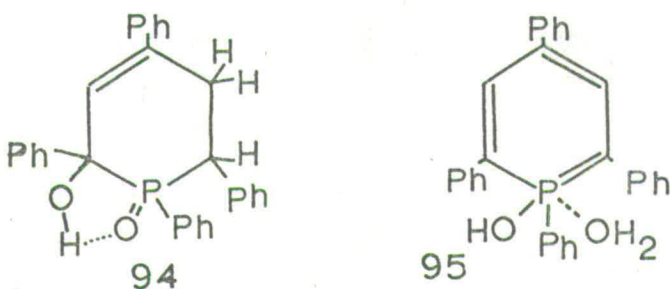


The phosphinoline (92) is unexpectedly stable towards hydrolysis but autoxidises readily in methanolic solution to various coloured methylenephosphoranes.

Märkl<sup>62</sup> suggested that considering the properties of comparable phosphoranes, notably 3,4-dihydro-1,1-diphenylphosphinoline (93) prepared at the same time, the phosphinoline (92) is

relatively stable. The author considered that this is due to cyclic conjugation involving the  $p\pi-d\pi$  double bond of the ylene (92b) in accordance with the small participation of the ylide form (92a) the compound proved unreactive towards benzaldehyde or nitrobenzaldehyde in the Wittig reaction.

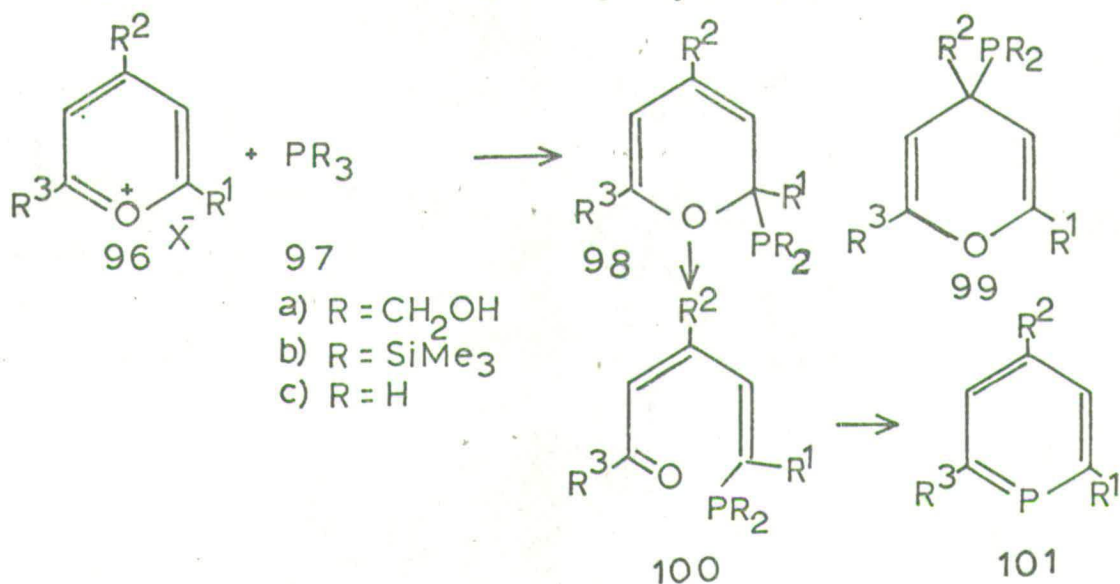
Another approach to the synthesis of the phosphorin (83) system was that of Price et al.<sup>63</sup> who isolated two isomers, of composition  $C_{29}H_{25}O_2P$ , from the reaction of phenylphosphine and 2,4,6-triphenylpyrilium fluoroborate (94). A considerable amount of evidence indicated that one had the hydrogen bonded structure and the other the hydrated phosphorin form (95).



Märkl<sup>64</sup> followed up this approach with the reaction of tris-(hydroxymethyl)phosphine (97a) with 2,4,6-triphenylpyrilium fluoroborate (96) in boiling pyridine and obtained the first phosphorin unsubstituted on the phosphorus atom (99). Dimroth et al.<sup>65</sup> have extended this method to a wide range of phosphorins including 2,4,6-tri-t-butylphosphorin, the first example with no aryl substituents.

Märkl et al.<sup>66</sup> improved this synthesis by replacing the tris(hydroxymethyl)phosphine (97a) with tris(trimethylsilyl)phosphine (97b) in acetonitrile. The authors suggested that an intermediate phosphine (100) was formed, which reacted intramolecularly to give

hexamethyldisiloxane and the phosphorin (101), which was isolated by chromatography. This method had the advantage that no basic solvent was required and that it also gave higher yields.



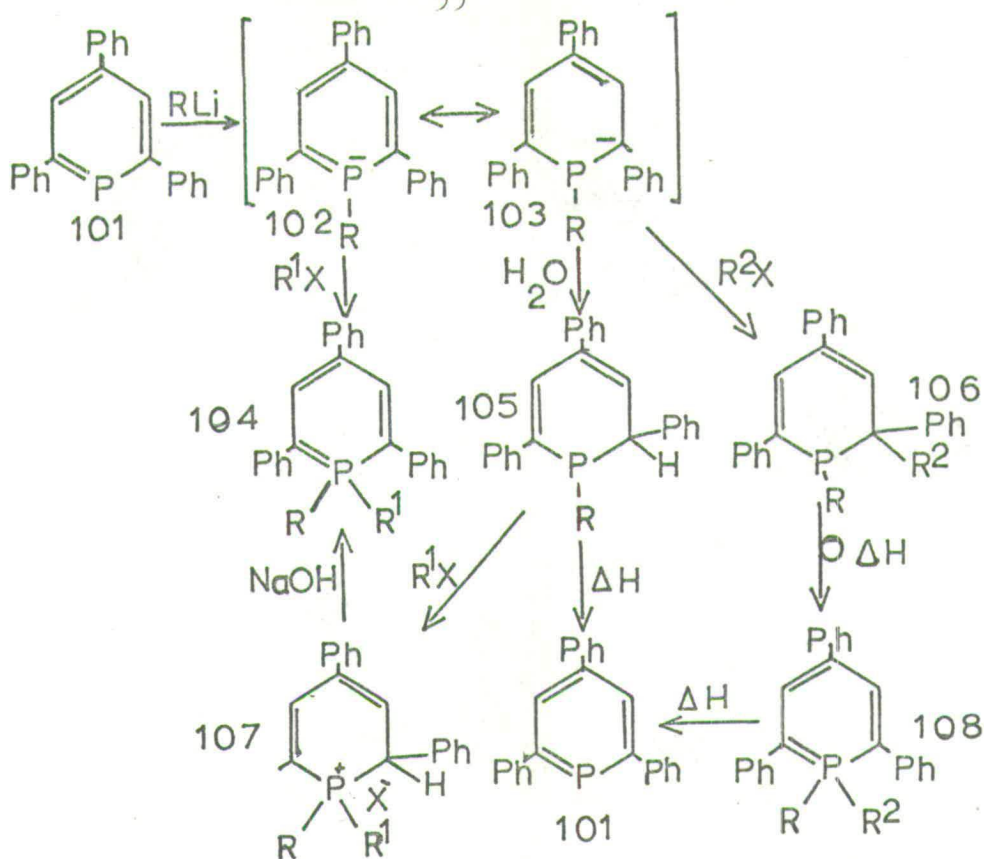
This synthesis of phosphorus from pyrilium salts and tris(hydroxymethyl)phosphine or tris(trimethylsilyl)phosphine has however, a fundamental steric limitation. Nucleophilic attack by (97a) or (97b), which could occur at C-2 or C-4 of the pyrilium salt, is rendered irreversible by the loss of formaldehyde or  $X-Si(CH_3)_3$  to form the pyrans (98) or (99). If R is smaller than  $R^1$  and  $R^2$  the phosphines (97a, 97b) react exclusively at C-4; thus 2,6-diphenylpyrilium perchlorate ( $R^1=R^3=Ph$ ;  $R^2=H$ ) is quantitatively dimerised to 2,2',6,6'-tetraphenyldipyrylene, while 2,6-diphenyl-4-methylpyrilium perchlorate does not give a phosphorin or the ketone (100). If the substituent R on the tertiary phosphine (97) is larger than  $R^1$  and  $R^3$ , but these are both smaller than  $R^2$ , nucleophilic attack is preferential at C-2 or C-6. Thus 2,4,6-triarylpyrilium salts, where  $R^1$  and  $R^3$  are larger than R, react with (97a) and (97b) to give the pyran (98). Ring opening of this intermediate yields the isomeric ketone (100), which forms the

phosphorin (101) by ring closure. 2,6-Dimethyl-4-phenylpyrilium fluoroborate, where  $R^1$  and  $R^3$  are smaller than R, does not, however, give the phosphorin presumably because the ketone (100) is not formed. This limitation was partially overcome by Märkl et al.<sup>66</sup>, when they applied to the intermediate (100) the principle, formulated by Buckler and Epstein<sup>68</sup>, that primary phosphines react with carbonyl groups under proton catalysis. Thus phosphine (97c, R=H), generated in situ from phosphonium iodide, reacted smoothly with 2-methyl-4,6-diphenylpyrilium fluoroborate, where R is smaller than  $R^1 = R^2 = \text{Ph}$  and  $R^3 = \text{Me}$ , to give the phosphorin (101) in reasonable yield. This extension of the basic reaction made phosphorins with alkyl substituents readily available.

Therefore, although the two groups of workers under Märkl and Dimroth could vary the substituent at will, a new approach is required to produce phosphorins without substituents in the chemically interesting ortho- and para- positions.

#### B) 4) Reactions of phosphorins.

Phosphorin derivatives (101) are unreactive to electrophilic reagents such as methyl iodide, but react readily with nucleophilic reagents such as phenyl lithium or phenyl magnesium bromide<sup>69</sup>. Thus phenyl lithium adds directly to the phosphorus atom of 2,4,6-triphenylphosphorin, expanding its electron shell to ten, to form the canonical structures (102) and (103). Addition of water to a solution of the anion yields 1,2-dihydro-1,2,4,6-tetraphenylphosphorin (105), which is readily oxidised and methylated like a normal tertiary phosphine.



Addition of base to 1,2-dihydro-1-methyl-1,2,4,6-tetraphenylphosphorinium iodide (107) solution yields 1-methyl-1,2,4,6-tetraphenylphosphorin (104). The latter is also obtained by the action of an alkyl halide, like methyl iodide that is normally susceptible to S.N.2. reactions, to the anion solution because the canonical form (102) is attacked<sup>70</sup>. If, however, a more sterically hindered halide like benzylchloride, that usually undergoes S.N.1. reactions, is used, the anion form (103) is attacked to yield 2-benzyl-1,2,4,6-tetraphenylphosphorin (106)<sup>70</sup>.

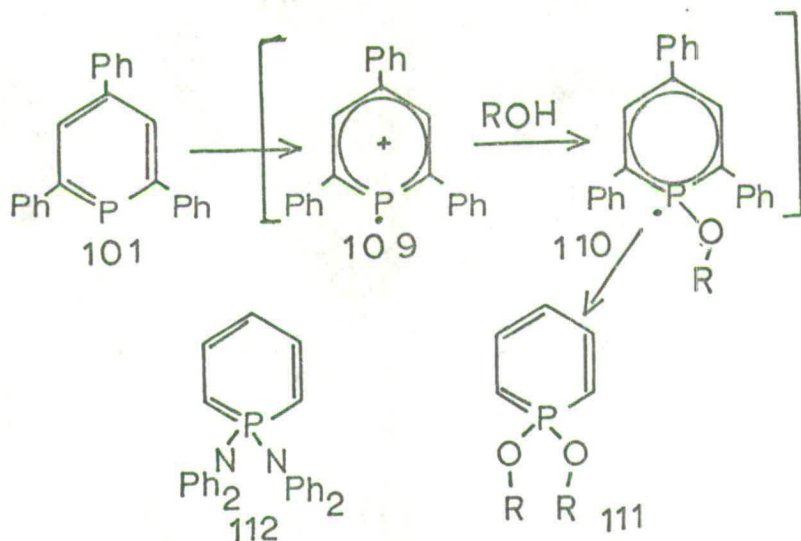
Märkl has studied the controlled thermolysis<sup>70</sup> of the tertiary phosphines (105,  $\text{R}=\text{CH}_3$ ;  $\text{PhCH}_2$ ;  $\text{pN}(\text{CH}_3)_2\text{C}_6\text{H}_4$ ). In each case 2,4,6-triphenylphosphorin was regenerated with loss of the appropriate hydrocarbon. Märkl also postulated the rearrangement of the phosphorin (106;  $\text{R}=\text{Ph}$ ,  $\text{R}^2=\text{Ph}$ ) to the 1,1-phosphorin (108) and subsequent loss of biphenyl to yield 2,4,6-triphenylphosphorin (101).

In the light of this reaction it is curious that Märkl has not reported an attempt at the thermolysis of 1,1-diphenylphosphorin, that he had prepared earlier, to phosphorin.

The group of reactive phosphorin intermediates was extended, initially by Dimroth, Greif, Perst and Steuber<sup>65</sup> with the formation of unusually stable radical anions from the oxidation of a wide range of phosphorins by triaryl phenoxyl's and lead or mercury acetate. Dimroth and Städe<sup>71</sup> made further detailed studies of the E.S.R. spectra of the radical cations (109) and have shown that interaction of phosphorus with the unpaired electron gave a coupling constant of  $|a|_p = 22-27$  gauss and proved that the ring remained intact.

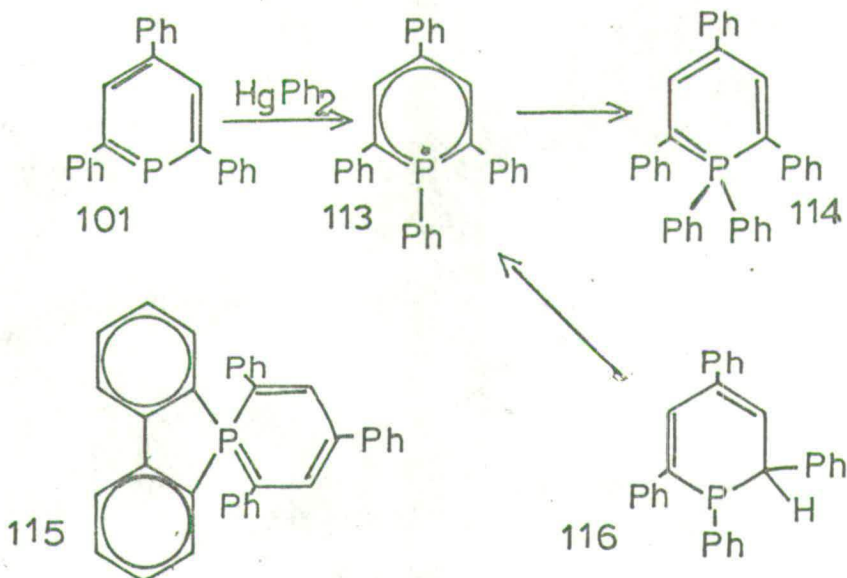
Reaction of the radical cation (109), formed by the action of mercury acetate on 2,4,6-triarylphosphorin with alcohols or phenols was also studied (110). The first 1,1-dialkoxy-2,4,6-triarylphosphorins (111) were prepared by this reaction and a careful study made of their n.m.r. spectra<sup>71</sup>. In 1,1-Dimethoxyl-2,4,6-trideuterophenylphosphorin C-3 and C-5 protons resonated at  $\tau$  2.07,  $J_{PH} = 36.5$  Hz, the region normally associated with aromatic compounds. The  $^{31}P$  n.m.r. signal of dialkoxyphosphorin was observed to be between -58 and -65 p.p.m.<sup>73</sup>, relative to 85% phosphoric acid, compared with -178.2 p.p.m. for 2,4,6-triphenylphosphorin<sup>66</sup>. No comment has been made on these extremely low field resonances of  $^{31}P$  in phosphorins but it suggests high delocalisation. Dimroth<sup>71</sup> does consider that the resonant position of the C-3 and C-5 protons implies an aromatic bonding state with contributions from  $\sigma$ - $\pi$  bonds.

Dimroth, Hettch, Städe, and Steuber<sup>73</sup> have prepared 1,1-bis(diphenylamino)-2,4,6-triphenylphosphorin (112) from diphenylamino radicals, formed on heating tetraphenylhydrazine, where the radical cation intermediate was detected in solution by E.S.R. This phosphorin had a  $^{31}\text{P}$  n.m.r. at  $-29.5$  p.p.m. which suggested that donation of the nitrogen lone pair nullifies the deshielding effect of delocalisation.



Dimroth and Steuber<sup>74</sup> also reported a three stage reduction of 2,4,6-triphenylphosphorin (101) with potassium and sodium metal. The first stage showed an E.S.R. spectra with a doublet ( $|a|_p$  32.4 gauss) due to a radical anion. At the second stage, further reduction caused the signal to disappear and formation of a dianion species, while a third reduction gave a trianion radical with a complex spectra. When an equimolar solution of the phosphorus, oxidised by phenoxy radicals, was mixed with the reduced solution the phosphorin was regenerated, even after the solution had been standing for several days. No mention was made of the implication of these extra electrons, to give a total of eleven, round the phosphorus atom.

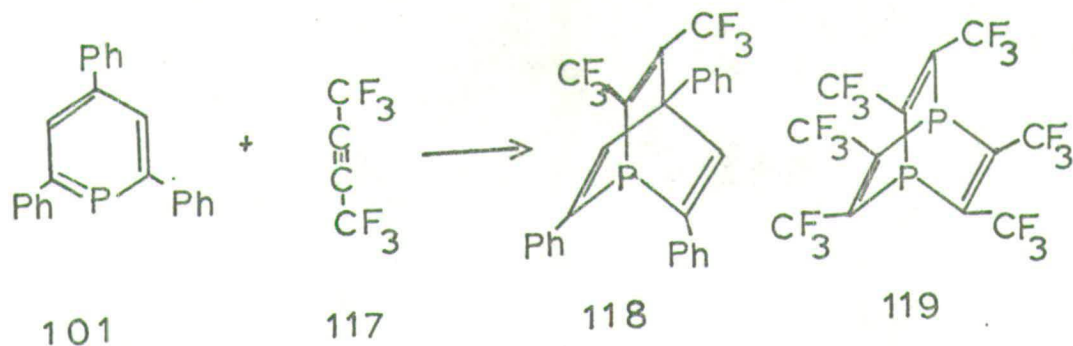
Markl and Merz<sup>69</sup> proposed radical phosphorin intermediates (113) during the reaction of diphenyl mercury with 2,4,6-triphenylphosphorin (101) which formed 1,1,2,4,6-pentaphenylphosphorin (114). They showed that this intermediate (113) was involved by forming it from 1,2-dihydro-1,2,4,6-tetraphenylphosphorin (115).



Although no radical intermediate was postulated, Markl<sup>69</sup> also obtained the interesting spirophosphorin (115) with diphenylene mercury.

Markl and Leib<sup>76</sup> observed that phosphorins have only slight diene reactivity since 2,4,6-triphenylphosphorin (101) failed to react with diethyl acetylenedicarboxylate or maleic anhydride. However, the highly reactive dienophile hexafluoro-2-butyne (117) reacted with the phosphorin (101) exclusively in the 1,4-position, as with durene, to yield a phosphabarrelene (118).

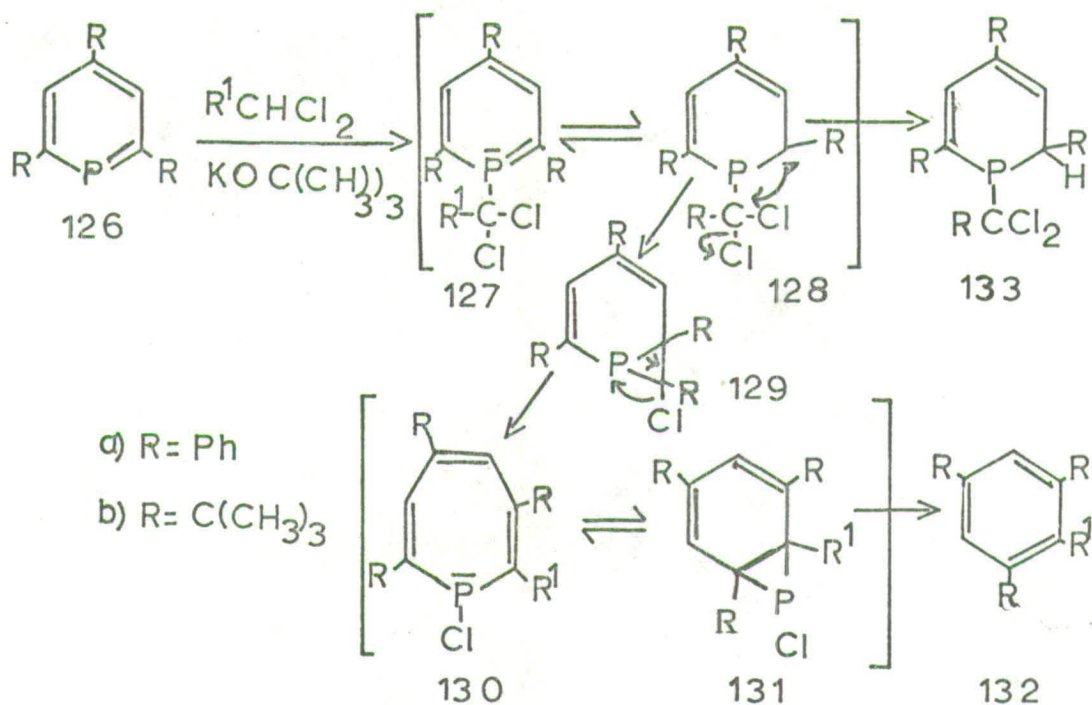
The authors suggested that the 1,4-diphosphabarrelene (119), observed by Krespan<sup>77</sup> in the reaction of red phosphorus on hexafluorobutyne, came from the corresponding tetrakis(trifluoromethyl)-1,4-diphosphorin, which has not been isolated.



Phosphabarrelene derivatives have also been prepared from the reaction of trialkyl and triarylphosphorins with 1-fluorophenyl magnesium bromide and the reaction is believed to involve an anion intermediate (121)<sup>76</sup>. These phosphabarrelenes (123) were also obtained from the reaction with benzenediazonium-O-carboxylate, an aryne generator. It is interesting to note that 2,4,6-tri-*t*-butylphosphorin (120b) gave 47% of phosphabarrelene (123b) whereas 2,4,6-triphenylphosphorin (120a) gave only 15% of phosphabarrelene (123a) and 10% of a 1:2 adduct. The authors postulated from special data, that a bridge-head phosphorane (125) was formed, not the possible alternative a spirophosphorin (124), and claimed that this demonstrated that the reaction is not limited to an aryne route. This point was supported by the fact that both phosphorins failed to react with anthranilic acid and isopropyl-nitrite, a well known aryne precursor<sup>78</sup>. The variation in the reaction products observed is an example of substituents affecting the electrophilic character of the phosphorin ring.



mechanism depicted in the scheme below, which they believe involves a phosphine anion (130) and a bicyclic anion (131) as an intermediate step.



They also suggested that the different electrophilic character of the two phosphorins used was responsible for the variations observed. They believe these variations are analogous to those observed in the aryne reaction mentioned earlier, but do not mention the different steric effect of the substituents.

The reactions described above summarize the important observations made so far on the chemistry of the phosphorin ring system. This is dominated by the amphoteric nature of phosphorus, which is able to form stable compounds with ten electrons on the phosphorus atom and also to form anion, radical or cation intermediates. The U.V. spectrum of 2,4,6-triphenylphosphorin  $\lambda_{\text{max}}=278$  nm shows a bathochromic shift compared to 1,3,5-triphenylbenzene  $\lambda_{\text{max}}=254$  nm, and 2,4,6-triphenylpyridine  $\lambda_{\text{max}}=254$  nm, which

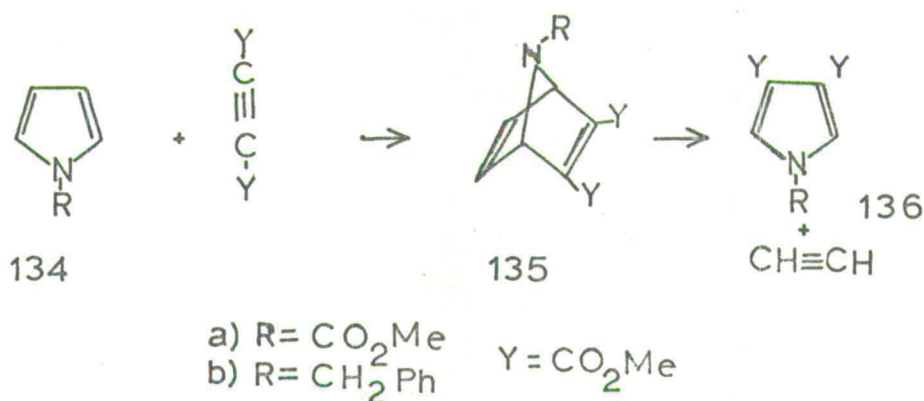
suggests at least an equal, if not greater degree of delocalisation.

X-ray crystallographic studies on 2,6-dimethyl-4-phenylphosphorin have been made by Bart and Daly<sup>80</sup>. These workers have shown that the molecule has four equal C-C bonds of  $1.388 \text{ \AA}$ , which agrees well with those in pyridine,  $1.395 \text{ \AA}$ , and benzene,  $1.397 \text{ \AA}$ . There are two equal P-C bonds in the ring of  $1.743 \text{ \AA}$ , which are shorter than a single bond  $1.828 \text{ \AA}$ , but longer than the P=C bond in  $\text{Ph}_3\text{PC}=\text{CH}_2$   $1.661 \text{ \AA}$ . The constituent atoms of the phosphorin ring essentially lie in a plane although minor buckling was observed. These authors consider that overall the evidence implies considerable six  $\pi$  electron delocalisation and is good evidence for substantial aromatic character.

The proton and  $^{31}\text{P}$  n.m.r. data described earlier for triarylphosphorins does suggest a considerable ring current effect and substantial delocalisation of the phosphorus electrons. The limitation of the synthesis of phosphorins explained earlier has restricted the chemical study to the only reactive centre available, phosphorus, and therefore makes realistic correlations to other aromatic systems difficult.

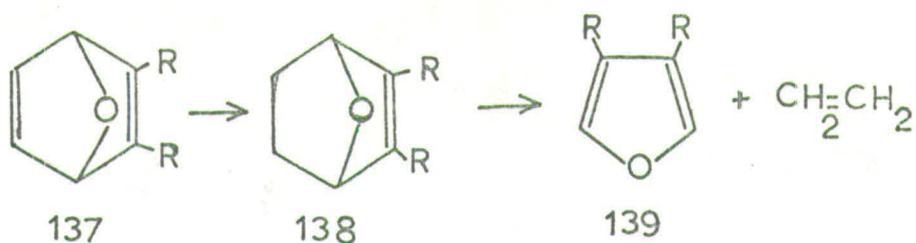
I. C) EXTRUSION REACTIONS OF DIELS-ALDER ADDUCTS AND RELATED COMPOUNDS.

The Diels-Alder reaction of acetylenedicarboxylic acid and esters with pyrroles is well known<sup>81</sup>. In the reaction of methyl pyrrole-1-carboxylate (1a) with dimethyl acetylenedicarboxylate extrusion of acetylene, presumed to be via the intermediate adduct (135a) gave trimethyl pyrrole-1,3,4-tricarboxylate<sup>82</sup> (3a). This has been utilised by Acheson and Vernon<sup>82</sup> as a route to 1,3,4-trisubstituted pyrroles (136a).

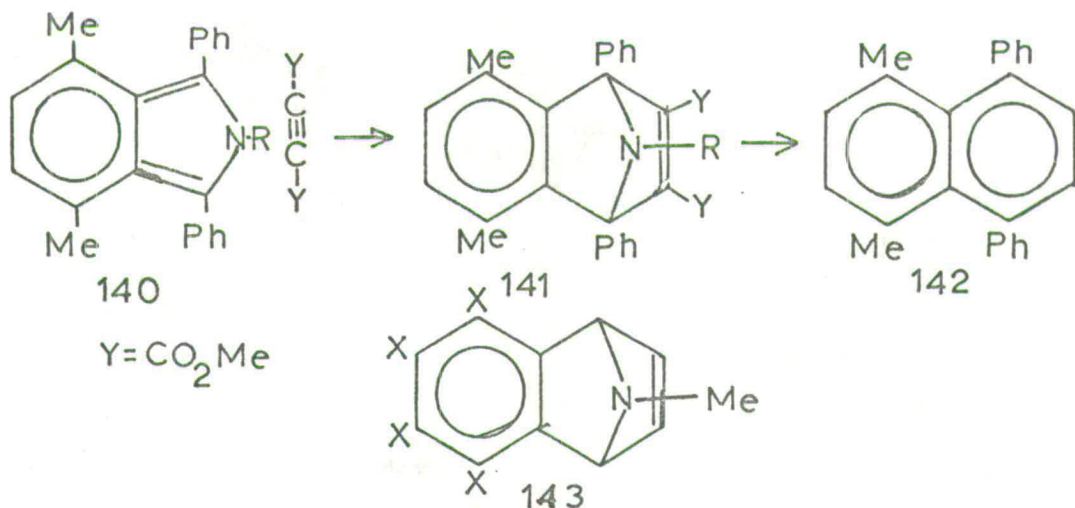


The intermediate bridged-ring adduct has been isolated in the reaction of 1-benzylpyrrole and acetylenic acid by Mandell and Blanchard<sup>83</sup> but then only in low yield contaminated by substitution products. There has been no report to date of this type of retro Diels-Alder reaction involving loss of the nitrogen bridgehead rather than the acetylene.

The analogous reaction of furans has been known from the original study of 1,4-cycloadditions<sup>85</sup>, in this case, however, the adduct (138) is readily isolated. Alder and Rickert<sup>86</sup> used the extrusion of ethylene from the reduced adduct (138) to prepare a wide range of 3,4-substituted furans (139) otherwise difficult to obtain. Analysis of the extruded ethylenic fragment has been used by Johnson<sup>87</sup> to diagnose the substituents on the original furan ring.



The related reaction of isoindoles is of interest because the retro Diels-Alder reaction would involve extrusion of either the bridgehead nitrogen, or a benzyne species. Kricka and Vernon<sup>84</sup> have studied the reaction of dimethyl acetylenedicarboxylate with polysubstituted isoindoles (140) and reported that the adduct (141) reacted further in an extrusion or deamination reaction, and gave the corresponding naphthalene (142). The authors observed a parallel reaction of naphthalene-1,4-imines (143) with the acetylenic ester in mild conditions, but have not been able to isolate a product containing the nitrogen fragment.



A precedent for the conversion of naphthalene-1,4-imines to naphthalene is the hitherto unexplained formation of small amounts of naphthalene from the reaction of benzyne with N-methylpyrrole<sup>88</sup>. Kricka and Vernon<sup>84</sup> believe that benzyne induces extrusion of the [NMe] fragment from the intermediate (144)

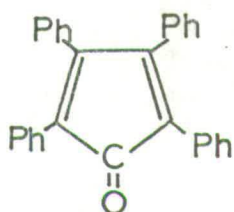
postulated by the original workers, Wittig and Behnisch<sup>88</sup>.

Benzynes is known to be involved in extrusion reactions following 1,4-additions to dienophiles like 2,3,4,5-tetraphenylcyclopentadienone (145). In this reaction the leaving group is carbon monoxide, considered by Kwart and King<sup>89</sup> to be a stable carbene. The stable adduct (147) of benzyne and the silicon heterocycle (146) were heated at 300° to give 1,2,3,4-tetraphenylnaphthalene and a dimethylpolysilane (Me<sub>2</sub>Si)<sub>n</sub>, obtained by Gilman et al.<sup>90</sup> When the decomposition was conducted in the presence of 1,2-diphenyl-1-yne, the disilane (148) was isolated. In the analogous reaction, in the presence of dimethyl acetylenedicarboxylate, although 1,2-dimethyl 3,4,5,6-tetraphenylphthalate was obtained, the corresponding disilane was not isolated.

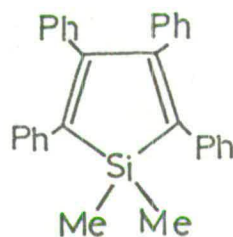
The possibility of carbene generation from cyclopentadiene adducts with dienophiles has interested several groups. McBee, Smith and Ungnade<sup>91</sup> reported the decomposition of a bridged adduct of (149a) at 480°, but although they obtained the phthalate in good yield the fate of the bridge, CF<sub>2</sub>, was not reported.



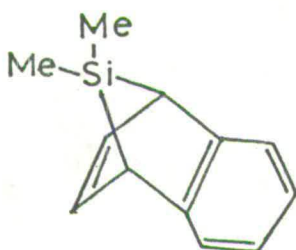
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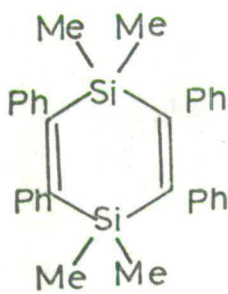
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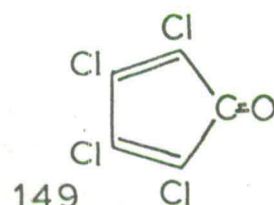
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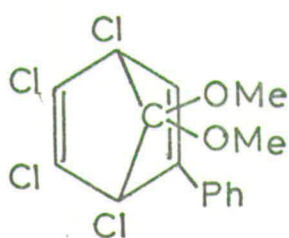
148



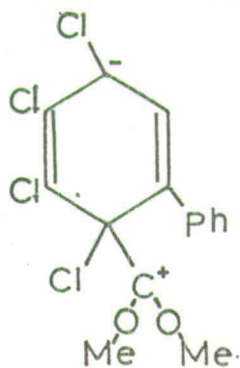
149



149a



150



151

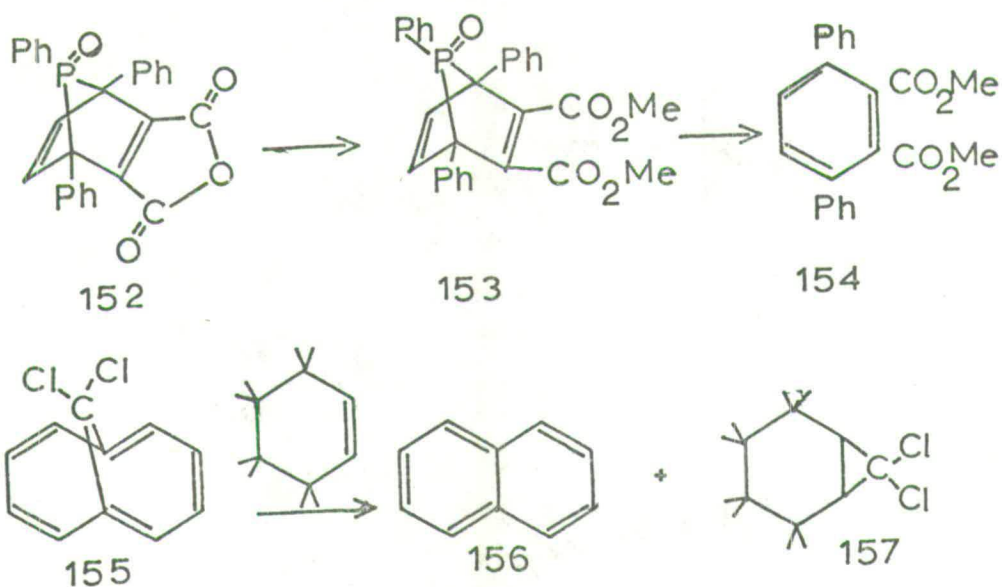
The fate of the ketal bridgehead during analogous decomposition at  $150^{\circ}$  of the adduct (150), formed from the chlorinated ketal (149) and 1-phenyleth-1-yne, is also uncertain. In the absence of air and water, tetramethyloxyethylene appeared to be the only product accountable to a carbene. The reaction was reported by Lemal et al.<sup>92</sup> to be very dependent on the solvent, which Kwart and King<sup>89</sup> considered implied a mechanism involving a zwitterion (151).

The Diels-Alder reaction of pentaphenylphosphole and dimethyl acetylenedicarboxylate at  $160^{\circ}$  was reported by Braye et al.<sup>33</sup>. Neither the intermediate adduct, nor the extruded [PhP] fragment were isolated, although good yields of 1,2-dimethyl 3,4,5,6-tetra-phenylphthalate were obtained.

Campbell et al.<sup>42</sup> reported a similar reaction of dimethyl acetylenedicarboxylate with 1,2,5-triphenylphosphole and the oxide, but in neither case identified the fragment. Hughes and Uaboonkul<sup>22</sup> used milder conditions but were more interested in the other adducts obtained, neither of which proved to be the normal Diels-Alder product. Schmidt et al.<sup>93</sup> followed up their work on the trapping of a phosphidene (PhP) intermediate, with dipropyldisulphide by attempting to isolate the bridged

adduct from another route. These authors formed the normal Diels-Alder adduct of 1,2,5-triphenylphosphole and  $\alpha$ -chloromaleic anhydride (152) and hydrolysed and methylated it to the adduct (153). An attempt to reduce the (PO) group by the standard chlorosilane method only gave the phthalate (154).

This summary demonstrates that this type of extrusion or retro Diels-Alder reaction is a potential generator of reactive species. The decomposition of the related bridged naphthalenes (155) gives greater encouragement, since Rautenstrauh et al.<sup>94</sup> have isolated 7,7-dihalonorcarane (157), the carbene adduct with cyclohexene, in over 95% yield.



Programme of Research.

The introduction has outlined the preparation and properties of some phosphines, phospholes and phosphorins, and mentioned that the most general phosphole synthesis is from the reaction of phenylphosphine with alkynes, while that of phosphorins is very limited. Atkinson and Cadogan<sup>95</sup> have shown that a thermal reaction of phenylphosphine with conjugated diynes gave phospholes, but the products were highly contaminated. They also investigated the reaction of phenylphosphine with diynols, a study which was examined more closely by Lim<sup>96</sup>. Cadogan and Gripper-Grey<sup>97</sup> made a brief study of the reaction of phenylphosphine with conjugated diynes, but did not characterise the products obtained.

One objective of the present study was, therefore, to collect these lines of research and examine the possibility of a synthesis of phosphorins unsubstituted in the para- position. The route proposed involved the reaction of phenylphosphine with diynes, as an extension of Märkl's phosphole synthesis. Since molecular rearrangements in basic conditions make it impossible to simply apply Märkl's conditions, a study of the thermal reaction of phenylphosphines with alkynes was necessary.

The properties that phosphorus contributes to heterocyclic systems is of considerable interest, particularly with reference to the degree of diene character of phosphole derivatives. This work therefore, also investigates the reaction of dimethyl acetylenedicarboxylate, a highly reactive dienophile, with some phosphole derivatives and the retro Diels-Alder reaction that occurs.

II EXPERIMENTAL

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Symbols and Abbreviations.

i.r.	infra-red.
$\nu$	wave number.
s	singlet.
d	doublet.
c	complex.
J	coupling constant.
U.V.	ultra-violet.
$\lambda$	wave length.
m/e	mass to charge ratio.
$P^+$	mass of parent ion.
e.s.r.	electron spin resonance.
b.p.	boiling point.
m.p.	melting point.
h.	hour.
g.l.c.	gas liquid chromatography.
t.l.c.	thin layer chromatography.



## II EXPERIMENTAL

### A) INSTRUMENTATION AND GENERAL PROCEDURES.

Infra-red Spectroscopy: Perkin Elmer grating spectrometers 257 and 237 were most commonly employed for infra-red spectroscopy. A polystyrene film was used as reference at 1601 and 1029  $\text{cm}^{-1}$ . Liquid samples were examined as thin films, solids as melts, nujol mulls or occasionally KBr pellets formed in a "Wilks mini-press". Solution spectra were obtained using a matched pair of sodium chloride cells with a path length of 0.1 mm.

Nuclear Magnetic Resonance Spectroscopy: A Perkin Elmer R-10 nuclear magnetic resonance spectrometer, operating at a frequency of 60 MHz, a field of 14,100 gauss and a probe temperature of  $35.5^{\circ}$ , or a Varian H.A. 100 nuclear magnetic resonance spectrometer, operating at a frequency of 100 MHz, a field of 23,490 gauss and a probe temperature of  $28^{\circ}$ , were used for observing proton resonances. Solutions of the samples in deuteriochloroform or carbon-tetrachloride were used with tetramethylsilane as internal reference.

The Varian H.A. 100 spectrometer was used for  $^{31}\text{P}$  phosphorus nuclear magnetic resonance spectra operating at 40.5 MHz, 23,490 gauss and a probe temperature of  $28^{\circ}$ .

Mass Spectroscopy: Mass spectra were obtained with an Associated Electrical industries MS-902 mass spectrometer using a direct insertion probe for all solid or involatile samples.

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

Gas Liquid Chromatography: A Pye 104 chromatograph with a flame-ionisation detector and 1.5 m x 4 mm packed columns or a Perkin Elmer F.11. chromatograph with a flame ionisation detector and

50m x 0.25mm capillary column were used for analytical work. A Pye 105 chromatograph with a flame-ionisation detector, sealed and cooled traps, and a heated outlet was used for preparative work. In all cases the carrier gas was nitrogen with all flow rates and split ratios as recommended by the manufacturers. Stationary phases were supported on 100-120 mesh celite and those employed were: neopentylglycol succinate (N.P.G.S.), polyethyleneglycol adipate (P.E.G.A.) and apiazon L grease (A.P.L.).

Column Chromatography: Alumina used was Laporte Industries Ltd. grade H 100-200 mesh. (Brockman activity 1-3), silica gel was Whatman Cromedia S.G.31.

Liquid Liquid Chromatography: Chromatograms were obtained using a Du Pont 820 liquid liquid chromatograph, with an O.D.S. permaphase column and methanol water mobile phase and an ultra-violet detector by Dr.J.Done.

Thin Layer Chromatography: Chromatograms were obtained using 0.25 mm layers of alumina (Merck Aluminium oxide G(type E) or silica gel (Merck Kieselgel G) on glass plates and developed under ultra-violet light or by the action of iodine vapour.

Dry Column Chromatography: Alumina (aluminium oxide Woelm Ltd.) was used following the method described by Loev and Goodman<sup>98</sup> for separation of small samples.

Elemental Analysis: Micro-analysis for carbon, nitrogen and hydrogen were performed by Mr.B.Clark, University of Edinburgh using a Perkin Elmer 240 Elemental Analyser.

Vapour Pressure Osmometry: A Hewlitt Packhard 301A vapour pressure osmometer with glass-coated thermistors was used for molecular weight measurements, after calibration with a standard solution of dibenzil.

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. Tetrahydrofuran and dioxan were dried over anhydrous calcium chloride, passed down an alumina column, distilled from lithium aluminium hydride and stored over sodium in the dark for no longer than two weeks before use. t-Butylbenzene was dried over calcium chloride, distilled from molten sodium and stored. All other solvents and reagents were distilled or recrystallised and stored over molecular sieves where appropriate.

## II B. PREPARATION OF STARTING MATERIALS.

### 1 Terminal Alkynes.

#### 1a) Hex-1-yne.

Sodium acetylide (3 mol) was prepared as a suspension in liquid ammonia and reacted with bromobutane as described in Vogel<sup>99</sup> p.899 to give hex-1-yne (61g., 45%) b.p. 71° (lit.<sup>100</sup> b.p.72.3°) Care was taken to avoid frothing of the acetylide suspension during this exothermic reaction and to ensure complete decomposition of excess acetylide with ammonium chloride at the end of the reaction.

#### 1b) Hept-1-yne.

Hept-1-yne was prepared following the method for 1a) b.p. 99-100° (lit.<sup>101</sup> b.p. 99.8°).

#### 1c) 1-Phenyleth-1-yne.

Dibromostyrene (510g., 2 mol) was dehydrobrominated following the method in Vogel<sup>99</sup> p.900 to give 1-phenyleth-1-yne (121g., 62%) b.p. 68° at 60 mm Hg. (lit.<sup>99</sup> b.p. 49° at 14 mm Hg.)

### 2. Non-terminal Alkynes.

#### 2a) Oct-4-yne.

Sodium acetylide (2.5 mol) was prepared in liquid ammonia and reacted with bromopropane (250g., 2 mol) to give pent-1-yne in solution. This was reacted with sodamide in liquid ammonia to give the acetylide, which was reacted with further bromopropane. Oct-4-yne (57g., 26%) was isolated by extraction with ether and distillation b.p. 131° (lit.<sup>102</sup> b.p. 131°).

#### 2b) 1-Phenylhex-1-yne.

Lithium 2-phenylethylide (0.5 mol) was prepared in liquid ammonia and allowed to dissolve in dioxan as the ammonia

was expelled, following the method of Schlubach and Repenning<sup>103</sup>.

Reaction of 1-bromobutane with the ethylide solution gave 1-phenylhex-1-yne (45g., 30%) b.p. 137° at 35 mm Hg. (lit.<sup>103</sup> 109-110° at 12 mm Hg.)

### 2c) 1-Phenylprop-1-yne.

An attempt to prepare 1-phenylprop-1-yne from 1-phenyleth-1-yne and iodomethane by the method for 1b) gave a mixture of product and starting alkyne, in spite of prolonged reaction times, that was not easily separated.

## 3 Alkyldiynes.

### 3a) Trideca-5,8-diyne.

The method used was based on that of Taniguchi et al.<sup>104</sup> Hex-1-ynylmagnesium bromide was prepared from hex-1-yne (57g., 0.69 mol) and ethylmagnesium bromide (0.71 mol) and reacted in ether with gaseous formaldehyde. The formaldehyde was carried over into the reaction mixture by a stream of nitrogen after thermal depolymerisation of paraformaldehyde at 160-180°. Hept-2-yne-1-ol (40g., 51%) b.p. 107° at 43 mm Hg. (lit.<sup>106</sup> b.p. 112° at 50 mm Hg.) was extracted after work up with ammonium chloride solution. Bromination by phosphorus tribromide in ether containing pyridene (6g.) by the method of Tchao Yin Lai gave 1-bromohept-2-yne (40g., 65%) b.p. 92-94° at 22 mm Hg. (lit.<sup>106</sup> b.p. 105-106° at 56 mm Hg.). Hex-1-ynylmagnesium bromide (0.2 mol) was coupled with 1-bromohept-2-yne (30g., 0.17 mol) in boiling anhydrous tetrahydrofuran in the presence of cuprous chloride catalyst (0.3g.). The reaction mixture was worked up with ammonium chloride solution and extracted with ether to give trideca-5,8-diyne (23.8g., 80%) b.p. 86-88° at 0.8 mm Hg (lit.<sup>107</sup> b.p. 63° at 0.06 mm Hg.).

3b) Nona-1,4-diyne.

Hex-1-ynylmagnesium bromide (0.7 mol) was coupled with 3-bromoprop-1-yne (57.0g., 0.48 mol) in a reaction similar to 3a) to give nona-1,4-diyne (21.7g., 25%) b.p. 72-74° at 24 mm Hg. (lit.<sup>107</sup> b.p. 83-84° at 41 mm Hg.).

3c) 1,5-Diphenyl-1,4-diyne.

1-Phenylprop-1-yne-3-ol, b.p. 840° at 0.04 mm Hg., was prepared from 1-phenyl-1-yne and paraformaldehyde, as for 3a), and brominated with phosphorus tribromide to give 3-bromo-1-phenylprop-1-yne, b.p. 82-84° at 0.05 mm Hg. (lit.<sup>105</sup> b.p. 107-108° at 6.0 mm Hg.).

2-Phenyleth-1-ynylmagnesium bromide was then coupled with 3-bromo-1-phenylprop-1-yne (8.7g., 0.045 mol) to give 1,5-diphenylpenta-1,4-diyne (4.1g., 57%) b.p. 135-140° at 0.03 mm Hg. (lit.<sup>104</sup> b.p. 151-153° at 0.2 mm Hg.) following the method for 3a).

An attempt at the direct synthesis from 2-phenyleth-1-ynylmagnesium bromide and dibromomethane in ether gave mostly starting materials and a little green oil that was not investigated.

3d) 5-Phenylpenta-1,4-diyne.

2-Phenyleth-1-ynylmagnesium bromide (0.31 mol) was coupled with 3-bromoprop-1-yne (15.5g., 0.13 mol) following the method for 3a) to give 5-phenylpenta-1,4-diyne (6.3g., 35%) b.p. 60-65° at 0.25 mm Hg. (lit.<sup>104</sup> b.p. 66° at 0.25 mm Hg.).

3e) Deca-4,6-diyne.

Deca-4,6-diyne b.p. 112-116° at 0.05 mm Hg. (lit.<sup>108</sup> b.p. 60° at 0.001 mm Hg.) was supplied by Dr. P.E. Atkinson.

3f) Tetradeca-6,8-diyne.

Tetradeca-6,8-diyne b.p. 136-138° at 6.0 mm Hg.

(lit. <sup>107</sup> b.p.  $118^{\circ}$  at 4.0 mm Hg.) was supplied by Dr. R.E. Atkinson.

3g) Hexadeca-7,9-diyne.

Hexadeca-7,9-diyne b.p.  $92^{\circ}$  at 0.05 mm Hg. (lit. <sup>110</sup> b.p.  $117^{\circ}$  at 0.6 mm Hg.) was supplied by Dr. R.E. Atkinson.

3h) 1,4-Diphenylbuta-1,3-diyne.

1,4-Diphenylbuta-1,3-diyne m.p.  $84-85^{\circ}$  (lit. <sup>109</sup> m.p.  $88^{\circ}$ ) was supplied by Dr. R.E. Atkinson.

4. Preparation of Azides.

4a) Phenyl Azide.

The method used was that of Lindsay and Allen <sup>111</sup>. Phenylhydrazine hydrochloride was reacted with sodium nitrite below  $5^{\circ}$  to give phenylazide, b.p.  $66-68^{\circ}$  at 21 mm Hg. (lit. <sup>111</sup> b.p.  $73^{\circ}$  at 23 mm Hg.) after steam distillation and extraction with ether.

4b) p-Nitrophenyl Azide.

The method used was based on that of Smith et al. <sup>112</sup> p-Nitroaniline was diazotised in excess conc. hydrochloric acid and the salt reacted with sodium azide. Extraction with ether and rapid recrystallisation from ethanol gave pure p-nitrophenyl azide m.p.  $69-70^{\circ}$  (lit. <sup>113</sup> m.p.  $71^{\circ}$ ) as transparent needles.

4c) p-Tolyl Azide.

p-Tolyl azide b.p.  $82-84^{\circ}$  at 21 mm Hg. (lit. <sup>114</sup> b.p.  $80^{\circ}$  at 10 mm Hg.) was prepared by the method described for 4b).

4d) Ethyl Azido-Formate.

The method used was based on that of Forster <sup>115</sup>. Ethyl chloroformate (7g) was stirred with an aqueous solution of sodium azide until the pungent smell was gone. Ethyl azido-formate was distilled b.p.  $25^{\circ}$  at 12 mm Hg. (lit. <sup>115</sup> b.p.  $25^{\circ}$  at 12 mm Hg.).

5. Preparation of Phosphines.5a) Preparation of Phenylphosphine.

The method used was based on that of Michaelis and Kohler<sup>116</sup> using the optimum quantities prescribed by Mann and Millar<sup>117</sup>.

Phenylphosphonous dichloride (250 ml.) was added slowly to ethanol (600 ml.) under nitrogen. Excess ethanol was removed under vacuum and the system converted to highly efficient condensation into a cooled receiver under nitrogen. A hot spot was created with a bunsen burner on the side of the flask until a vigorously exothermic reaction started and phenylphosphine distilled over, b.p.  $160^{\circ}$ . The product (25-30%) was redistilled, b.p.  $89^{\circ}$  at 35 mm Hg. precautions being taken against the nauseating smell.

6. Preparation of Phospholes, Phosphole Oxides and Pyrroles.6a) 1,2,5-Triphenylphosphole.

The method used was based on that of Campbell et al.<sup>42</sup>. A mixture of 1,4-diphenylbuta-1,3-diene (26.5g., 0.13 mol), prepared following the method of Corson<sup>118</sup>, and phenylphosphonous dichloride (35g., 0.2 mol) was heated on an oil bath maintained between  $210^{\circ}$  and  $220^{\circ}$ , under nitrogen, until evolution of hydrogen chloride had finished 6h. The cooled mixture was triturated with petrol to remove starting materials and the solid residue dissolved in chloroform. This solution was filtered to remove a fine white powder, washed with sodium bicarbonate solution and water, dried over magnesium sulphate and then evaporated. 1,2,5-Triphenylphosphole was obtained from chloroform as yellow needles (8g., 19%) m.p.  $187-188^{\circ}$  (lit.<sup>142</sup> m.p.  $187-189^{\circ}$ ).

6b) 1,2,5-Triphenylphosphole-1-oxide.

A suspension of finely powdered 1,2,5-triphenylphosphole (5g., 16 mmol) in ethanol (500 ml.) and ethyl acetate (100 ml.) was stirred with a solution of hydrogen peroxide (30 ml. of 30 vol.) for 36 h. The yellow prisms (4.5g., 85%) obtained after recrystallisation from ethanol had m.p. 236-237° (lit.<sup>142</sup> m.p. 237-239°). I.r. (nujol)  $\nu_{\max}$ ; 1440 (PPh), 1170 (PO)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.0-2.3 (2H, c, P-Ph ortho), 2.3-2.9 (13H, c, aromatic) 2.58 and 2.94 (2H, d,  $J_{\text{PH}}$  36Hz. phosphole ring protons).

6c) 2,5-Dipentyl-1-phenylphosphole.

The method used was based on that of Märkl<sup>34</sup>. Tetradeca-6,8-diyne (5.7g., 0.03 mol) was added to a solution of phenylphosphine (3.3g., 0.03 mol) in a benzene/ether solution of phenyllithium (6 ml., 1.5 molar) and the mixture stirred for 3 h. at room temperature. The solvents were removed and 2,5-dipentyl-1-phenylphosphole (2.8g., 28%) distilled, b.p. 120-122° at 0.05 mm Hg.

I.r.  $\nu_{\max}$ ; 1430 (PPh), 740 and 690 (Ph)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.6-2.8 (5H, c, aromatic), 3.61 (2H, d,  $J_{\text{PH}}$  13 Hz. phosphole ring), 7.4-9.3 (22H, c, alkyl)

m/e 300 calc. for  $\text{C}_{20}\text{H}_{29}\text{P}$  m/e 300.

6d) 2,5-Di-t-butyl-1-phenylphosphole.

2,5-Di-t-butyl-1-phenylphosphole m.p. 36°, b.p. 158° at 10 mm Hg., was supplied by Dr. R.E. Atkinson.

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.4-2.8 (5H, c, aromatic), 3.44 (2H, d,  $J_{\text{PH}}$  14 Hz., phosphole ring), 8.95 (18H, c, t-butyl). Small impurity peaks of phosphole oxide appear  $\tau$  3.50 ( $J_{\text{PH}}$  39 Hz.).

6e) 1,2,5-Triphenylpyrrole.

The method used was that of Schultz et al.<sup>119</sup>. Aniline

(3g., 0.035 mol), 1,4-diphenylbuta-1,3-diyne (6g., 0.03 mol) and cuprous chloride catalyst (1g.) were maintained at 180° for 3 h. 1,2,5-triphenylpyrrole (1.70g., 23%) was obtained, by crystallisation from ethanol, as white needles m.p. 244° (lit.<sup>119</sup> m.p. 228-229°). I.r. (nujol)  $\nu_{\max}$ ; 1600 (C=C), 770, 745, 705 and 690 (Ph). N.m.r. (CDCl<sub>3</sub>)  $\tau$ ; 2.7-3.1 (15H, c, aromatic) 3.54 (2H, s, pyrrole ring).

#### 7. 1,8-bis(dimethylamino)naphthalene.

The method used was that of Alder<sup>121</sup>. 1,8-Diamino-naphthalene was suspended in sodium hydroxide solution (2N; 12 mol per mol of diamine) and dimethyl sulphate (12 mol per mol of diamine) added slowly and the mixture heated at 80° until t.l.c. (alumina/ethyl acetate) showed one spot. Extraction with dichloromethane gave a crude product that was purified by extraction at PH 8 from a solution in petrol. Pure 1,8-bis(dimethylamino)naphthalene was obtained by making the abstracts alkaline and sublimation 90° at 0.05 mm Hg. m.p. 46° (lit.<sup>121</sup> m.p. 47-48°).

#### 8. Preparation of Authentic Compounds.

##### 8a) Diocetylphenylphosphine oxide.

Octylmagnesium bromide (0.05 mol) was reacted with phenylphosphonous dichloride (4.5g., 0.025 mol). Diocetylphenylphosphine was extracted from the reaction mixture in ether and, without further purification, was oxidised in acetone solution by hydrogen peroxide (5 ml., 100 vol.). The diocetylphenylphosphine oxide (7.0g., 80%) obtained had m.p. 36-37° and b.p. 180-182° at 0.05 mm Hg.

I.r. (nujol)  $\nu_{\max}$ ; 1435 (PPh), 1160 (P=O) cm<sup>-1</sup>.

N.m.r. ( $\text{CDCl}_3$ )  $\tau$  ; 2.0-3.0 (5H, c, aromatic), 7.8-9.2 (34H, c, alkyl).  
 m/e; 350 (100), 238 (40,  $-\text{C}_8\text{H}_{16}$ ), 237 (20,  $-\text{C}_8\text{H}_{17}$ ),  $\text{C}_{22}\text{H}_{39}\text{PO}$  requires  
 m/e 350.

8b) Phenyl-bis(2-phenylethyl)phosphine oxide.

1-Bromo-2-phenylethane b.p.  $90^\circ$  at 10 mm Hg. (lit.  
 b.p.  $92^\circ$  at 11 mm Hg.) was prepared from 2-phenylethan-1-ol and  
 phosphorus tribromide and reacted with magnesium and phenylphosphon-  
 ous dichloride following 8a). Phenyl-bis(2-phenylethyl)phosphine  
 oxide b.p.  $160^\circ$  (block temp.) at 0.04 mm Hg. was obtained as a  
 solid m.p.  $85-87^\circ$  (lit. <sup>122</sup>  $90-91^\circ$ )

I.r. (nujol)  $\nu_{\text{max}}$  ; 1435 (PhP), 1160 (P=O)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$  ; 2.1-2.35 (2H, c, o-protons to P=O), 2.4-2.55  
 (3H, c, PhP aromatic m and p), 2.6-2.9 (10H, c, aromatic), 6.8-7.9  
 (8H, c,  $-\text{CH}_2-\text{CH}_2-$ ).

m/e 334 (100), 229 (200- $\text{PhCH}_2\text{CH}_2$ ) 202 (100,  $-\text{PhCH}_2\text{CH}_2$ ,  $-\text{C}_2\text{H}_3$ ) calc.  
 for  $\text{C}_{22}\text{H}_{23}\text{PO}$  m/e 334.

## II C. REACTION OF PHENYLPHOSPHINE WITH UNSATURATED COMPOUNDS.

### 1. Reaction of Phenylphosphine with Terminal Alkynes.

#### 1a) 1,Phenyleth-1-yne and Chemical Identification of the Product.

i) Reaction: A mixture of 1-phenyleth-1-yne (10.2g., 0.1 mol) and phenylphosphine (5.5g., 50mmol) was stirred at 160° for 12 h. under nitrogen. The dark tar was distilled and redistilled, b.p. 180-185° at 0.03 mm Hg. to yield a 2:1 adduct (4g., 26%) to which the structure phenyl-bis,1,1'(2-phenyleth-1-ene)ylphosphine was assigned.

I.r.  $\nu_{\max}$ ; 1590 (PC=C), 1435 (PPh)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.4-2.8 (15H, c, aromatic), 3.05 (2H, d,  $J_{\text{PH}}$  14 Hz, vinyl), 3.18 (2H, d,  $J_{\text{PH}}$  8Hz, vinyl).

m/e 314 (100%), 288 (50,  $-\text{C}_2\text{H}_2$ ), 206(150,  $-\text{PhP}$ ), a 2:1 adduct  $\text{C}_{22}\text{H}_{19}\text{P}$  requires m/e 314.

#### ii) Oxidation of Phenyl-bis,1,1'(2-phenyleth-1-ene)ylphosphine.

The phosphine (0.31g., 0.9 mmol) was dissolved in water (10 ml.) and oxidised with hydrogen peroxide (2 ml., 100 vol.). A white precipitate of phenyl-bis,1,1'(2-phenyleth-1-ene)ylphosphine oxide was obtained (0.3g., 95%), m.p. 204-205°.

(Found C, 74.9; H, 9.3; m/e 330,  $\text{C}_{22}\text{H}_{17}\text{OP}$  requires C, 75.5; H, 9.7%, m/e 330)

I.r. (nujol)  $\nu$ ; 1595 (PC=C), 1435 (P-Ph), 1160 (P=O)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.06-2.16 (2H, c, o-protons to P=O), 2.4-2.8 (13H, c, aromatic), 3.25 (1H, d,  $J_{\text{PH}}$  20 Hz, vinyl), 3.14 (1H, d,  $J_{\text{PH}}$  22 Hz, vinyl).

#### iii) Reduction of Phenyl-bis,1,1'(2-phenyleth-1-ene)ylphosphine oxide.

10% palladium on charcoal catalyst (0.3g.) was

added to the phosphine oxide (lg., 3 mmol) in ethanol (20 ml.) and the mixture hydrogenated (94 ml. of  $H_2$ ) at room temperature. Distillation (block temp.  $240^\circ$ ) at 0.04 mm Hg. gave phenyl-bis,1,1'-(2-phenyleth)ylphosphine oxide (0.6g., 55%), m.p.  $84-85^\circ$ , mixed m.p.  $85^\circ$ .

(Found: m/e 334 (100%), 229 (200,  $-CH_2CH_2Ph$ ), 202 (100,  $-C_4H_7Ph$ ), calc. for  $C_{22}H_{23}OP$ . m/e 334).

I.r. (nujol)  $\nu_{max}$ ; 1435 (PPh), 1160 (P=O)  $cm^{-1}$ .

N.m.r. ( $CDCl_3$ )  $\tau$ ; 2.6-2.35 (2H, c, o-protons to P=O), 2.4-2.9 (13 H, c, aromatic), 6.8-7.4 (2 H, c, P- $CH_2$ ), 7.4-7.9 (2 H, c,  $CH_2Ph$ ).

All spectra were identical to those of an authentic compound.

1b) Oct-1-yne and Chemical Identification of the Product.

i) Reaction with Phenylphosphine: A mixture of Oct-1-yne (23.2g., 0.2 mol) and phenylphosphine (11.0g., 0.1 mol) was boiled under nitrogen for 5 h. Distillation of the reaction mixture gave oct-1-yne (3g.) and a 2:1 adduct (13.6g., 45%), b.p.  $140-142^\circ$  at 0.05 mm Hg. to which the structure di-oct-1-enylphenylphosphine was assigned.

I.r.  $\nu_{max}$ ; 1595 (PC=C), 1435 (PPh)  $cm^{-1}$ .

N.m.r. ( $CDCl_3$ )  $\tau$ ; 2.4-2.9 (5 H, c, aromatic), 3.34-4.1 (4 H, c, vinyl), 7.5-9.2 (26 H, c, alkyl).

m/e; 330 (100%), 315 (10,  $-CH_3$ ), 301 (20,  $-C_2H_5$ ), 273 (110,  $-C_4H_9$ ).  $C_{22}H_{35}P$  requires m/e; 330.

ii) Oxidation of Di-oct-1-enylphenylphosphine: The phosphine (6.6g., 0.02 mol) was oxidised with hydrogen peroxide (5 ml., 100vol.) by stirring vigorously for 12 h. The emulsion formed was extracted with dichloromethane, the extract washed,

dried and distilled, b.p.  $175^{\circ}$  at 0.03 mm Hg. to give dioct-1-enylphenylphosphine oxide. (6.0g., 85%).

I.r.  $\nu_{\max}$ ; 1610 (PC=C), 1180 (P=O)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.0-2.6 (5 H, c, aromatic), 2.9-4.7 (4 H, c, vinyl), 7.0-9.2 (26H, c, alkyl)

m/e 346 (100), 317 (10,  $-\text{C}_2\text{H}_5$ ), 303 (25,  $-\text{C}_3\text{H}_7$ ), 289 (110,  $-\text{C}_4\text{H}_9$ )  
 $\text{C}_{22}\text{H}_{35}\text{OP}$  requires m/e 346.

N.m.r. chemical spin decoupling experiments of dioct-1-enylphenylphosphine oxide using cobalt and europium complexes failed to give any useful shifts in the observed resonances and only caused broadening.

iii) Reduction of Dioct-1-enylphenylphosphine oxide;

10% palladium on charcoal catalyst (0.25g.) was added to the phosphine oxide (1.73g., 5.0 mmol) in ethanol (25 ml) and the mixture hydrogenated (250 ml.  $\text{H}_2$ ) at room temperature. The reaction mixture was filtered and distilled b.p.  $180-182^{\circ}$  at 0.05 mm Hg. to give a white waxy solid m.p.  $36-37^{\circ}$  of dioctylphenylphosphine oxide (1.6g., 92%).

I.r.  $\nu_{\max}$  (nujol); 1440 (PhP), 1180 (P=O)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.0-2.6 (5H, c, aromatic), 7.0-9.2 (34 H, c, alkyl).

m/e 350  $\text{C}_{22}\text{H}_{39}\text{OP}$  requires m/e 350. All spectra were identical to those of the compound prepared by another route (Ch II. sect. B 8).

iv) Equimolar Oct-1-yne and Phenylphosphine; A slight

excess of phenylphosphine (3g., 27 mmol) and oct-1-yne (2.5g., 23 mmol) were heated at  $135^{\circ}$  under nitrogen for 0.5 h. Starting materials were removed, b.p.  $60^{\circ}$  at 22 mm Hg. and the residue distilled. One fraction, b.p.  $115^{\circ}$  at 0.05 mm Hg. (0.6g., 12%) was collected and a second, b.p.  $142^{\circ}$  at 0.05 mm Hg. of

dioct-1-enylphenylphosphine (1.6g., 16%), (spectra identical to an authentic sample).

The first fraction had i.r.  $\nu_{\max}$ ; 2280 (PH), 1595 (PC=C)  $\text{cm}^{-1}$ . m/e 222 and 220 (ratio 100:80), 207 and 205 (ratio 20:15), 193 and 191 (ratio 20:15). The ratio of the peak heights m/e 222 and 220 at 70e.v. was the same as that at 20e.v. This distillate was therefore assigned to a mixture of oct-1-enylphenylphosphine and octylphenylphosphine.

1c) Hept-1-yne and chemical identification of the product.

i) Reaction with Phenylphosphine: Phenylphosphine (5.5g., 0.05 mol) and hept-1-yne (9.6g., 0.1 mol) were boiled under nitrogen for 12 h. Distillation gave starting material (3.6g.) b.p. 90-100° and a 1:2 adduct (2.8g., 18%) to which the structure dihept-1-enylphenylphosphine was assigned.

I.r.  $\nu_{\max}$ ; 1595 (PC=C), 1435 (PPh)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.4-2.8 (5H, c, aromatic), 3.5-4.1 (4H, c, vinyl), 7.4-9.4 (22H, c, alkyl).

(Found: C, 79.2; H, 10.2; m/e 302,  $\text{C}_{20}\text{H}_{31}\text{P}$  requires; C, 79.5; H, 10.2; m/e 302).

ii) Oxidation of Dihept-1-enylphenylphosphine: The phosphine was oxidised as 1a) to give dihept-1-enylphenylphosphine oxide. (Found: C, 74.9; H, 9.4;  $\text{C}_{20}\text{H}_{31}\text{OP}$  requires C, 75.5; H, 9.7).

I.r.  $\nu_{\max}$ ; 1610 (PC=C), 1180 (P=O)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.2-2.7 (5H, c, aromatic), 3.1-3.44 (4H, c, vinyl), 7.5-9.4 (22H, c, alkyl).

The structural assignment was made by analogy to 1b) but does not distinguish between the possible geometric isomers.

ld) Phenylphosphine with Hex-1-yne.

i) Thermal reaction: Phenylphosphine (1.1g., 0.01 mol) and hex-1-yne (0.8g., 0.01 mol) were boiled under nitrogen for 5 days. Distillation of the reaction mixture gave only starting materials.

ii) Ultra-violet Irradiation of Reactants: Phenylphosphine (1.6g., 0.015 mol), hex-1-yne (1.1g., 0.015 mol) and cyclohexane (0.2g.) as g.l.c. marker, were placed in a silica glass round bottomed flask and irradiated from below with a Hanovarian medium pressure U.V. lamp (350 watts). G.l.c. (2% A.P.L. 90°) of samples taken at 0, 0.5, and 6 h. showed the same relative peak area to the marker cyclohexane indicating that no reaction had occurred.

II C 2. Reaction of Phenylphosphine with Disubstituted Alkynes.

2a) Oct-4-yne.

Phenylphosphine (5.5g., 0.05 mol) and oct-4-yne (11.0g., 0.1 mol) were boiled for 12 h. under nitrogen. The reaction mixture was distilled to give a 1:1 adduct, b.p. 85° at 0.03 mm Hg. to which the structure phenyl-1(1-propylpent-1-ene)ylphosphine (4g., 35%) was assigned.

I.r.  $\nu_{\max}$ ; 2280 (PH), 1595 (PC=C), 1440 (PhP)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.4-3.0 (5H, c, aromatic), 4.03 (1H, d of t,

$J_{\text{PH}}$  21 Hz,  $J_{\text{HH}}$  8 Hz, vinyl), 5.65 (1H, d of t,  $J_{\text{PH}}$  218 Hz,  $J_{\text{HH}}$

12 Hz, PH), 7.5-9.4 (14H, c, alkyl),

m/e; 220 (100), 205 (35,  $-\text{CH}_3$ ), 191, (90,  $-\text{C}_2\text{H}_5$ ),  $\text{C}_{14}\text{H}_{21}\text{P}$  requires m/e 220.

In a similar reaction the reactants were boiled under nitrogen for 2 days but the same product was isolated.

2b) 1-Phenylhex-1-yne.

Phenylphosphine (2.8g., 0.025 mol) and the alkyne (7.9g., 0.05 mol) were maintained at 160° for 12 h. under nitrogen. Distillation of the reaction mixture gave a 2:1 adduct (5.4g., 50%) b.p. 175-180° at 0.05 mm Hg. that was assigned the structure phenyl-bis,1,1'(1-n-butyl-2-phenyleth-1-en)ylphosphine.

I.r.  $\nu_{\max}$ ; 1590 (C=C), 1435 (PPh), 740 and 690 (aromatic).

N.m.r. (CDCl<sub>3</sub>)  $\tau$  ; 2.2-3.1 (15H, c, aromatic), 7.4-9.5 (18H, c, alkyl). The peaks are broad and poorly resolved and no assignment to the expected vinyl resonance can justifiably be made. It is possible that these protons are coupled both to phosphorus and the alkyl groups and the resulting resonances lie partially under the aromatic region as a broad complex.

m/e; 426 (100), 383 (90, -C<sub>3</sub>H<sub>7</sub>), 370 (100, -C<sub>4</sub>H<sub>8</sub>), 327 (120, -C<sub>5</sub>H<sub>8</sub>P): C<sub>20</sub>H<sub>35</sub>P requires, m/e, 426). The unusually large peak at m/e 327 is associated with the loss of the fragment, P≡C-C<sub>4</sub>H<sub>8</sub> by substantial structural rearrangement under electron impact.

In a similar experiment excess of equimolar phenylphosphine (5.5g., 0.05 mol) to alkyne (4.0g., 0.024 mol) was used. The product (2.8g.) was distilled b.p. 145-150° at 0.05 mm Hg.

I.r.  $\nu_{\max}$ ; 2280 (PH), 1435 (PhP) cm<sup>-1</sup>.

N.m.r. (neat)  $\tau$  ; 2.4-3.0 (5H, c, aromatic), 5.76 (d of d, J<sub>PH</sub> 210 Hz, J<sub>HH</sub> 4Hz) and 5.90 (d of d, J<sub>PH</sub> 210 Hz, J<sub>HH</sub> 6 Hz) (total accountancy 1H, PH), 7.0-7.4, 7.6-7.9, 8.8-8.9 and 9.0-9.3 (12H, broad complex alkyl).

N.m.r. (CDCl<sub>3</sub>) identical aromatic and alkyl region but no resonances appear for PH.

I.r. of  $\text{CDCl}_3$  solution from n.m.r. show a large peak at 1180 ( $\text{P}=\text{O}$ )  $\text{cm}^{-1}$ . m/e 270  $\text{C}_{18}\text{H}_{23}\text{P}$  required m/e 270. No peak of any significance was recorded at m/e 268 for the non-reduced 1:1 adduct. The product (2.8g., 42%) was assigned to a mixture of (1-phenylhexyl)phenylphosphine and the isomer (1-benzylpentyl)phenylphosphine.

## II C 3 Reduction reactions with Phenylphosphine.

### 3a) Reaction of Dioct-1-enylphenylphosphine.

Phenylphosphine (2g., 18 mmol) and dioctyl-1-enylphenylphosphine (2g., 6 mmol) were maintained at  $160^\circ$  for 12 h. under nitrogen. Distillation of the reaction mixture gave some phenylphosphine b.p.  $60^\circ$  at 22 mm Hg., a little of the phosphine reactant (0.2g.) and a main fraction b.p.  $90-94^\circ$  at 0.03 mm Hg. which was assigned the structure octylphenylphosphine (6.8g., 58%).

I.r.  $\nu_{\text{max}}$ ; 2280 (PH), 1435 (PhP)  $\text{cm}^{-1}$ .

N.m.r. (neat)  $\tau$ ; 2.4-3.0 (5H, c, aromatic), 5.90 (1H, d of t,

$J_{\text{PH}}$  206 Hz,  $J_{\text{HH}}$  6 Hz, PH). N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; PH peak lost.

m/e 222 (100), 207 (10,  $-\text{CH}_3$ ), 124 (200,  $-\text{C}_7\text{H}_{14}$ ) calc. for

$\text{C}_{14}\text{H}_{23}\text{P}$  m/e ; 222.

### 3b) Reaction of Dioct-1-enylphenylphosphine Oxide.

Excess phenylphosphine and the phosphine oxide were maintained at  $160^\circ$  for 2 days. Distillation of the reaction mixture at 20-25 mm Hg. and at 0.05 mm Hg. gave only starting materials whose spectra were identical to those of authentic samples.

### 3c) Reaction of Dec-1-ene.

Dec-1-ene (1.4g., 10 mmol) and phenylphosphine (2.2g., 2.0 mol) were boiled for 12 h. under nitrogen. Distillation of the reaction mixture gave starting materials (1.8g.), b.p.  $63^\circ$  at 20-25 mm Hg. of decylphenylphosphine (0.3g., 12% based on decene).

I.r.  $\nu_{\max}$ ; 2280 (PH), 1435 (PPh)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.4-2.8 (5H, c, aromatic), 8.0-9.4 (21H, c, alkyl), -0.75 (t, PH of oxidised product), 6.45 (t, PH). It is likely that the low field half of the PH resonance of the normal product lies under the aromatic region. This would require  $J_{\text{PH}}$  215 Hz a normal coupling for phosphorus bonded directly to hydrogen. The resonance at -0.75 is almost certainly due to the oxidised product.

In a similar reaction, samples were taken and g.l.c. (P.E. Fl1 capillary column  $80^\circ$ , 9 lb.) showed decane (2 min. 45 sec.), decene (3 min.) and phenylphosphine (3 min. low F.I.D. response). All retention times corresponded to authentic samples. Addition of decane to a sample enhanced the peak height (2 min. 45 sec.), g.l.c. (10% A.P.L.,  $98^\circ$ ) gave phenylphosphine (5 min. 30 sec.), decene (11 min.) and decane (11 min. 50 sec.). Mass Spec./g.l.c. (2% A.P.L.,  $40^\circ$ ) gave a first peak m/e 140 (decene) and a second peak m/e 140 (100): 142 (20) proving that decane was present.

II D. REACTION OF PHENYLPHOSPHINE WITH ALKYLDIYNES.I.) Conjugated Alkyldiynes.1a) Butadeca-6,8-diyne.

Phenylphosphine (7.2g., 0.065 mol) and butadeca-6,8-diyne (10g., 0.053 mol) were heated slowly, with stirring to 140° on an oil bath under nitrogen. A vigorous exothermic reaction was observed that lasted for five minutes. The mixture was maintained at 150° for 8 h. The black tarry reaction mixture was distilled and collected over the range b.p. 120-140° at 0.05 mm Hg. (6.0g., 29%). The combined distillates were adsorbed onto silica and chromatographed. Elution with ether/light petrol (1:10) gave a yellow oil, which was distilled into two fractions.

The first (2.16g., 13%) b.p. 118° at 0.05 mm Hg. had:  
 I.r.  $\nu_{\max}$ : 1595 (C=C), 1430 (PhP), 740 and 690 (aromatic)  $\text{cm}^{-1}$ .  
 N.m.r. ( $\text{CDCl}_3$ ) (see Appendix II)  $\tau$ , 2.4-2.8 (5 units, c, aromatic), A, 2.95 (0.4 units, d of d,  $J_{\text{PH}}$  10 Hz,  $J_{\text{HH}}$  3 Hz, vinyl), B, 3.2-3.3 (0.4 units, c, vinyl), C, 3.6 (0.2 units, c, vinyl), D, 3.96 (0.4 units, d of complex,  $J_{\text{PH}}$  13 Hz phosphole ring protons), 7.0-9.4 (22H, c, alkyl).

m/e 302 and 300  $\text{C}_{20}\text{H}_{31}\text{P}$  and  $\text{C}_{20}\text{H}_{29}\text{P}$  require m/e 302 and 300 respectively and were assigned to a mixture of 2,5-dipentyl-1-phenylphosphole and 2,5-dipentyl-1-phenylphosphol-2-ene.

The second distillate (1.6g., 9.5%) b.p. 138° at 0.05 mm Hg. had:  
 I.r.  $\nu_{\max}$ : 1595 (C=C), 1440 (PhP), 1190 (P=O)  $\text{cm}^{-1}$ .  
 N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.2-2.8 (5H, c, aromatic), 2.85-3.65 (1.5H, c, vinyl), broad peaks at  $\tau$ ; 3.20 and  $\tau$ ; 3.60 possibly represent the phosphole oxide ring protons  $J_{\text{PH}}$  40 Hz, 7.0-9.3 (25H, c, alkyl).

m/e 318 and 316  $C_{20}H_{31}OP$  and  $C_{20}H_{29}OP$  requires m/e 318 and 316 and was assigned to 2,5-dipentyl-1-phenylphosphole oxide and 2,5-dipentyl-1-phenylphosphol-2-ene oxide.

1b) Deca-4,6-diyne.

Deca-4,6-diyne (2.68g., 0.02 mol) and phenylphosphine (2.2g., 0.02 mol) were maintained at  $160^{\circ}$  under nitrogen for 8 h. Distillation and redistillation of the tarry residue gave two fractions.

The first (1.2g., 31%) b.p.  $97^{\circ}$  at 0.05 mm Hg. was analogous to 1a) and assigned to 2,5-dipropyl-1-phenylphosphole and 2,5-dipropyl-1-phenylphosphol-2-ene.

I.r.  $\nu_{\max}$ ; 1595 (C=C), 1435 (PPh)  $cm^{-1}$ .

N.m.r. ( $CDCl_3$ )  $\tau$ ; 2.4-2.8 (5H, c, aromatic), 2.8-3.98 (1.6H, c, vinyl and ring protons), 7.6-9.2 (17H, c, alkyl)

m/e; 246 (50) and 244 (100), 217 and 215 ( $-C_2H_5$ ), 204 and 202 ( $-C_3H_7$ ), 175 and 173 ( $-C_5H_{11}$ );  $C_{16}H_{23}P$  and  $C_{16}H_{21}P$  require m/e; 248 and 246.

The second distillate (0.5g., 12%) b.p.  $158^{\circ}$  at 0.05 mm Hg. had an i.r. spectrum as inconclusive as the first.

I.r.  $\nu_{\max}$ ; 1595 (C=C), 1435 (PhP)  $cm^{-1}$ .

m/e; 382 (30) and 380 (100) and 378 (80);  $C_{26}H_{25}P$  and  $C_{26}H_{23}P$  and  $C_{26}H_{21}P$  require m/e; 382, 380 and 378 respectively and represent addition of two molecules of diyne to one of phenylphosphine and two reduced stages. A small group of peaks at m/e; 480, 488 and 486 implies addition of two molecules of diyne to two molecules of phenylphosphine.

In a similar reaction an excess of phenylphosphine (3.5g., 0.031 mol) to diyne (2.68g., 0.02 mol) was used. A similar

first fraction (1.1g., 20%) b.p. 90-94° at 0.05 mm Hg. was obtained but with m/e; 246 (100) and 244 (50), thus showing that increased reduction had occurred. A second fraction (0.6g., 9%) b.p. 94-125° at 0.05 mm Hg. had m/e; 354,  $C_{22}H_{28}P_2$  requires m/e; 354 thus indicating that two molecules of phenylphosphine have added to one of diyne.

A third fraction (0.3g., 4%) b.p. 158° at 0.05 mm Hg. was identical to the second, obtained in the previous experiment, and was diaddition of the diyne to phenylphosphine.

lc) Hexadeca-7,9-diyne.

Excess phenylphosphine (3.0g., 0.023 mol) and hexadeca-7,9-diyne (2.06g., 9.5 mmol) were maintained at 150° for 12 h. under nitrogen. Distillation of the black tar formed gave two fractions. The first (1.8g., 18%) b.p. 135° at 0.04 mm Hg. had: I.r.  $\nu_{max}$ ; 1435 (PhP), 740 and 690 (aromatic)  $cm^{-1}$ . N.m.r. ( $CDCl_3$ )  $\tau$ ; 2.40-2.8 (5H, c, aromatic), 2.8-3.9 (0.5H, c, vinyl and phosphole ring), 7.0-9.2 (29H, c, alkyl and methylene protons).

m/e; 330 (100) and 328 (20):  $C_{22}H_{35}P$  and  $C_{22}H_{33}P$  require m/e 330 and 328 and the distillate was assigned to a mixture of 2,5-dihexyl-1-phenylphosphole and phospholene. The excess of phosphine led to increased reduction.

A second fraction (0.7g., 6%) b.p. 140-145° at 0.05 mm Hg. had an inconclusive i.r. spectrum.

N.m.r. ( $CDCl_3$ ) showed broad peaks at  $\tau$ ; 2.2-2.8 (10H, c, aromatic), 7.4-9.2 (26H, c, alkyl).

m/e; 440 (20) and 438 (100),  $C_{28}H_{42}P_2$  and  $C_{28}H_{40}P_2$  requires m/e 440 and 438 respectively for diaddition of two further molecules

of phenylphosphine to one of diyne. A further small group of peaks appears at  $m/e$ ; 552 (1) and 550 (2) showing diaddition of two molecules of phosphine to two of diyne.

## II D 2. Nonconjugated Alkyldiynes.

### 2a) Trideca-5,8-diyne.

i) Thermal reaction: Phenylphosphine (3.2g., 0.029 mol) and trideca-5,8-diyne (5.1g., 0.029 mol) were maintained at  $160^{\circ}$  for 4 h. under nitrogen with vigorous stirring. Distillation and redistillation of the red tar gave two main fractions. The first b.p.  $106-115^{\circ}$  at 0.04 mm Hg. was shown to be a mixture of 1:1 cyclic adducts (2.14g., 38.5%), 1,2-dihydro-2,6-di-n-butyl-1-phenylphosphorin, 2-n-butyl-5-pentylidene-1-phenylphosphol-2-ene and a minor component of 2-n-butyl-5-pentyl-1-phenylphosphole.

I.r.  $\nu_{\max}$ ; 1595 (C=C), 1430 (PhP), 740 and 690 (aromatic).

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.4-2.8 (5H, c, aromatic), 3.52 (0,2H, d,  $J_{\text{PH}}$  13 Hz phosphole ring), 3.9-4.3 (1.4H, c, phospholene and dihydrophosphorin ring), 6.5-7.0 (1.4H, c, phospholene and dihydrophosphorin methylene) 7.2-8.1 (c, exocyclic methylene), 8.4-9.0 (c,  $-\text{C}_2\text{H}_4-$ , butyl group) 9.0-9.3 (t, terminal  $-\text{CH}$ ). Total integral of alkyl groups 20H.

N.m.r.  $^{31}\text{P}$  ( $\text{CDCl}_3$ ) external ref. 85%  $\text{H}_3\text{PO}_4$ :  $-4.68^{\pm}0.02$  p.p.m. and  $+7.22^{\pm}0.02$  p.p.m. and a small peak at  $-4.1$  approx.  $^{\pm}0.1$  p.p.m.

N.m.r. variable temperature spectra from  $+55^{\circ}$  to  $-40^{\circ}$  observing the region 6.5-7.0  $\tau$ , which remained essentially unchanged except for broadening due to increased viscosity at low temperatures.

N.m.r. spin decoupling studies were made on the region 3.9-4.3  $\tau$  with respect to 6.5-7.0  $\tau$  and the results are discussed in (Ch. III. sect. B).

U.V. (ethanol)  $\lambda_{\max}$ ; 210,225 and a shoulder at 250 nm. (found:

C, 72.2; H, 9.2;  $C_{19}H_{27}P$  requires; C, 79.0, H, 9.0%).

m/e; 286 (100), 271(20,  $-CH_3$ ), 257 (40,  $-C_2H_5$ ), 244 (80,  $-C_3H_6$ ), 230 (30,  $-C_4H_8$ ), 215 (20,  $-C_5H_{11}$ ), 201 (10,  $-C_6H_{13}$ ), 187 (10,  $-C_7H_{15}$ ), 173 (20,  $-C_8H_{17}$ ). This pattern is commensurate with loss of both butyl groups.

G.l.c. (preparative) on a solution in  $CHCl_3$  of the first distillate (5%, N.P.G.S. at  $154^\circ$ ) with manual operation gave three fractions at 50 min., 1 h. 15 min., and (after a temperature increase to  $201^\circ$ ) 2 h. 10 min.

The first fraction had:

I.r.  $\nu_{\max}$ ; 2240 (PH, a shoulder), 2210 ( $C\equiv C$ , broad), 1430 (PhP)  $cm^{-1}$ .

N.m.r. (fresh  $CDCl_3$  solution)  $\tau$ ; 2.2-2.8 (5H, c, aromatic), 3.8-4.2 (1.1H, c, vinyl), 6.5-7.7 (1.5H, c, methylene), 7.6-9.4 (18H, c, alkyl).

m/e; 286, with a cracking pattern commensurate with the loss of alkyl chains.  $C_{18}H_{27}P$  requires m/e; 286. After standing the  $CDCl_3$  solution had an i.r. spectrum that included a strong  $\nu_{\max}$  1170 ( $P=O$ )  $cm^{-1}$ . The n.m.r. spectrum had also changed with stronger resonances at  $\tau$ , 3.2 and  $\tau$ , 3.6 and a single broad complex at  $\tau$ , 6.6. (m/e; 302.  $C_{18}H_{27}OP$  requires m/e; 302.).

The second g.l.c. (preparative) fraction had:

I.r. ( $CDCl_3$ )  $\nu_{\max}$ ; 2220 ( $C=C$ ), 1440 (PhP) 1175 ( $P=O$ )  $cm^{-1}$ .

N.m.r. ( $CDCl_3$ )  $\tau$ ; 2.2-2.4 (2H, c, o-protons to  $P=O$ ), 2.2-2.4 (3H, c, aromatic), 3.2 and 3.52 (1H, c, vinyl protons), 6.6-6.8 (1.5H, c, methylene), 7.6-9.2 (18H, c, alkyl).

m/e; 302.  $C_{18}H_{27}OP$  requires m/e; 302.

In view of these results the third and minor g.l.c. - fractions were not investigated. (retention 2 h. 20 min. at 201°)

The second main distillate (1.2g., 15%) b.p. 162° at 0.03 mm Hg. had:

I.r.  $\nu_{\max}$ ; 2280 (PH, broad), 1585 (C=C), 1435 (PhP)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ ),  $\tau$ ; 2.59 (10H, c, aromatic), 3.3-4.2 (2.1H, c, vinyl), 6.4-6.9 (2H, c, methylene), 7.2-9.2 (18H, c, alkyl). Two small peaks resonating at  $\tau$ , 4.25 and  $\tau$ , 6.34 could be assigned to PH  $J_{\text{PH}}$  215 Hz.

N.m.r.  $^{31}\text{P}$  ( $\text{CDCl}_3$ , external reference 85%  $\text{H}_3\text{PO}_4$ ) gave two peaks, +17.8 $\pm$ 0.2 p.p.m. and 22.9  $\pm$  0.2 p.p.m. and was assigned to a doublet  $J_{\text{PH}}$  206  $\pm$  10 Hz.

m/e; 394.  $\text{C}_{22}\text{H}_{44}\text{P}_2$  requires m/e; 396. This would have implied addition of two molecules of phenylphosphine to one of the diyne.

ii) Reaction of the first main distillate with methyl iodide and base: The distillate (1g., 5.4 mmol) was mixed with excess methyl iodide and stirred under nitrogen for 1 h. An exothermic reaction was observed that gave an orange oil. Excess methyl iodide was removed and sodium hydroxide solution (5 ml. 1 molar) was added and the mixture maintained at 50° for 2 h. The mixture was extracted twice with dichloromethane, the extracts washed, dried and evaporated. The oily residue was distilled b.p. 175° (block temp.) at 0.03 mm Hg. and assigned to a mixture of methylphenylalkenylphosphine oxides that will be discussed in Ch. III sect. B.

I.r.  $\nu_{\max}$ ; 1620 (C=C), 1435 (PhP), 1170 (PO)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.2-2.5 (2H, c, o-protons to P=O), 2.5-2.8 (3H, c, aromatic), 3.2-4.9 (1.9H, c, vinyl), 7.0-7.4 (2H, c,

methylene), 7.6-9.4 (22H, c, alkyl), 8.24 (d,  $J_{PH}$  12Hz, P-CH<sub>3</sub>)  
overlying the alkyl groups.

N.m.r. <sup>31</sup>P (CDCl<sub>3</sub>) external ref. 55% H<sub>3</sub>PO<sub>4</sub>, -32.4 ± 0.02 p.p.m.  
m/e; 318. C<sub>20</sub>H<sub>31</sub>OP requires m/e; 318.

In a similar experiment triethylamine was used as base. The residue after extraction was adsorbed onto alumina and chromatographed but no pure products were obtained.

In another experiment a non-nucleophilic base 1,8-bis(dimethylamino)naphthalene was used but distillation of the residue failed to separate any phosphorus containing products.

In another experiment pyridene was used as base, but t.l.c. (alumina/ethyl acetate) of the reaction mixture showed that no deprotonation had occurred and the phosphonium salt remained.

iii) Thermolysis of the First main Distillate: The distillate (1 g. 3.5mmol) was heated to 200° on a Woods metal bath, while nitrogen was passed slowly over the surface into an ethanol trap. U.V. of the resultant ethanol showed that no benzene had been collected. Thus the 1,4-dihydrophosphorin component does not follow the thermolysis of 1,2-dihydrophosphorins reported by Markl<sup>70</sup>.

## 2b) Nona-1,4-diyne.

Phenylphosphine (5.5g., 0.05 mol) and the diyne (6.0g., 0.05 mol) were heated slowly under nitrogen, to 130° when a reaction occurred. The temperature of the reaction mixture was maintained at 130° for 5 h. when excess phenylphosphine was removed (b.p. 60° at 14 mm Hg. The residue was distilled to give two fractions. The first (1.8g., 15%) b.p. 90° at 0.1 mm Hg. was a water white viscous liquid.

I.r.  $\nu_{max}$ ; 3300 (C≡CH), 2280 (PH), 1590 (C=C), 1430 (PPh) cm<sup>-1</sup>.

N.m.r.  $\tau$  ; 2.4-2.7 (5H, c, aromatic), 3.4-4.5 (2H, c, vinyl), 6.6 and 7.0 (2H, c, methylene), 7.2-9.2 (10H, c, alkyl). The spectrum gave a poor integral and no obvious peak to assign to PH or  $C\equiv CH$ .

m/e; 230.  $C_{15}H_{17}P$  requires m/e; 230. The distillate was considered to be a mixture of open chain 1:1 adducts.

The second fraction b.p.  $168^{\circ}$  at 0.01 mm Hg. (lg., 7%) was considered to be addition of two molecules of phenylphosphine to one molecule of diyne.

I.r.  $\nu_{\max}$ ; 2300 (PH), 1445 (PPh)  $cm^{-1}$ .

N.m.r. ( $CDCl_3$ )  $\tau$  ; 2.4-2.7 (10H, c, aromatic), 3.5-4.4 (2.5H, c, vinyl), 6.6 and 7.0 (1.5H, c, methylene), 7.4-9.2 (10H, c, alkyl).

m/e; 340.  $C_{29}H_{26}P_2$  requires m/e 340.

In a similar experiment the reagents were lowered into an oil bath at  $180^{\circ}$ , a vigorous reaction ensued, and the residue was distilled to give two main fractions. The higher boiling fraction  $140-146^{\circ}$  at 0.02 mm Hg. was essentially the same as the second of the previous experiment. The lower boiling fraction  $78-80^{\circ}$  0.03 mm Hg. (28%) gave:

I.r.  $\nu_{\max}$ ; 1595 (C=C), 1435 (PhP)  $cm^{-1}$ .

N.m.r. ( $CDCl_3$ )  $\tau$  ; 2.4-2.8 (5H, c, aromatic), 3.4-3.8 (2H, c, vinyl), 6.5-6.7 (1.2H, c, methylene), 7.6-9.3 (11H, c, alkyl).

m/e; 230 (100), 215 (10,  $-CH_3$ ), 201 (40,  $-C_2H_5$ ), 188 (90,  $-C_3H_7$ ), 173 (30,  $-C_3H_7$ ,  $-CH_3$ ).  $C_{15}H_{17}P$  requires m/e; 230.

U.V. (ethanol)  $\lambda_{\max}$ ; 210, 225 and 253, nm. This distillate was assigned to a phospholene and dihydrophosphorin mixture by analogy to 2a).

2c) 1,5-Diphenylpenta-1,4-diyne.

Phenylphosphine (1.12g., 0.01 mol) and the diyne (2.2g., 0.01 mol) were heated at 160° under nitrogen for 3 h. The black glass formed was distilled b.p. 190° (block temp.) at 0.03 mm Hg. to give a vivid yellow oil that was assigned to a 50:50 mixture of 2-benzyl-1,5-diphenylphosphole and 1,2-diphenyl-5(1'-phenylmethylidene)phosphol-2-ene. (0.7g., 21%).

I.r.  $\nu_{\max}$ ; 1595 (C=C), 1440 (PhP), 760 and 700 (aromatic)  $\text{cm}^{-1}$ .  
 N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.4-2.9 (15H, c, aromatic) 3.02 (1H, d  $J_{\text{PH}}$  11 Hz phosphole ring), 3.5-3.65 (0.5H, c, phospholene ring, possibly a doublet of triplets,  $J_{\text{PH}}$  7 Hz,  $J_{\text{HH}}$  1.5 Hz), 6.8 and 6.84 (1H, d,  $J_{\text{PH}}$  5 Hz phosphole benzyl protons).  
 U.V. (ethanol)  $\lambda_{\max}$ ; 210 (adsorbance 1.4) 230 (1.52) 370 (1.1) nm.  
 m/e; 326 (100), 249 (5, -Ph), 235 (50,  $-\text{CH}_2\text{Ph}$ ).  $\text{C}_{23}\text{H}_{19}\text{P}$  requires m/e 326.

In a similar experiment phenylphosphine (1.2g., 0.01mol) and the diyne (2.2g., 0.01 mol) in t-butylbenzene were boiled under nitrogen for 12 h. The solvent was removed and the tarry residue adsorbed onto alumina and chromatographed. Elution with light petrol gave a little t-butylbenzene. Elution with light petrol/benzene (10:1) gave a white solid (8mg. approx.) that was not investigated further. Elution with light petrol/benzene (5:1) gave a yellow solid (0.05g., 1.5%) that was recrystallised from ethanol and assigned the structure, 1(1,5-diphenylpenta-1-ene-4-yne)-ylphenylphosphine.

I.r.  $\nu_{\max}$ ; ( $\text{CDCl}_3$ ), 2250 (PH), 2230 (C=C), 1595 (C=C), 1440 (PhP),  $\text{cm}^{-1}$ .  
 N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.4-2.9 (15H, c, aromatic), 3.35 (1H, d of t,

$J_{PH}$  9 Hz,  $J_{HH}$  2 Hz), 6.14 (2H, c, methylene)

U.V.  $\lambda_{max}$ : (ethanol) 210 (adsorbance 1.36), shoulder 225 (0.92), 255 (1.05).

m/e; 326, 249 (60, -Ph).  $C_{23}H_{19}P$  requires m/e 326. An impurity peak at m/e 342 was observed and assigned to the phosphine oxide.

Elution with ethyl acetate and methanol gave some tars.

2d) 1-Phenylpenta-1,4-diyne.

Phenylphosphine (2.4g., 0.02 mol) and the dialkyne (3.0g., 0.02 mol) were heated to 160° at which point a violent reaction occurred. The intractable tar formed was dissolved in chloroform and adsorbed onto alumina. Elution with petrol, ether and methanol mixtures failed to isolate any significant amounts of products.

II E. FORMATION OF PHOSPHOLIMINES.E 1 From Phospholes and Azides.1a) N-Phenyl-1,2,5-triphenylphospholimine.

Phenyl azide (4g., 35 mmol) was added during 1 h. to a solution of 1,2,5-triphenylphosphole (10g., 31 mmol) in deoxygenated dioxan (250 ml.) and boiled for 12 h. under nitrogen. The solution darkened to a deep red colour. The dioxan was removed and the red solid dissolved in a minimum of hot chloroform and added to ether. Red prisms of N-phenyl-1,2,5-triphenylphospholimine (5.24g., 42%) m.p. 218-219<sup>o</sup> crystallised from the cooled solution. (Found: C, 83.45; H, 5.25; N, 3.30; m/e 403. C<sub>28</sub>H<sub>22</sub>NP requires C, 83.3; H, 5.46; N, 3.47%. m/e 403).

I.r.  $\nu_{\max}$ : 1580 (C=C), 1470 (PPh), 1280 (P=N) cm<sup>-1</sup>.

N.m.r. (CDCl<sub>3</sub>)  $\tau$ ; 1.8-2.1 (2H, c, P-Ph ortho protons), 2.4-3.4 (20H, c, aromatic), 2.4 and 2.73 (J<sub>PH</sub> 33 Hz, phospholimine ring protons).

U.V. (ethanol)  $\lambda_{\max}$ : 208 (37,000), 235 (29,500), 390 (17,500) nm.

1b) N-phenyl-2,5-di-t-butyl-1-phenylphospholimine.

Phenyl azide (1g., 9.2 mmol) and 2,5-di-t-butyl-1-phenylphosphole (2g., 7.4 mmol) were reacted following the method for 1a) and gave yellow needles of the phospholimine (1.7g., 64%) m.p. 174-175<sup>o</sup> from hot ether.

(Found: C, 79.2; H, 8.32; N, 4.4%. m/e; 363. C<sub>24</sub>H<sub>30</sub>NP requires C, 79.3; H, 8.26; N, 3.86%. m/e; 363).

I.r.  $\nu_{\max}$ : 1585 (C=C), 1315 (P=N) cm<sup>-1</sup>.

N.m.r. (CDCl<sub>3</sub>)  $\tau$ ; 2.9-3.1 (2H, c, ortho protons of P-Ph), 2.5-2.7 (3H, c, aromatic P-Ph), 2.84, 2.94, 3.02 and 3.25, 3.3, 3.39 (5H, m, NPh). Double irradiation at  $\tau$ , 3.28 caused the first set

to collapse to a broad singlet.  $\tau$ , 3.1 and 3.48 (2H,  $J_{PH}$  36 Hz phospholimine ring protons), 8.1 (18H, s, t-butyl).

U.V. (ethanol)  $\lambda_{max}$ ; 210 (22,400), 249 (14,700), 287 (9,000) nm.

lc). N-p-tolyl-1,2,5-triphenylphospholimine.

1,2,5-triphenylphosphole (3.12g., 10 mmol) and p-tolyl azide (1.33g., 10 mmol) were reacted following the method for la) and gave burgundy plates of the phospholimine (3.87g., 92% m.p. 195-196<sup>o</sup> from hot ethanol.

(Found: C, 83.7; H, 5.62; N, 3.24.

m/e; 417.  $C_{29}H_{24}NP$  requires, C, 83.4; H, 5.25; N, 3.25%. m/e; 417).

I.r.  $\nu_{max}$ ; 1600 (C=C), 1435 (PhP), 1285 (P=N)  $cm^{-1}$ .

N.m.r. ( $CDCl_3$ )  $\tau$ ; 1.8-2.1 (2H, c, ortho protons P-Ph), 2.2-2.9

(15H, c, aromatic and phospholimine ring protons,  $J_{PH}$  33Hz), 3.16

(4H, s, tolyl ring protons), 7.86 (3H, s,  $CH_3$ ). (App. II).

U.V. (ethanol)  $\lambda_{max}$ ; 208 (41,700), 242 (30,200), 370 (17,900) nm.

ld). N-p-nitrophenyl-1,2,5-triphenylphospholimine.

1,2,5-triphenylphosphole (3.12g., 10 mmol) and p-nitrophenyl azide (1.74g., 10 mmol) were reacted following the method for la) and gave red prisms of the phospholimine (3.00g., 67%) m.p. 212-214<sup>o</sup>, from a chloroform/ether mixture. (1:10).

(Found: C, 74.7; H, 4.7; N, 6.3. m/e; 448.  $C_{28}H_{21}N_2O_2P$  requires C, 75.0; H, 4.68; N, 6.24%. m/e; 448).

I.r.  $\nu_{max}$ ; 1580 (C=C), 1450, (PPh), 1290 (P=N)  $cm^{-1}$ .

N.m.r. ( $CDCl_3$ )  $\tau$ ; 1.8-2.2 (4H, c, ortho protons PPh, and nitro

aromatic ring), 2.4-2.9 (13H, c, aromatic), 2.30 and 2.64 (2H,  $J_{PH}$

34 Hz, phospholimine ring protons), 3.1-3.3 (2H, c, half of  $A_2B_2$

nitro ring system). (App. II).

U.V. (ethanol)  $\lambda_{max}$ ; 206 (24,700), 225 (20,700) 394 (25,800).

le). N(ethyl carboxylate)-1,2,5-triphenylphospholimine.

Ethyl azidoformate (1.4g., 1.3 mmol) and 1,2,5-triphenylphosphole (3.12g., 10 mmol) were reacted following the method for la) and gave yellow cubes of the phospholimine (3.2g., 82%) m.p. 221-222<sup>o</sup> directly.

(Found: C, 74.2; H, 5.61; N, 3.75. m/e; 399. C<sub>25</sub>H<sub>22</sub>NO<sub>2</sub>P requires C, 75.2; H, 5.5; N, 3.5%. m/e; 399).

I.r.  $\nu_{\max}$ ; 1620 (C=O), 1450 (PhP), 1380 (P=N) cm<sup>-1</sup>.

N.m.r. (CDCl<sub>3</sub>)  $\tau$ ; 1.9-2.1 (2H, c, ortho protons PhP), 2.4-2.9 (13H, c, aromatic), 2.38 and 2.74 (2H, J<sub>PH</sub> 36 Hz, phospholimine ring protons), 6.1 (2H, q, OCH<sub>2</sub>), 8.88 (3H, t, CH<sub>3</sub>),

U.V. (ethanol)  $\lambda_{\max}$ ; 210 (42,500), 223 (41,000) 399 (21,200) nm.

lf). Reaction of 1,2,5-Triphenylphosphole with Diphenylphosphinyl Azide.

i) Diphenylphosphinyl azide (5.12g., 25 mmol) and 1,2,5-triphenylphosphole (3.0g., 9.5 mmol) were dissolved in dioxan and boiled under reflux for 12 h. The solvent was removed and the tarry residue recrystallised from ethanol to yield only starting materials.

ii) The reaction was repeated using t-butylbenzene as solvent and boiling for two days under nitrogen. Two apparently different solids were separated by crystallisation from ethanol. The first, m.p. 185-186<sup>o</sup> mixed m.p. 185<sup>o</sup>, was starting material. The second solid in low yield (0.15g., 8%) m.p. 165-170<sup>o</sup> was found to be mostly starting material contaminated by a substance that showed m/e; 527 at 220 but this peak did not appear at 120<sup>o</sup>.

I.r. spectrum suggested  $\nu_{\max}$ ; 1445 (PPh), 1170 (P=N), 1330 (P=O).

The mass spectrum at 220<sup>o</sup> was however the only evidence

for the formation of N-(diphenylphosphinyl)-1,2,5-triphenylphospholimine.

II E. 2. From the Reaction of Phospholes with Chloramine T.



2a). N-tosyl-1,2,5-triphenylphospholimine.

Anhydrous chloramine T (3.5g., 15 mmol) in absolute ethanol (20 ml.) was added slowly to 1,2,5-triphenylphosphole (3.12g., 10 mmol) in absolute ethanol (200 ml.) following the method of Cadogan and Moulden<sup>125</sup> for formation of triethyl N-tosylphosphorimidate. The mixture was boiled under reflux for 12 h. Water (100 ml.) and ether (200 ml.) were added to the cooled solution, the aqueous layer separated and extracted with more ether, the combined extracts dried and finally evaporated. N-tosyl-1,2,5-triphenylphospholimine (2.5g., 54%) m.p. 245-247° was obtained as yellow needles from hot ethanol.

(Found: C, 72.1; H, 4.73; N, 3.04; m/e; 481.  $\text{C}_{29}\text{H}_{24}\text{NO}_2\text{PS}$  requires C, 72.4; H, 5.0; N, 2.92%, m/e; 481).

I.r. (nujol);  $\nu_{\text{max}}$ ; 1595 (C=C), 1440 (P-Ph), 1260 (P=N), 1130 (S=O)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 1.98-2.2 (2H, doublet of double doublets,  $J_{\text{PH}}$  12 Hz,  $J_{\text{HoHm}}$  8 Hz,  $J_{\text{HoHp}}$  2 Hz, o-protons PhP), 2.4-2.9 (15 H, c, aromatic) 2.41 and 2.81 (2H,  $J_{\text{PH}}$  41 Hz, phospholimine ring protons), 3.14 and 3.23 (2H, half of  $\text{A}_2\text{B}_2$  complex of tosyl ring protons), 7.80 (3H, s,  $\text{CH}_3$ ). (App. II).

U.V. (ethanol)  $\lambda_{\text{max}}$ ; 208 (25,000), 225 (30,000), 405 (9,900).

2b). Reaction of 2,5-Dipentyl-1-phenylphosphole with Chloramine T.

The phosphole (1.8g., 6 mmol) and chloramine T (1.8g., 8.2 mmol) were reacted following the method for 2a). The mixture

was boiled under nitrogen for 12 h., when t.l.c. (alumina/ether) showed that the reaction was complete. Water (20 ml.) and chloroform (25 ml.) were added to the cooled solution, the aqueous layer extracted with more chloroform, the combined organic extracts, washed, dried over sodium sulphate and the solvent removed. An attempt to crystallise the oily residue failed, so the sample was dry chromatographed on alumina with ether. Five fractions were collected from the middle band and three gave identical i.r.  $\nu_{\max}$ : 1559 (C=C), 1440 (P-Ph), 1260 (P=N), 1130 (S=O)  $\text{cm}^{-1}$ . N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.0-3.0 (9H, c, aromatic), 3.38 (2H, d, phospholimine ring protons), 7.65 (s) overlying 7.6-9.5 (total 26H, c, alkyl).

The poor n.m.r. integral and large impurity peaks showed that the sample was impure. It was therefore distilled at 0.05 mm Hg and block temp.  $200^\circ$  to give (0.62g.) of a yellow oil.

(Found: m/e; 362.  $\text{C}_{27}\text{H}_{36}\text{NO}_2\text{PS}$  requires m/e; 469).

I.r.  $\nu_{\max}$ : 1320, 1150 (S=O). No peaks were observed for P-Ph or P=N.

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.1-2.8 (5.9H, c, aromatic), 3.51 (1, d, J<sub>PH</sub> 40 Hz ring protons), 7.6-9.4 (22.6H, c alkyl protons).

N-Tosyl-2,5-dipentyl-1-phenylphospholimine decomposed on distillation possibly with loss of nitrosobenzene.

II F. REACTION OF DIMETHYL ACETYLENEDICARBOXYLATE WITH SOME  
PHOSPHOLE AND PYRROLE DERIVATIVES.

F 1. Phospholimines

1a) N-Phenyl-1,2,5-triphenylphospholimine.

The phospholimine (0.31g., 0.7 mmol) and the alkyne (0.14g., 1 mol) in the minimum of t-butylbenzene were maintained at 105° until t.l.c. (alumina/ether) demonstrated that reaction was complete (24 h.). The solvent was removed b.p. 60° at 20 mm Hg. to leave an oily solid. Fractional crystallisation from ethanol gave slightly impure dimethyl 3,6-diphenylphthalate (10%) m.p. and mixed m.p. 185°.

I.r. (nujol)  $\nu_{\max}$ ; 1730 and 1745 (C=O)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.52 and 2.64 (12H, aromatic), 6.42 (s, 6H, OMe).

The second substance, m.p. 208-210°, was a 1:1 adduct and was assigned the structure, 1,2,5-triphenyl-eth(1',2'-dimethyl carboxylate-2'-N-phenylimine)ylphospholidene (10%).

I.r.  $\nu_{\max}$ ; 1720 (CO), 1660 (C=N), 1580 (PC=C), 1435 (PPh), 1350 (P=C)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.2-3.2 (c), and 3.52, 3.62 (22H, aromatic and heterocyclic ring), 3.44 (s) and 3.64 (s) (6H, OMe).

(Found; C, 75.1; H, 5.2; N, 2.36. m/e; 545 (100), 486 (100,  $-\text{CO}_2\text{Me}$ ), 383 (15,  $-\text{PhN}=\text{CCO}_2\text{Me}$ ).  $\text{C}_{34}\text{H}_{28}\text{NO}_4\text{P}$  requires: C, 75.0; H, 5.15; N, 2.57% m/e; 545).

The products of a reaction of the alkyne (0.56g., 4 mmol) and the phospholimine (1.6g., 4 mmol) under similar conditions were adsorbed onto alumina and chromatographed. Elution with ether gave the phthalate (0.079g., 5.6%) m.p. 189-190°, mixed m.p. 189°

and an i.r. (nujol) spectrum identical to that of an authentic sample. Further elution with ether gave the ethylphospholidene (0.131g., 6.0%) m.p. 215°. I.r. (nujol) identical to a sample from the previous experiment. Elution with ether: ethyl acetate 4:1 gave slightly impure 1,2,5-triphenylphosphole oxide (0.09g., 7.8%), m.p. 210° (lit. m.p. 237°). I.r. (nujol) identical to an authentic sample. T.l.c. on alumina/ether gave the same retention time as an authentic sample and the same green fluorescence under U.V. irradiation. Elution with ethyl acetate gave a brown solid (1.2g.) m.p. 205-215°.

I.r. (nujol) broad characterless peaks.

N.m.r. (CDCl<sub>3</sub>)  $\tau$  ; 2.0-3.4 (30 units, aromatic), 6.0-7.0 (7 units, OCH<sub>3</sub>).

m/e; 705 (5), 563 (100), 545 (4), 531 (30), 446 (200). The solid gave a positive phosphorus test.

Elution with methanol gave a buff solid (0.580g.) m.p. 300° (sticky). I.r. gave broad characterless peaks and the n.m.r. showed broad characterless peaks. The mass spectrum at 310° showed a continuous spectrum of peaks up to m/e 800 and above. Vapour pressure osmometry (ethanol) gave a mass of 140 ± 20. The solid gave a positive phosphorus test.

A sample of the residue before chromatography was crystallised once from ethanol to give a solid that appeared under a microscope as a mixture of needles and red prisms. Liquid-liquid chromatography (70° : methanol/water: O.D.S. permaphase on zipase support) proved it to contain phthalate and phospholidene as expected. A shoulder was present on the phospholidene peak that was assigned to syn- and anti- structural isomers of the phenylimine

group. Hydrolysis to 1,2,5-triphenylphosphole oxide must also be considered possible under these high pressure conditions.

1b) N phenyl-2,5-di-t-butyl-1-phenylphospholimine.

The phospholimine (0.21g., 0.6 mmol) and the alkyne (0.1g., 0.6 mmol) in t-butylbenzene (5ml) were boiled under reflux for 12 h. under nitrogen. The entire reaction mixture was chromatographed on alumina. Elution with light petrol gave t-butylbenzene. Elution with light petrol:ether (10:1) gave the phospholimine (0.022g., 10%) m.p. 172-173° , mixed m.p. 171° . Elution with ether gave a 1:1 adduct (0.080g., 30%) m.p. 130-135° whose structural assignment will be examined in the discussion (Ch. III sect. C).

I.r. (nujol)  $\nu_{\max}$ ; 1725 (C=O), 1460 (C=N), 1435 (P-Ph), 1350 (P=C)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.0-3.7 (12H, c, aromatic and phosphole ring), 6.4-6.5 (6H,  $\text{OCH}_3$ ), 8.8-9.0 (18H, t-butyl). The methoxyl region consisted of 1 peak at  $\tau$ , 6.42 and two others  $\tau$ , 6.48 and 6.50. The t-butyl region consisted of 3 peaks at  $\tau$ , 8.86 and 8.92 (same integral) and 8.98.

m/e; 505 (100), 490 (75,  $-\text{CH}_3$ ), 446 (150,  $-\text{CO}_2\text{CH}_3$ ), 416 (90).

Accurate mass measurement of  $m^+$  gave a mass of 505.238182 (error 4.5 p.p.m.) as required by  $\text{C}_{30}\text{H}_{36}\text{NO}_4\text{P}$ .

1c) N-p-Tolyl-1,2,5-triphenylphospholimine.

The phospholimine (0.83g., 2 mmol) and the alkyne (0.3g., 0.22 mmol) in the minimum of t-butylbenzene were maintained at 105° for 24 h. when t.l.c. (silica/ether) showed complete reaction. Dark orange crystals of 1,2,5-triphenyl-eth(1',2'-dimethyl carboxylate-2'-N-tolylimine)ylphospholidene,

(0.45g., 40.2%) m.p. 183-184° precipitated from the cooled solution.

I.r. (nujol)  $\nu_{\max}$ ; 1730 (C=O), 1660 (C=N), 1435 (PPh), 1350 (P=C)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.2-2.8 (17H, c, aromatic and phospholidene ring), 3.14, 3.20 and 3.63, 3.70 (4H,  $\text{A}_2\text{B}_2$ , tolyl ring), 6.40 (3H, s,  $\text{OCH}_3$ ), 6.63 (3H, s,  $\text{OCH}_3$ ), 7.85 (3H, s,  $\text{CH}_3$ ).

m/e; 559 (100), 530 (5,  $-\text{C}_2\text{H}_5$ ), 500 (90,  $-\text{CO}_2\text{CH}_3$ ), 469 (10,  $-\text{C}_7\text{H}_6$ ), 383 (10,  $-\text{CH}_3\text{CO}_2-\text{C}=\text{NC}_6\text{H}_4\text{CH}_3$ ). Accurate mass measurement of  $m^+$  gave 559.191234 (error 4.5 p.p.m.) as required by  $\text{C}_{35}\text{H}_{30}\text{NO}_4\text{P}$ .

The product mixture of a reaction of the phospholimine (0.83g., 2 mmol) and the alkyne (0.3g., 2mmol) under identical conditions was chromatographed on alumina. Elution with light petrol: ether (10:1) gave a yellow oil (0.008g.) that was not investigated. Elution with ether gave dimethyl 3,6-diphenylphthalate (0.03g., 4.1%) m.p.  $189^\circ$ , mixed m.p.  $189^\circ$ . I.r. (nujol) identical to an authentic sample. Elution with ether:ethyl acetate (10:1) gave the phospholidene (0.60g., 53.9%) m.p.  $170-175^\circ$ , mixed m.p.  $173-175^\circ$  identical to a sample from the previous experiment. Elution with methanol gave a range of buff solids (0.21g.).

ld). N-p-Nitrophenyl-1,2,5-triphenylphospholimine.

The phospholimine (0.89g., 2 mmol) and the alkyne in the minimum of t-butylbenzene were maintained at  $105^\circ$  for 24 h. Red crystals of starting material (0.44g., 49%) precipitated from the cooled solution. The solvent was removed on a Buchi evaporator at 60 mm Hg. and the residue crystallised from ethanol to yield two solids.

The first was assigned the structure 1,2,5-triphenyl-eth(1',2'-dimethyl carboxylate-2'-N-p-nitrophenylimine)ylphospholidene. (0.043g. 8%)

I.r. (nujol)  $\nu_{\max}$ ; 1730 (C=O), 1550 (C=N), 1430 (P-Ph), 1320 (P=C)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.0-3.65 (21H, c, aromatic), 6.39 (3H, s,  $\text{OCH}_3$ ), 6.60 (3H, s,  $\text{OCH}_3$ ). It is possible to clearly distinguish at  $\tau$  2.9, 3.56 and 3.64 three of the expected four peaks of an  $\text{A}_2\text{B}_2$  pattern for the nitro ring protons. Accurate mass measurement gave 590.160660 (error 3 p.p.m.) as required by  $\text{C}_{34}\text{H}_{27}\text{N}_2\text{O}_6\text{P}$ .  
 m/e; 590 (100), 575 (5,  $-\text{CH}_3$ ), 561 (10,  $-\text{C}_2\text{H}_5$ ), 531 (100,  $-\text{CO}_2\text{CH}_3$ ), 383 (10,  $-\text{CO}_2\text{CH}_3, -\text{C}=\text{NC}_6\text{H}_4\text{NO}_2$ ).

In a similar reaction but at  $160^\circ$ , the phospholimine (0.71g., 1.6 mmol) and the alkyne (0.3g., 2 mmol) in t-butylbenzene were reacted for 24 h. The solvent was removed and the residue chromatographed on alumina. Elution with ether gave dimethyl 3,6-diphenylphthalate (0.45g., 70.8%) m.p.  $190-191^\circ$  mixed m.p.  $190^\circ$ . Elution with ether and ethyl acetate mixtures gave several fractions of less than 10 mg., which were not investigated. Elution with methanol gave a buff solid (0.333g) that gave no clear melting point. Vapour pressure osmometry (ethanol) gave a molecular weight of 68.

le) N(ethyl carboxylate)-1,2,5-triphenylphospholimine.

The phospholimine (0.8g., 2 mmol) and the alkyne (0.3g., 2.1 mmol) in the minimum of t-butylbenzene were maintained at  $130^\circ$  for 12 h. when t.l.c. (silica/ether) had shown the reaction to be finished. Filtration of the solid precipitated, and crystallisation from ethanol of the residue after the solvent had been removed, gave dimethyl 3,6-diphenylphthalate (0.41g., 57%) m.p.  $190-191^\circ$ , mixed m.p.  $189^\circ$ . I.r. identical to one of an authentic sample.  
 m/e; 346 calc. for  $\text{C}_{22}\text{H}_{18}\text{O}_4$  m/e; 346.

The mother liquors from the crystallisations were collected and evaporated to give a tarry residue.

lf) N-p-Tosyl-1,2,5-triphenylphospholimine.

i) Reaction at 105° and 80°: The phospholimine and alkyne failed to react when dissolved in t-butylbenzene and maintained at 105°, since only solid starting materials were recovered, m.p. 247-248°, i.r. identical to an authentic sample. When dioxan was used as solvent no reaction was observed at 101°.

ii) Reaction at 160°: (0.18g., 0.4 mmol) and the alkyne (0.5g., 3.5 mmol) in t-butylbenzene (25 ml.) were boiled under reflux under nitrogen for 12 h. The solvent was removed and a tarry residue crystallised from ethanol to give impure dimethyl 3,6-diphenylphthalate (0.14g., 100%) m.p. 189°. I.r. and n.m.r. spectra were identical to an authentic sample.

The mother liquors were collected and evaporated to dryness, the residue adsorbed onto alumina, and chromatographed. Elution with ether gave phthalate (0.01g.) m.p. 191°, mixed m.p. 191°.

Elution with ether:ethyl acetate (10:1) gave the phospholimine (0.008g., 40%) m.p. 247°, mixed m.p. 246°. Elution with methanol gave a buff solid (0.05g.) m.p. above 300° when it was still a tacky solid. I.r. (nujol) gave broad characterless peaks. The solid gave a positive phosphorus test.

iii) Reaction in 1,4-Dimethoxybenzene: The phospholimine (0.48g., 1 mmol) and the alkyne (0.14g., 1 mmol) in 1,4-dimethoxybenzene were maintained at 170° for 12 h. The solvent was distilled off (b.p. 100° at 20 mm Hg.) and g.l.c. (2% P.E.G.A. 150°) of a sample proved that no volatile components had been lost from the reaction mixture. The residue was adsorbed onto alumina and

chromatographed. Elution with light petrol:ether (10:1) gave a little solvent. Elution with ether gave the phthalate (0.156g., 32%) m.p.  $189^{\circ}$ . I.r. spectrum was identical to an authentic sample. Further elution with ether gave impure p-tolylsulphonamide. (0.01g., 10%) m.p.  $130^{\circ}$  (lit.<sup>124</sup> 138.5-139 anhydrous). I.r. (nujol)  $\nu_{\max}$ ; 3250 and 3350 (NH)  $\text{cm}^{-1}$  and n.m.r. were identical to an authentic sample except for a few impurity peaks. (Found: m/e; 171 calc. for  $\text{C}_6\text{H}_6\text{NO}_2\text{S}$  m/e; 171). Elution with methanol gave a buff solid (0.260g) m.p. above  $300^{\circ}$ , insoluble in all solvents except methanol. I.r. gave characterless smudges.

A similar reaction using N,N-dimethylaniline as solvent failed because the alkyne reacted with this amine to give brown tars.

## II F 2. Phospholes and Phosphole Oxides.

### 2a) 1,2,5-Triphenylphosphole.

Finely powdered 1,2,5-triphenylphosphole (0.04g., 0.1 mmol) was suspended in a solution of the alkyne (0.018g., 0.1 mmol) in cyclohexane (25 ml.) and the mixture boiled under reflux for 2 days. The solvent was removed and crystallisation of the residue gave dimethyl 3,6-diphenylphthalate (0.03g., 70%) m.p.  $189-191^{\circ}$ , mixed m.p.  $189^{\circ}$ . I.r. and n.m.r. identical to those of an authentic sample.

### 2b). 1,2,5-Triphenylphosphole Oxide.

The phosphole oxide (0.32g., 1 mmol) and the alkyne (0.14g., 1 mmol) in t-butylbenzene were maintained at  $105^{\circ}$  for 20 h. under nitrogen. The solution was cooled overnight at  $0^{\circ}$  and gave white needles of dimethyl 3,6-diphenylphthalate (0.3g., 87%) m.p.  $190-191^{\circ}$ , mixed m.p.  $191^{\circ}$ . I.r. identical to an authentic sample.

In a similar experiment in cyclohexene the phosphole oxide (0.65g., 2 mmol) and the alkyne (0.28g., 2 mmol) gave the phthalate (0.21g., 33%) m.p. 190-191<sup>o</sup>, mixed m.p. 191<sup>o</sup>, and a yellow oily distillate b.p. 120-130<sup>o</sup>, 12 mm Hg. The oil had a sweet ester like odour and failed to crystallise from various solvents. N.m.r. failed to show an aromatic resonance therefore the phosphorus fragment was not present. The oil was not investigated further.

In a similar experiment the phosphole oxide (0.65g., 2 mmol) and the alkyne (0.3g., 2.1 mmol) in 1,4-dimethoxybenzene were maintained at 110<sup>o</sup> for 3 days. The solvent was removed b.p. 100<sup>o</sup> 12.0 mm Hg. and a sample was g.l.c. (P.E.G.A. 150<sup>o</sup>) but did not show any volatile component. The black residue was dissolved in chloroform, adsorbed onto alumina, and chromatographed. Elution with light petrol gave some pure solvent. Elution with ether gave dimethyl 3,6-diphenylphthalate (0.45g., 76%) m.p. 190<sup>o</sup>. I.r. was identical to an authentic sample. Elution with ether:ethyl acetate (10:1) gave needles of phosphole oxide (0.1g., 15%). m.p. 234-235<sup>o</sup> mixed m.p. 234<sup>o</sup>. T.l.c. (alumina/ether) gave the same retention as an authentic sample. Elution with methanol gave a buff solid, the mass spectrum was unobtainable because of a low ion pressure even at 310<sup>o</sup> and the sample remained on the probe. Vapour pressure osmometry gave a molecular weight of 49 ± 10. The solid gave a positive but faint phosphorus test.

## II F. 3. Pyrrole Derivatives.

### 3a) N-Phenylpyrrole.

N-Phenylpyrrole (1.43g., 0.01 mol) and the alkyne (1.42g., 0.01 mol) in t-butylbenzene (5 ml.) were boiled under nitrogen for 24 h. The solvent was removed and the residual tar

crystallised from ethanol to give dark brown crystals m.p. 116-117° that was assigned the structure 3,4-dimethyl N-phenylpyrroledicarboxylate.

I.r.  $\nu_{\max}$ ; (nujol), 1720 (C=O),

N.m.r. (CDCl<sub>3</sub>)  $\tau$  ; 2.4-2.7 (7H, c, aromatic and pyrrole ring),  
6.15 (6H, s, Me).

(Found: C, 64.71; H, 4.87; N, 5.59. m/e; 259. calc. for C<sub>14</sub>H<sub>13</sub>NO<sub>4</sub>;  
C, 64.9; H, 5.01; N, 5.4%. m/e 259).

In a similar experiment the product 3,4-dimethyl N-phenylpyrroledicarboxylate was used as reactant but was retrieved unchanged at the end of the reaction period.

### 3b) 1,2,5-Triphenylpyrrole.

1,2,5-Triphenylpyrrole (0.7g., 2 mmol) and excess alkyne (0.3g., 2.2 mmol) in t-butylbenzene were boiled for 12 h. under nitrogen. The solid obtained from the cooled solution was 1,2,5-triphenylpyrrole m.p. 239°, mixed m.p. 238°. I.r. identical to that of an authentic sample.

In a similar experiment a large excess of alkyne was used and no solvent. The tar obtained after 2 days at 160° was adsorbed onto alumina and chromatographed. Elution with ethyl acetate gave some oils that had no aromatic resonance in the n.m.r. spectra and were polymers of the alkyne.

II G. OTHER EXPERIMENTS.1a) Methylation of N-phenyl-1,2,5-triphenylphospholimine.

N-Phenyl-1,2,5-triphenylphospholimine (0.4g., 1 mmol) was dissolved in dioxan and iodomethane (0.5g., 3.5 mmol) added and boiled under reflux under nitrogen for 12 h. An oil precipitated from the cooled mixture, was recrystallised from ethanol and assigned the structure 1(methylphenylamino)-1,2,5-triphenylphospholium iodide m.p. 244-245° . (0.43g., 55%).

I.r. (nujol)  $\nu_{\max}$ ; 1595 (C=C), 1445 (PPh)  $\text{cm}^{-1}$  .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$  ; 1.66 and 2.32 (phospholium ring protons,  $J_{\text{PH}}$  45 Hz), 1.6-3.0 (22H, c, aromatic), 6.48 (3H, d,  $J_{\text{PH}}$  10 Hz Me).

1b) Reaction of 1(methylphenylamino)-1,2,5-triphenylphospholium iodide with phenyl lithium.

Phenyl lithium solution (2.0 ml. of 1.65 molar) was added to a suspension of finely powdered 1(methylphenylamino)-1,2,5-triphenylphospholium iodide (0.25g., 0.45 mmol) and stirred for two days. The solvent was removed and the tarry residue adsorbed onto alumina and chromatographed. Elution with light petrol gave biphenyl with a retention on g.l.c. (5% P.E.G.A. 130<sup>9</sup>) identical to an authentic sample. Elution with light petrol/ether (50:1) gave a fluorescent oil (0.02g.)

I.r. ( $\text{CDCl}_3$  solution from n.m.r.)  $\nu_{\max}$ ; 1435 (PhP), 690 and 740 (aromatic)  $\text{cm}^{-1}$  .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$  ; 2.4-3.0 (c, aromatic),

m/e; 388 (100), 309 (20), 233 (40),  $\text{C}_{28}\text{H}_{21}\text{P}$  requires m/e; 388.

Sublimation of the sample failed to give an analytically pure sample and the oil was assigned the structure 1,2,3,5-tetra-phenylphosphole on n.m.r. and mass spectra data but with considerable reservation.

2) Reduction of N-p-nitrophenyl-1,2,5-triphenylphospholimine.

The phospholimine (3.2g., 7.0 mmol) was added to a mixture of iron powder (2.3g.), ethanol (10 ml.), water (10 ml.) and conc. hydrochloric acid (0.2 ml.) and boiled under reflux under nitrogen for 12 h. The reaction mixture was neutralised with sodium hydroxide, filtered through celite, washed with water and extracted with chloroform. The extracts were evaporated to give 1,2,5-triphenylphosphole oxide (1.8g., 68%) m.p. 234-235° , mixed m.p. 235° . T.l.c. alumina (ether) had the same retention time as an authentic sample and i.r. indistinguishable from an authentic sample.

3) Photolysis of N-Phenyl-1,2,5-triphenylphospholimine in Diethylamine.

The phospholimine (0.3g., 0.7 mmol) in deoxygenated diethylamine (120 ml.) was photolysed (350 watt. medium pressure) for 16 h. The orange suspension gave a pale yellow solution g.l.c. (2% A.P.L. 90° programed after 10 min. to heat to 185° ) failed to show any aniline or 2-diethylamino-3H-azapine. The diethylamine was removed and the tarry residue adsorbed onto alumina and chromatographed.

Elution with ether/ethanol (20:1) gave a little yellow oil that t.l.c. (ether/alumina) showed consisted of several components and it was not investigated further. Elution with ethanol gave a buff solid. (chloroform/ether) that had:

I.r. (nujol) characterless broad peaks 1475 (PhP possibly)  $\text{cm}^{-1}$ .

N.m.r. ( $\text{CDCl}_3$ )  $\tau$ ; 2.4-3.0 (c, aromatic) 8.6-9.2 (c, alkyl).

m/e (260 ); the sample remained on the probe and peaks above 400 and half masses 351.5, 355.5 suggest doubly charged ions of mass

730, 711 were present, implying polymeric material.

III DISCUSSION.

Page No.

- A) THE REACTION OF PHENYLPHOSPHINE WITH ALKYNES. 99
- B) THE REACTION OF PHENYLPHOSPHINE WITH ALKYLDIYNES. 111
- C) THE FORMATION AND REACTIONS OF PHOSPHOLIMINES. 119
- D) THE REACTION OF PHOSPHOLE AND PYRROLE DERIVATIVES WITH 125  
DIMETHYL ACETYLENEDICARBOXYLATE.

### III A) THE REACTION OF PHENYLPHOSPHINE WITH ALKYNES.

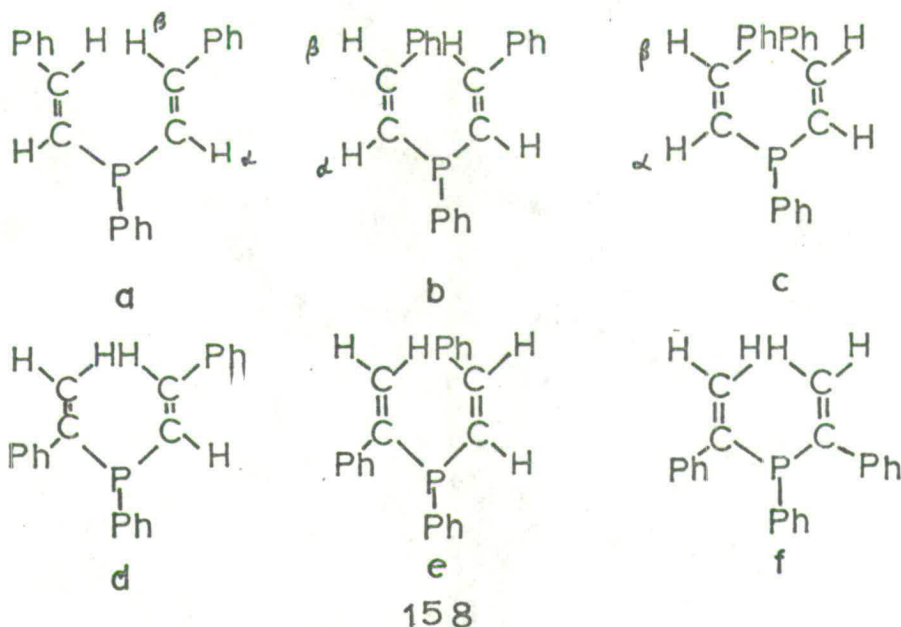
The reactions of a variety of phosphines with alkenes have been reviewed in the Introduction. One significant point raised is that phenylphosphine reacts under a variety of conditions. Rauhut et al.<sup>8</sup> have shown that cis-2-cyanoethylphosphine was formed from phenylphosphine in strongly basic conditions at room temperature. The ionic mechanism for this reaction and the nucleophilic initiation step in the polymerisation of 1-cyanoeth-1-ene<sup>4</sup> are indisputable. Mann and Millar<sup>1</sup> looked at the reaction of phenylphosphine at 130<sup>o</sup> and found no catalytic effect with base or acid present. This suggests that a different mechanism, possibly involving radicals, operates at this temperature. That phosphine itself undergoes radical reactions with alkenes was demonstrated conclusively by Stiles et al.<sup>7</sup> and Rauhut et al.<sup>8</sup>. These workers observed a reaction with radical initiators or U.V. irradiation.

The reactions of alkynes with phosphines have also been shown to involve a variety of mechanisms. Work by Aguir and Archibald<sup>14</sup> demonstrated that diphenylphosphinolithium added reversibly to 1-phenyleth-1-yne ( $\text{PhC}\equiv\text{CH}$ ) but that a different mechanism occurred to that of the reaction observed by Hoffmann and Diehr<sup>15</sup> at 100<sup>o</sup>. Rauhut et al.<sup>8</sup> found a free radical reaction of a secondary phosphine, bis(2-cyanoethyl)phosphine ( $(\text{CNCH}_2\text{CH}_2)_2\text{PH}$ ) with oct-1-yne. These workers also obtained a reaction with a primary phosphine, 2-cyanophosphine ( $\text{CNCH}_2\text{CH}_2\text{PH}_2$ ) with hept-1-yne, but the work was a coda to their more detailed work on alkenes.

The present study is concerned with the thermal reaction of phenylphosphine with a variety of alkynes. The aim was to establish

the generality of the reaction, to prove the position of attack by the phosphine and to decide if this can be directed by the choice of substituents.

1-Phenyleth-1-yne with Phenylphosphine: When 1-phenyleth-1-yne ( $\text{PhC}\equiv\text{CH}$ ) and phenylphosphine ( $\text{PhPH}_2$ ) were heated to  $160^\circ$ , a reaction occurred that gave an adduct of two molecules of the alkyne with one of the phosphine. The yield of this thermal reaction was low (26%) and much polymeric material was left after distillation. Analysis of the spectral data taken presented several problems and it was not possible to assign a structure from this data alone. The mass and infra-red spectra were consistent with any one of the six forms shown below (158; a-f).



The nuclear magnetic spectrum gave two doublets at  $\tau$ : 3.05 and 3.18 with coupling constant  $J_{\text{PH}}$  14 and 8 Hz respectively for the vinyl protons. Splittings of this order could be due to the interaction of cis- or trans- protons or the interaction of phosphorus<sup>56</sup>. In theory, if first order rules applied, the resonance of each vinyl proton in the six isomers would involve a doublet

of doublets, i.e.  $J_{H_\alpha H_\beta}$  and  $J_{H(\alpha \text{ or } \beta)P}$ . It is therefore impossible to decide between any of the isomers on this evidence, although (158, b), c) and e)) are less likely on steric grounds. The vinyl region in the n.m.r. spectrum was confused by peaks due to an oxide impurity, the product was, therefore, oxidised.

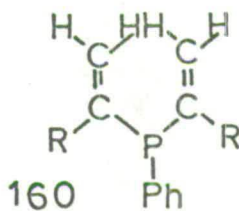
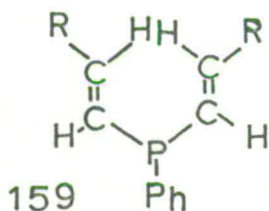
Infra-red, mass spectra and elemental analysis agreed well with a tertiary phosphine oxide (158 a-f,  $R_2PhPO$ ) but the n.m.r. spectrum again produced unexpected problems. Two doublets appeared at  $\tau$ ; 3.25 and 3.14 with splittings  $J$  20 and 22 Hz. Since oxidation of phosphorus is unlikely to change the coupling of cis- and trans- protons with each other, the observed splitting was considered to be due to an interaction with phosphorus. Thus protons in two different environments were involved. The area of these peaks, relative to that of the aromatic protons, indicated that only two protons were involved. This suggested that the high electron withdrawing power of  $P=O$  had pulled the adjacent protons' resonance into the aromatic region by further deshielding. A similar deshielding effect was observed with the ortho- protons of the  $O=P-Ph$  group. These results suggested that isomers (158 a), b) or c)) had been formed. Since two different vinyl protons were observed the isomer (158 b)) is preferred to the other two.

The unexpected lack of an observed coupling between (158  $H_\alpha$  and  $H_\beta$ ) can be explained by a different interpretation. This requires the splitting of 20 and 22 Hz to be due to the cis- and trans- coupling between two protons and a very large splitting of 50-65 Hz, that results in half of the pattern overlying the aromatic region. Large  $J_{PH}$  values are observed for systems like phosphole oxides  $^{13}O$  ( $J_{PH}=36$  Hz) but the value required is

nearly twice as large. This explanation does not distinguish between any of the isomers (158 a-f), although the large coupling  $J_{PH}$  required could imply a proton on an adjacent carbon<sup>56</sup>.

Confirmation of terminal addition was obtained by hydrogenation of the double bonds in the compound and by comparing spectral data with that of an authentic sample prepared by another route. No fragmentation of  $m/e$ ;  $P^+ - 15$  (for loss of a methyl radical) was observed in the mass spectrum, which supported the conclusion of terminal addition. Thus phenylphosphine reacts with 1-phenyleth-1-yne to give phenyl-bis 1,1'(2-phenyleth-1-ene)ylphosphine (158 b)) and probably does so with cis- and trans- addition.

Oct-1-yne and Phenylphosphine: The reaction of oct-1-yne with phenylphosphine at 125° also gave an adduct of two molecules of alkyne with one of the phosphine. Infra-red and mass spectral data support the assignment to dioct-1-enylphenylphosphine (159) or bis 1,1'(1-methylhept-1-ene)ylphenylphosphine (160) but gave no information as to the position of attack or configuration of the product. The n.m.r. spectra of the vinyl region was extremely complex and although the peaks integrated well for four protons, as expected, the pattern was too complex for useful analysis.



In an attempt to avoid confusing impurities the material was oxidised to the less reactive tertiary phosphine oxide. This compound gave i.r. and mass spectra supporting the assignment to (159 or 160), but it was still impossible to deduce the position

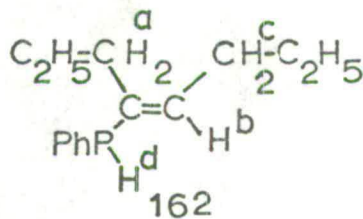
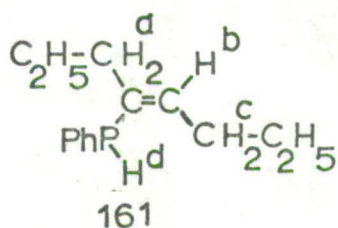
of attack from n.m.r. spectral data. The vinyl proton region appeared as a broad complex spreading from  $\tau$  ; 2.9-4.7. Engls<sup>126</sup> has reported that trialkyl phosphites can complex with paramagnetic transition metals such as cobalt and nickel. The metal causes a decrease in spin-lattice relaxation time of adjacent nuclei. This results in a more rapid exchange between the spin states of the nuclei, which are in effect, decoupled. An attempt to decouple phosphorus in the phosphine oxide (159, 160;  $R_2PhPO$ ) was made using  $Co(ClO_4)_2$  in deuterioacetone. The phosphine oxide solution gave a characteristic "cobalt blue" colour due to complex formation but the n.m.r. spectra of the aromatic and vinyl region were shifted downfield and broadened beyond recognition.

Since spectral studies had failed to elucidate the position of addition, the compound was hydrogenated and found to be identical to a sample of dioctylphenylphosphine oxide ( $(C_8H_{17})_2PhPO$ ) prepared by another route. This proved terminal addition had occurred forming dioct-1-enylphenylphosphine (159) but the geometry of the compound remains unknown.

Hept-1-yne and Phenylphosphine: A similar reaction was observed between phenylphosphine and hept-1-yne at  $125^\circ$ . The product of the reaction was distilled under nitrogen several times to give reasonable analytical, infra-red, n.m.r., and mass spectral data in agreement with an assignment to dihept-1-enylphenylphosphine. In neither the phosphine nor its oxide were the vinyl proton resonances in the n.m.r. spectra any less complex than before and the assignment was made by analogy to the case for oct-1-yne discussed above.

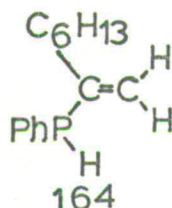
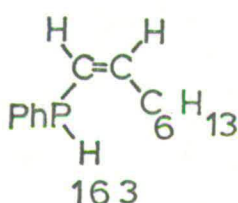
Hex-1-yne and Phenylphosphine: An attempt to react hex-1-yne at  $71^{\circ}$  failed. In a prolonged reaction with di-t-butyl peroxide, as a radical reaction initiator, no addition products were observed. This could, however, be due to a low decomposition rate of the peroxide at the boiling point of the reaction mixture. An experiment with small scale apparatus and irradiation with a U.V. lamp onto neat reactants also failed to form addition products.

Oct-4-yne and Phenylphosphine: The reaction of oct-4-yne with phenylphosphine was observed at  $131^{\circ}$ . The product was shown to consist exclusively of a 1:1 adduct that was assigned to the geometric isomers of 1(1-propylpent-1-en)ylphenylphosphine (161 or 162). Spectral data agreed with this assignment and the n.m.r. spectrum, unlike those for products discussed previously, was conclusive for either of the isomers shown below.



The alkyl proton resonances, including [ 161 or 162 a) and c) ] formed a broad complex. The proton resonance for b) was a doublet of triplets  $J_{\text{Phb}}$  21 Hz,  $J_{\text{HbHc}}$  8 Hz which correlates with values expected from observations on similar systems<sup>23</sup>. The proton resonance for d) appeared to be a doublet of triplets  $J_{\text{PHd}}$  218 Hz,  $J_{\text{HdHa}}$  12 Hz. The coupling constant  $J_{\text{PHd}}$  is large but similar to that observed for diphenylphosphine<sup>142</sup>. When the reaction was repeated with longer reaction times no 2:1 adducts were observed. This suggested that a steric limitation was present for non-terminal alkynes at this temperature.

Since such clear coupling constants had been observed for this secondary phosphine, an experiment to utilise this knowledge with respect to the problems of isomer identification was made. If the analogous secondary phosphine could be prepared from oct-1-yne and phenylphosphine, the nature of the n.m.r. adsorbtion and size of coupling constants could distinguish between 163 and 164.



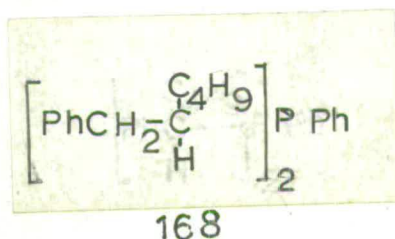
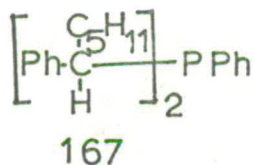
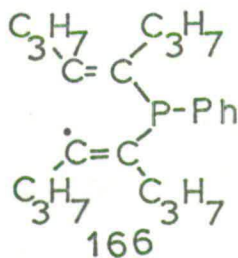
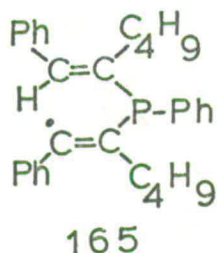
Therefore, oct-1-yne and phenylphosphine (slight excess) were reacted and dioct-1-enylphenylphosphine was obtained as before. This demonstrated that if the secondary phosphines 163 or 164 were intermediates then they were at least as reactive as phenylphosphine. This is a parallel to the study by Pellon<sup>127</sup> on chain transfer to primary and secondary phosphine and implies that a radical reaction is involved. A lower boiling distillate was also obtained and found to consist of a 1:1 adduct and a 1:1 adduct where the double bond had been reduced. This complication ruled out the possibility of deciding between isomers from coupling constants since the n.m.r. spectra were too complex.

1-Phenylhex-1-yne with Phenylphosphine: In another experiment 1-phenylhex-1-yne ( $\text{PhC}\equiv\text{C}-\text{C}_4\text{H}_9$ ) was allowed to react with phenylphosphine and gave an adduct of two molecules of alkyne and one of the phosphine. This assignment was based on i.r. and mass spectral data. The n.m.r. spectrum gave a reasonable peak integral for fifteen aromatic protons relative to eighteen alkyl protons. No justifiable

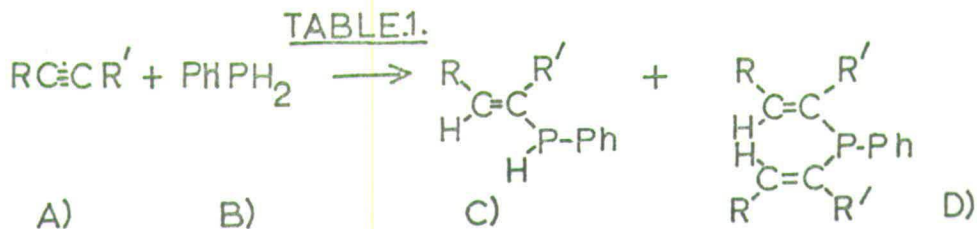
assignments could be made for the expected two vinyl protons.

It is possible that these resonances are coupled to adjacent alkyl protons and to phosphorus with the result that part of the sextet of peaks expected lies under the aromatic region.

It is interesting to note that this alkyne has not suffered the same limitation of the oct-4-yne adduct, since diaddition of phenylphosphine has occurred. This difference is almost certainly due to the higher reaction temperature of  $160^{\circ}$ , although the greater stability of possible radical intermediates 165 over 166 following reversible additions could be involved.



In a reaction with excess phenylphosphine and 1-phenylhex-1-yne at  $160^{\circ}$  for 12 h. the only product isolated was shown to be a mixture of reduced 1:1 adducts. The assigned structures 1(1-phenylhexyl)phenylphosphine (167) and 1(1-benzylpentyl)phenylphosphine (168) agreed with i.r. and mass spectral data. The suggestion that two isomers were involved was based on the observation of two sets of double doublets with slightly different resonance positions, both with  $J_{PH}$  210 Hz, but one with  $J_{HH}$  6 Hz and the other with  $J_{HH}$  8 Hz. The similarity of these peak integrals,



R	R'	Temp. <sup>a)</sup>	Ratio of Reactants A:B	Product
C <sub>4</sub> H <sub>9</sub>	H	71	2:1	no reaction
C <sub>5</sub> H <sub>11</sub>	H	100	2:1	D
C <sub>6</sub> H <sub>13</sub>	H	125	2:1 1:1	D C&D&reduction
Ph	H	140	2:1	D
C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>	131	2:1	C
C <sub>4</sub> H <sub>9</sub>	Ph	140	2:1 1:1	D&reduction C&reduction

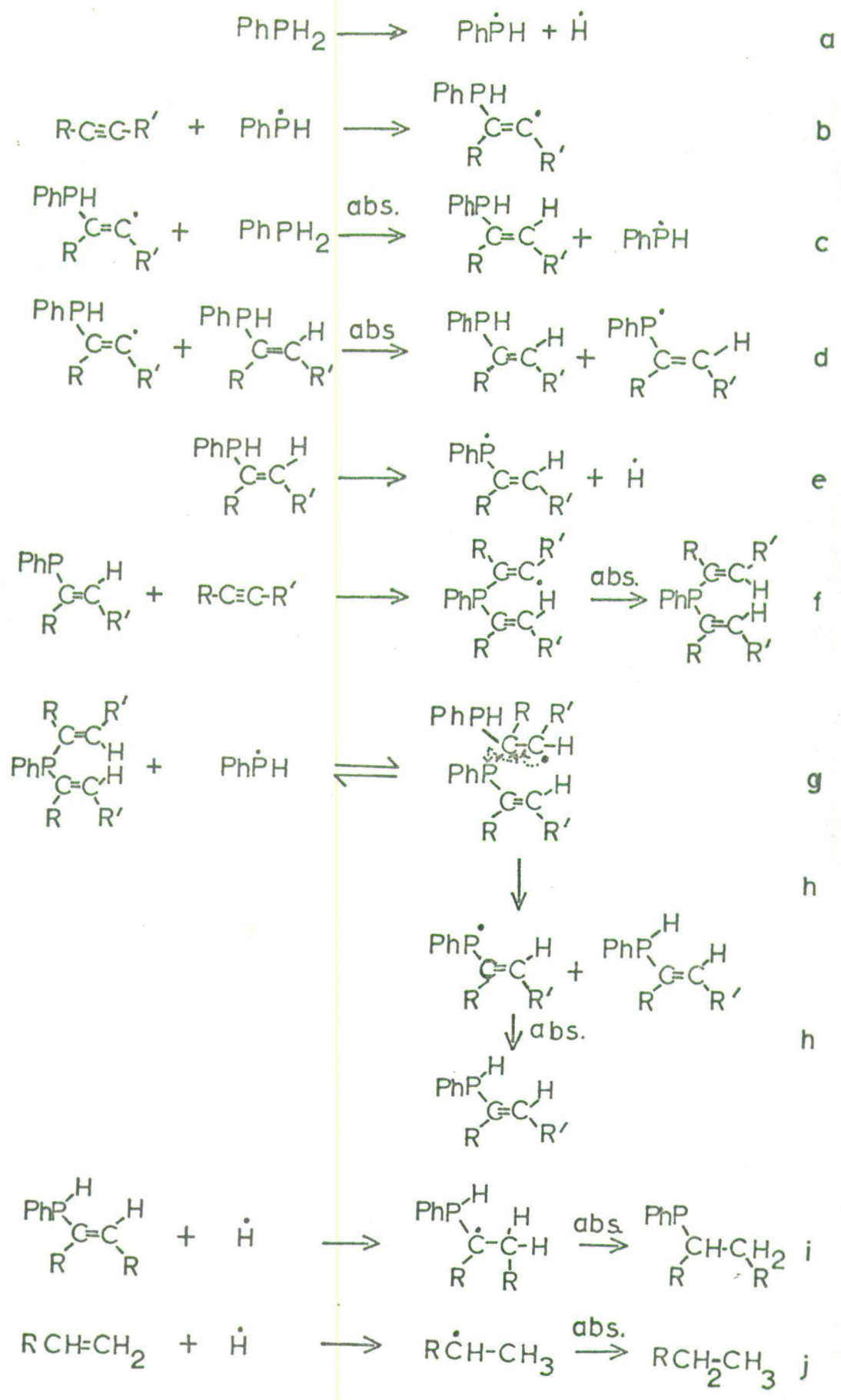
Note a) These temperatures are the boiling points of the alkynes or the oil bath, whichever was the lower.

although close together, ruled out an impurity of oxide causing a second set of peaks because there was no strong P=O frequency in the i.r. spectrum.

The results of these experiments are summarised in table 1. When investigating the addition reaction of phenylphosphine with these substituted alkynes a reduction of some of the double bonds in some of the products has been observed. Before discussing the possible mechanism of these addition reactions it is necessary to introduce the results of experiments designed to test the nature of this reduction step.

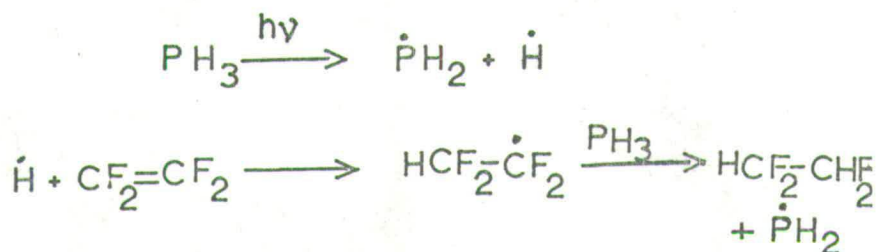
Reduction Reactions of Phenylphosphine: Dioctyl-1-enylphenylphosphine ( $(C_6H_{13}CH=CH)_2-PPh$ ) was allowed to react with a molar excess of phenylphosphine and gave a 58% yield of octylphenylphosphine ( $C_8H_{17}PPh$ ), a secondary phosphine. This product showed that an unusual reaction had occurred, which included reduction and fragmentation steps. A reaction with the corresponding phosphine oxide ( $(C_6H_{13}CH=CH)_2P(O)Ph$ ) failed to give either a reduced or fragmented product. This suggests that the reaction involves a similar reversible step to that of phosphine radicals to alkenes, reported by Pellon<sup>9</sup>, but that this reversible addition does not occur with phosphine oxides. The work by Pellon involved observations of the characteristic trans-alkene adsorption in the i.r. spectrum but the author did not analyse for products due to a reduction step.

A reaction of phenylphosphine with dec-1-ene is reported here and the presence of reduced alkene, decane, was observed besides the expected reduction product, decylphenylphosphine. The choice of such a long chain alkene was made to ensure that the temperature was sufficiently high to obtain a reaction without



resorting to high pressure systems.

Observations by Burch et al.<sup>12</sup> have shown that a radical chain mechanism occurs in the reaction of phosphine with fluoredated alkenes and have reported reduced products. These authors explain the reduced product by the addition and abstraction steps below:



The addition, reduction and fragmentation products of the reactions reported here suggest that a similar radical process is involved and the scheme (opp.) is proposed. All the reactions in the literature reported to proceed by radical chain mechanisms have been initiated by the decomposition of peroxide or azonitrile compounds or irradiation by U.V. light. In the reactions reported here no initiation was used and the process of the first step is in some doubt, because thermal fragmentation must have occurred as low as 100°. It is possible that some impurity of a biphosphine, dissolved oxygen, or incident U.V. light starts chain reactions by steps a) or e).

The steps a) to f) satisfactorily explain the addition products obtained with aryl and alkyl substituted alkynes. The step d) or e) involves chain transfer to a secondary phosphino radical and competes favourably with steps a) and c) which involve a primary phosphino radical. Thus even in the reaction of oct-1-yne, with equimolar phenylphosphine, diaddition of alkyne to the phosphine does occur. This observation indicates that a stepwise

mechanism does not operate. The observation of reduced products in experiments with excess phenylphosphine is explained by step i) and is a parallel to that proposed by Burch et al.<sup>12</sup>. The unexpected saturated secondary phosphine isolated from the reaction of phenylphosphine with dioct-1-enylphenylphosphine is explained by steps g) and h), which incorporate a reversible addition. This suggestion of a reversible addition is supported by observations on the isomerisation, during a reversible addition, of cis- to trans- but-2-ene made by Pellon<sup>9</sup> and was discussed earlier. That the corresponding phosphine oxide did not undergo this unusual fragmentation reaction also supports the reversible step suggested.

The critical temperature for these addition and reduction reactions appeared to lie between about 71° and 100°, the boiling point at atmospheric pressure of hex-1-yne, which did not react, and hept-1-yne which did. Hoffmann<sup>15</sup> reported a slow reaction between diphenylphosphine and 1-phenyleth-1-yne ( $\text{PhC}\equiv\text{CH}$ ) at 100° and it is possible that this is the limiting temperature.

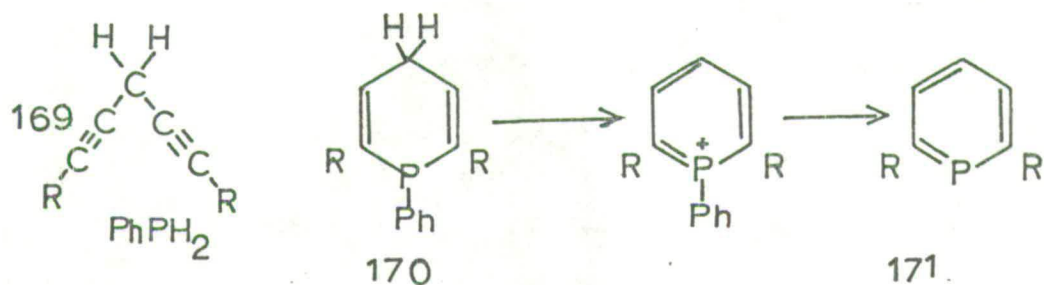
All the reactions from the literature used in evidence for a radical process have in fact been induced chemically or photochemically. The products reported here do suggest that a radical mechanism operates, but these temperatures are low for homolytic cleavage. The possibility that several different mechanisms operate cannot therefore be ruled out.

The main object of studying the reaction of phenylphosphine with alkynes was to identify the position of attack. It has been proved that a general thermal reaction occurs between phenylphosphine and alkynes and that the phosphine reacts preferentially in the terminal position with monosubstituted alkynes. With

disubstituted alkynes a similar general reaction occurs, but it was not possible to distinguish between isomers and thus prove whether the addition is on the alkyl or aryl substituted carbons in examples such as 1-phenylhex-1-yne ( $\text{PhC}\equiv\text{C}-\text{C}_4\text{H}_9$ ). During this investigation an unusual fragmentation and reduction reaction was observed and a mechanism for this reaction has been proposed.

III B. THE REACTION OF PHENYLPHOSPHINE WITH ALKYLDIYNES.

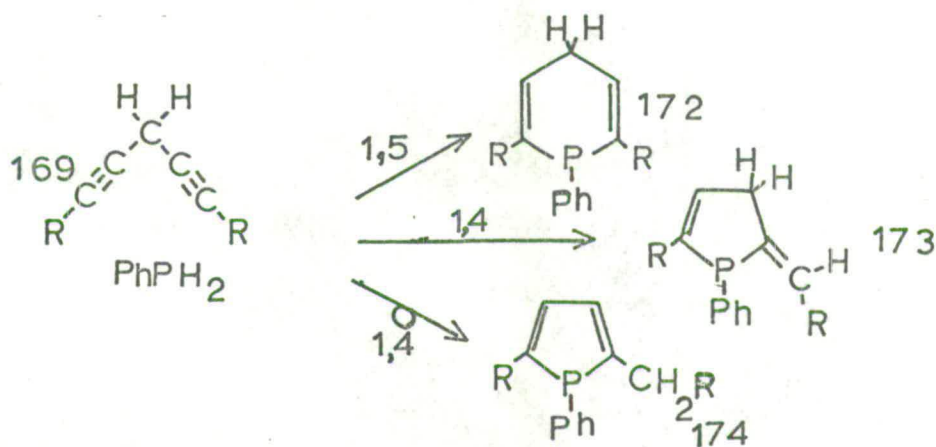
Märkl and Potthast<sup>34</sup> have used a base catalysed reaction of phenylphosphine with conjugated alkyldiynes ( $RC\equiv C-C\equiv C-R$ ) to form phospholes. The present study investigated the possible extension of this type of reaction using the reaction of a nonconjugated penta-1,4-diyne ("skipped" diyne) (169) with phenylphosphine, Märkl's basic conditions could not, however, be used because the diyne (169) would have isomerised<sup>104</sup>. The intention was that thermal addition of the phosphine followed by 1,5-cyclisation could form a 1,4-dihydrophosphorin (170), hydride transfer and electrolytic cleavage of P-Ph would then lead to a phosphorin (171).



The work discussed previously (Ch. III. A) did not indicate that alkyl or aryl substituents of the alkyldiyne (169) would promote addition specifically to the 1 and 5 positions. Therefore it was decided to start the investigation with trideca-5,8-diyne (169:  $R=C_4H_9$ ).

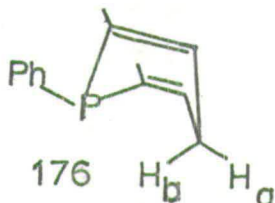
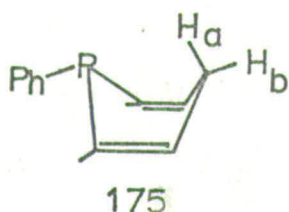
Trideca-5,8-diyne with Phenylphosphine: When phenylphosphine and trideca-5,8-diyne were heated to  $160^\circ$  a reaction was observed that gave two main distillates. The first distillate was found to consist of three components, which could not be separated by high vacuum distillation and were too readily oxidised for separation by column chromatography. The components were distinguished by peaks

in the  $^{31}\text{P}$  n.m.r. spectrum at  $-4.1$ ,  $-4.68$  and  $+7.72$  p.p.m., normal positions for phospholes<sup>56</sup> and aryl and alkyl substituted tertiary phosphines<sup>128</sup>. This distillate was proved to be a mixture of 1:1 adducts by good analytical data and a clear mass spectrum, which showed a cracking pattern commensurate with the breakdown of butyl chains. The mixture definitely contained cyclised products because no alkyne ( $\text{C}\equiv\text{C}$ ), or ( $\text{P}-\text{H}$ ) adsorptions appeared in the i.r. spectrum at  $2190$  or  $2220\text{ cm}^{-1}$ . The ( $\text{P}-\text{C}=\text{C}$ ) adsorption was weak at  $1595\text{ cm}^{-1}$ <sup>129</sup>. This evidence suggests that addition had occurred in the 1 or 2 positions and then cyclisation in the 4 or 5 positions to give (172), (173) and a proton or hydrogen migration to form (174).



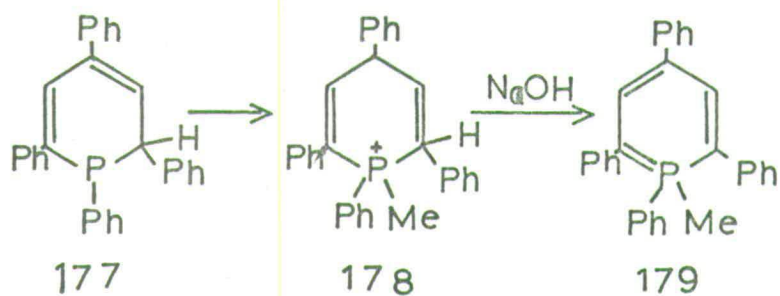
N.m.r. studies support this suggestion showing a doublet at  $\tau$ ; 3.52, which was assigned to the phosphole (174)  $J_{\text{PH}}$  13 Hz, which is normal for phosphole rings of this type<sup>130</sup>. A complex resonance was observed at  $\tau$ ; 3.9-4.3 and assigned to the vinyl protons of the hydrophosphorin (172) and the phosphol-2-ene (173) structures. Another complex pattern at  $\tau$ ; 6.5-7.0 was due to the cyclic methylene groups of the hydrophosphorin (172) and phospholene (173) rings. This methylene pattern consisted of

two distinct, overlying complexes with fine structure apparent to the low field side, (App. II. fig. 1). These complexes did not alter when spectra were taken at intervals from  $-40^{\circ}$  to  $+55^{\circ}$ . This implied that the two complex patterns were due to different compounds and not different conformations (175 or 176).

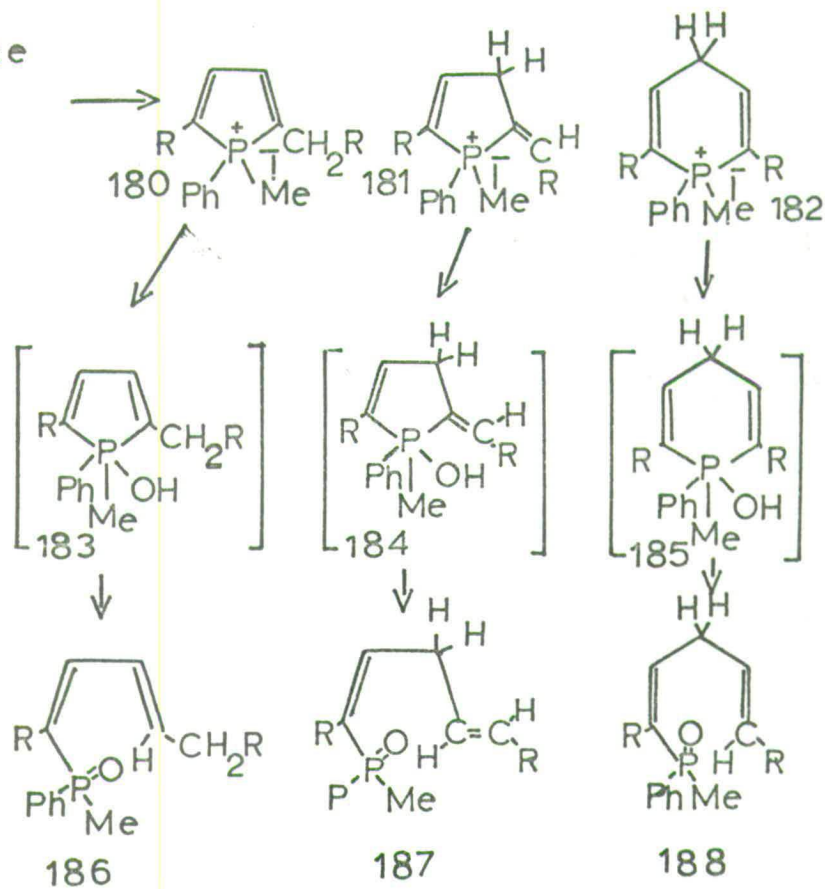


Spin decoupling experiments were performed on the region  $\tau$ ; 3.9-4.3 with respect to  $\tau$ ; 6.5-7.0. Irradiation corresponding to  $\tau$ ; 6.63 caused the complex centred at  $\tau$ ; 3.98 to collapse to two doublets,  $J_{PH}$  4 Hz and  $J_{PH}$  2.5 Hz, and was assigned to the phospholene (173) vinyl protons. A complex to the side at  $\tau$ ; 4.18 was also affected and gave a broad singlet that could represent a geometric isomer of (173). Irradiation corresponding to  $\tau$ ; 6.68 caused the complex centred at  $\tau$ ; 4.08 to change, and although it did not yield the expected symmetric pattern, it was assigned to the dihydrophosphorin (172). The proximity of the peaks makes execution of these spin decoupling experiments difficult and analysis of the results speculative.

Preparative g.l.c. was performed on this first distillate and gave several fractions. The first of these had a parent ion of  $m/e$ ; 286 (calc. for  $C_{19}H_{27}P$ ,  $m/e$ ; 286) in the mass spectrum showing that decomposition had not occurred. This oil oxidised rapidly in deuteriochloroform to give a compound, which now had a parent ion  $m/e$ ; 302 (calc. for  $C_{19}H_{27}OP$ ,  $m/e$ ; 302). Thin film i.r. studies showed adsorption at  $2240\text{ cm}^{-1}$  for (P-H) and  $2210\text{ cm}^{-1}$  for



First distillate  
 mixture  
 +  
 MeI



(C≡C) and oxidation on exposure to the atmosphere rapidly gave an adsorption at  $1170\text{ cm}^{-1}$  for (P=O). Thus from material that originally contained only cyclised components straight chain compounds were obtained that oxidised rapidly in solution. This conclusion was supported by n.m.r. studies, where the fine structure originally observed on the methylene region was soon lost.

The second preparative g.l.c. fraction obtained, gave a molecular ion of  $m/e$ ; 302 (calc. for  $\text{C}_{19}\text{H}_{27}\text{OP}$ ,  $m/e$ ; 302) and i.r. and n.m.r. spectra very similar to those observed for the first fraction after oxidation. It is possible that the solution used for chromatography was oxidising slowly and that the column phase ring opened both these components. Oxidation of the uncyclised first component subsequently gave identical products. The ease of ring opening is supported by observations on the reversibility of addition of phosphines to alkenes made by Pellon<sup>9</sup>. The present work proved that g.l.c. could not be used to separate the components contained in the original distillate.

In an attempt to demonstrate the nature of the components of the first distillate a set of sequential reactions were designed. The intention was to form a phosphorin with pentavalent phosphorus from the dihydrophosphorin component (172).

Märkl and Potthast<sup>69</sup> reported that a reaction between 1,2,4,6-tetraphenyl-1,2,-dihydrophosphorin (177) and methyl iodide followed by base gave 1-methyl-1,2,4,6-tetraphenylphosphorin (179).

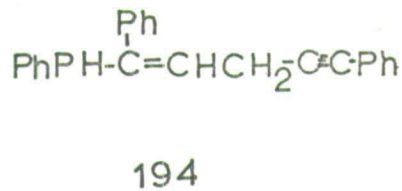
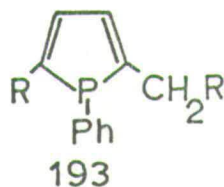
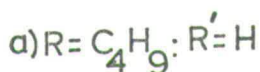
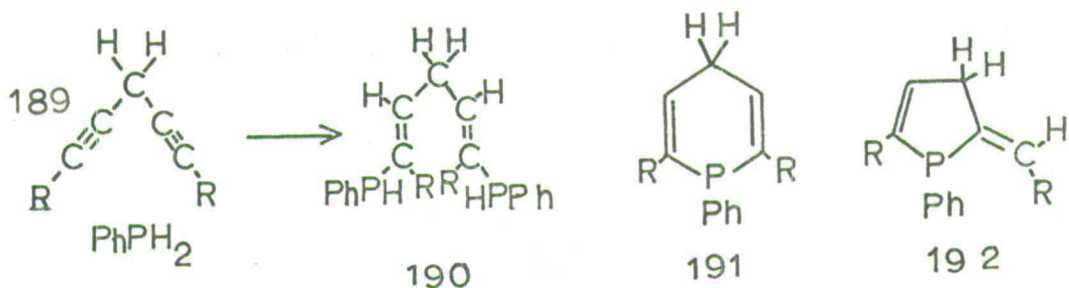
The first distillate, from the reaction reported here of phenylphosphine with trideca-5,8-diyne, was found to give an exothermic reaction with methyl iodide. Reaction of the oily product with sodium hydroxide solution gave nucleophilic attack at

the phosphonium centres of (180, 181, 182) and ring opening of the intermediates (183, 184, 185) under the driving force of formation of a P=O bond. The mixture of straight chain phosphine oxides obtained gave absorptions at  $1620\text{ cm}^{-1}$  for (P=C=C) and  $1170\text{ cm}^{-1}$  for (P=O) in the i.r. spectrum. Other spectral evidence, including  $^{31}\text{P}$  n.m.r. studies, support the assignment to a mixture of tertiary phosphine oxides. It was however impossible to separate or distinguish between the isomers formed (186, 187, 188). The ring opening reaction observed is a parallel to the report by Bergesen<sup>50</sup> on the reaction of 1-methyl-1,2,5-triphenylphosphonium iodide mentioned in the Introduction. Other bases used were triethylamine, pyridine and the sterically hindered 1,8-bis(dimethylamino)naphthalene, but no products containing a phosphorus ring were obtained.

Nona-1,4-diyne and Phenylphosphine: Results of work discussed previously has shown that phenylphosphine readily adds to the terminal position of alkynes. Ideally then, penta-1,4-diyne should be reacted with two terminal positions available. Since this substance would be gaseous, and require high pressures to give an addition reaction, nona-1,4-diyne (189a),  $\text{R}=\text{C}_4\text{H}_9$ ;  $\text{R}'=\text{H}$ ) was used and was found to require a temperature of  $160^\circ$  to obtain cyclised 1:1 adducts. A higher boiling fraction was obtained and shown to be the adduct formed by addition of two molecules of phenylphosphine to one of diyne. This compound probably has the structure (190a) although the integral of the n.m.r. resonances was not good.

The lower boiling fraction containing 1:1 cyclised adducts gave an n.m.r. spectrum very similar to that obtained for the trideca-5,8-diyne products, particularly in the methylene region. This complex had a well defined fine structure on the low

field side of the spectrum but less so to the high field side. The vinyl complex was also quite similar with two broad complex resonances. No doublet due to a phosphole component was observed although the U.V. spectrum had a comparable envelope to the previous case. The mixture is concluded to be a mixture of the dihydrophosphorin (191) and the phosphol-2-ene (192).



1,5-Diphenyl-1,4-diyne and Phenylphosphine: Similar experiments to those discussed above were performed using diynes with aryl substituents (189b)). In these cases more vigorous reactions were observed giving mixtures containing the phosphole (193 b)  $\text{R}=\text{R}'=\text{Ph}$ ) and the phosphol-2-ene (192,b)), but did not appear to contain a dihydrophosphorin component (191,b)). The n.m.r. spectrum of the mixture showed a doublet at  $\tau$ ; 6.82 J = 5 Hz assigned to the benzyl protons of the phosphole (193,b)). This resonance could not be due to the dihydrophosphorin (191,b)) methylene protons because these would give a triplet arising from coupling with two adjacent vinyl protons. The observed doublet at  $\tau$ 3.02 J = 11 Hz for the phosphole ring protons is normal for these compounds<sup>130</sup>. The other vinyl proton resonance observed was due to the phosphol-2-ene (192) component and is a doublet of triplets.

A similar reaction with t-butylbenzene as solvent was carried out and the reaction mixture was chromatographed. Anomalous results were obtained and the only identifiable product was a straight chain secondary phosphine (194). This suggests that the conditions were too mild to overcome a steric limitation to cyclisation. No realistic conclusions can, however, be made from a single product in low yield.

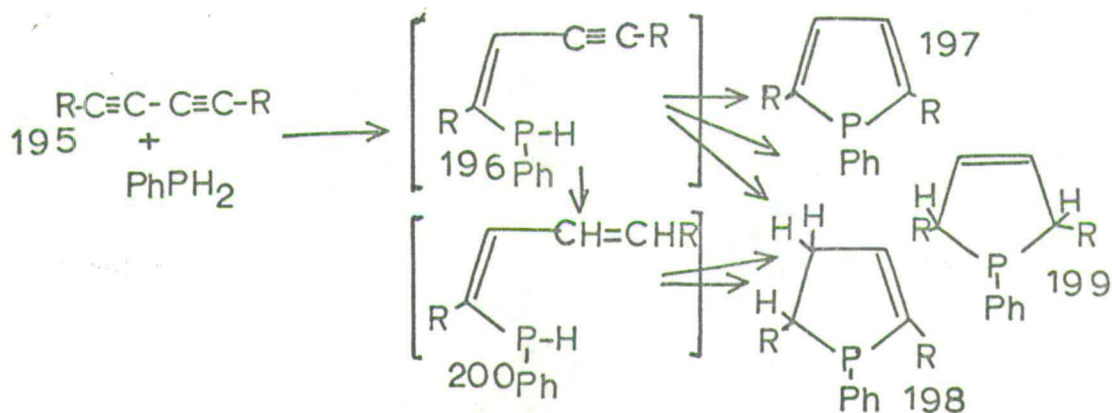
1-Phenyl-1,4-diyne ( $\text{PhC}\equiv\text{C}-\text{CH}_2-\text{C}\equiv\text{CH}$ ) gave an extremely vigorous reaction and only polymeric tars were obtained.

These results indicate that the thermal reaction of phenylphosphine and alkyl-1,4-diyne is not a simple route to 1,4-dihydrophosphorin, precursors of phosphorins unsubstituted in the o- or p- position. Experiments with phenylphosphine and alkyl-1,4-diyne-3-ol ( $\text{R}-\text{C}\equiv\text{C}-\text{CHOH}-\text{C}\equiv\text{C}-\text{R}$ ) were made by Lim<sup>131</sup>, who found similarly complex product mixtures. This worker did, however, observe a variation of products that appeared to depend on the steric influence of the substituents chosen.

Conjugated Dienes and Phenylphosphine: The simple thermal reaction of 1,3-dienes (195) with phenylphosphine as a route to phospholes was also considered. A very vigorous reaction was observed that gave several products that could not be separated by distillation or chromatography. The product from butadeca-6,8-diyne (195;  $\text{R}=\text{R}'=\text{C}_5\text{H}_{11}$ ) was shown to be a mixture of phosphole (197) and phospholene (198 and 199) components, indicating that a similar reduction process to that observed with simple alkynes had occurred.

The presence of both isomeric phospholenes (198 and 199) is inferred from the complexity of the vinyl region in the n.m.r. spectrum (App. II. fig. 2). A doublet at  $\tau$  ; 2.95 was observed for

the phosphol-3-ene and a complex at  $\tau$  ; 3.2-3.3 for the phosphol-2-ene. A broad doublet was observed at  $\tau$  ; 3.96 and assigned to the phosphole (197) on the basis that a similar position and coupling was observed with pure 2,5-di-*t*-butyl-1-phenylphosphole and values reported by Märkl<sup>34</sup>. The sample had oxidised during column chromatography and impurities confused the picture further.

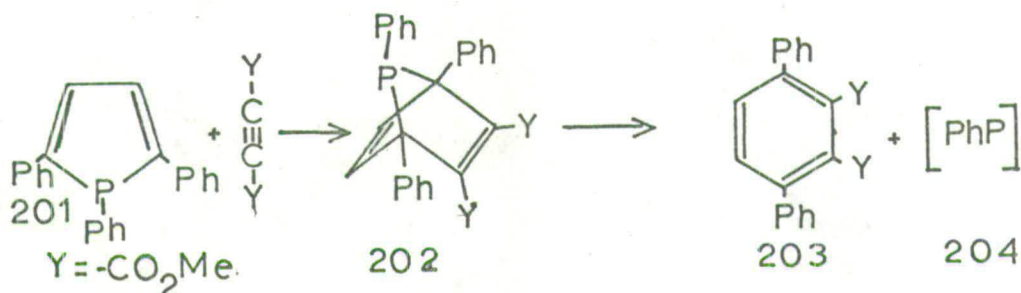


Other experiments using diynes with shorter alkyl chains were also performed and gave exactly comparable results. High boiling fractions were observed and were associated with diadditions of phenylphosphine to the diynes and addition of two molecules of the diyne to two of the phosphine. These fractions were obtained even when the relative molar proportions of the reactants were changed. Thus the low yields observed in the original experiments (29%) are probably due to polymerisation and reduction side reactions.

Thus an increase in phenylphosphine molar ratio led to increased reduction, while an increase in diyne molar ratio led to double addition to the phosphine. These results indicated that the simple thermal reaction could not be used to prepare pure phospholes from diynes and phenylphosphine.

III C THE FORMATION AND REACTIONS OF PHOSPHOLIMINES.

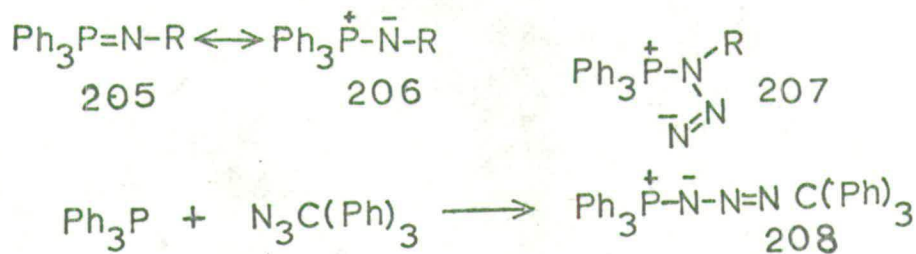
The reactions and properties of phosphole derivatives have been reviewed in the Introduction. This has shown that doubt exists concerning the degree of aromatic character of phospholes and phosphole derivatives. One interesting type of reaction reported by Campbell et al.<sup>42</sup>, which demonstrated the diene character of 1,2,5-triphenylphosphole (201), was that involving dimethyl acetylenedicarboxylate. In this reaction a phosphorus containing fragment, so far unidentified, was extruded in a retro Diels-Alder step, probably via intermediate (202), to form dimethyl 3,6-diphenylphthalate (203).



It was therefore decided that the present study should attempt to extend the range of phosphole derivatives to include larger substituents on phosphorus.

The Reaction of Phospholes with Azides: The reaction used to extend the available phosphole derivatives was that between a variety of substituted azides and some phospholes. This reaction also indicates the availability of the phosphorus lone pair of electrons. It is a parallel to that reported by Staudinger<sup>132</sup> between triphenylphosphine (Ph<sub>3</sub>P) and some azides, for the formation of phosphinimines (205:206). A later study by Leffler et al.<sup>133</sup> isolated a triaza- intermediate from the reaction of triphenylphosphine with triphenylmethyl azide. These workers postulated

a straight chain form (208). In a similar reaction Horner and Gross<sup>134</sup> assumed that an intermediate of the form (207) had been involved following their kinetic studies. This work suggested that nucleophilic attack by the phosphine on the azide had occurred.

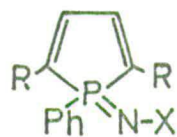


Franz and Osuch<sup>135</sup> isolated an intermediate with tosylazide that they believed was in the straight chain form because no adsorbance at  $2100\text{ cm}^{-1}$  for an azide frequency was observed. They did report that different products were obtained in different solvents. Johnson<sup>136</sup> has reviewed these reactions and concluded that the structures of the products and mechanism of the reaction require a detailed study for clarification.

This present investigation revealed a reaction between 1,2,5-triphenylphosphole (209;  $\text{R}=\text{R}'=\text{Ph}$ ) and a variety of azides. Evolution of nitrogen just below the boiling point of the solvent (dioxan) was observed and the novel phosphole derivatives, phospholimines (212) (App. III. fig. 3,4,5.) isolated by crystallisation. The relatively low temperature indicated that a discrete nitrene intermediate could be excluded and suggested that a dipolar or ylid species was involved. If a straight chain ylid (210) is involved then the triazaphosphetane intermediate (211) must also take part. Phosphorus is known to readily undergo four centre reactions and in this case forms the phospholimine (212) and nitrogen. The alternative dipolar species (213) cannot be ruled out on the

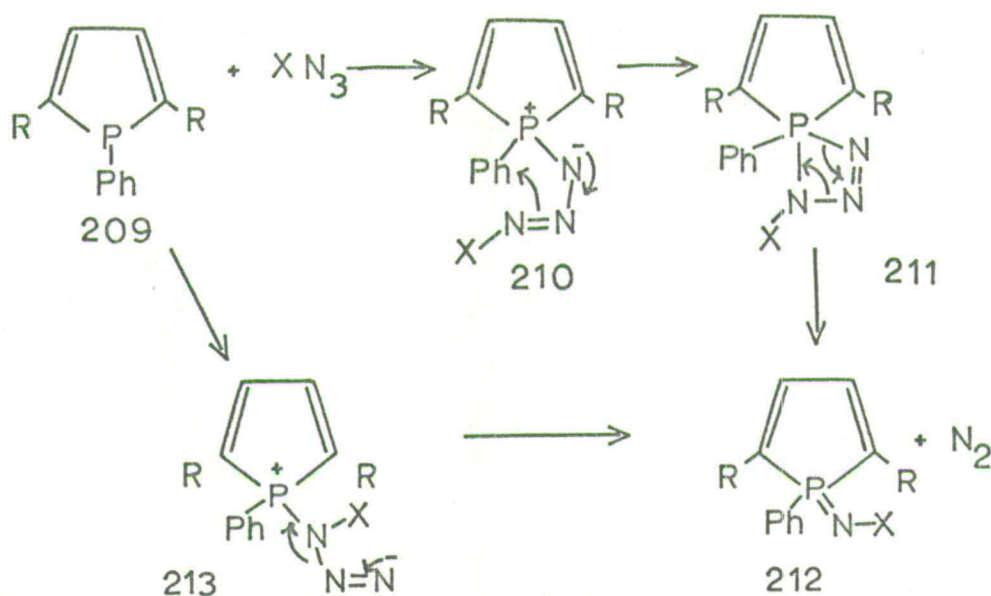
TABLE.2.

Spectral Data on Phospholimines :



R	X	-P=N- cm <sup>-1</sup>	Ring Protons at 100MHz, $\tau$ :	J <sub>PH</sub>	
Ph	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -	1285	2.46 & 2.79	33	
Ph	Ph-	1280	2.40	2.73	33
Ph	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> -	1290	2.30	2.64	34
Ph	p-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> -	1260	2.41	2.81	41
Ph	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> -	1380	2.38	2.74	36
t-butyl	Ph-	1315	3.10	3.48	36
Ph	1,2,5-triphenyl- phosphole oxide	-	2.58	2.96	36

evidence obtained. The reaction of phospholes with chloramine T was found to give a similar phospholimine (212;  $X = -SO_2C_6H_4CH_3$ ).



The i.r. spectra of this series of compounds gave a stretching frequency of  $1260\text{--}1380\text{ cm}^{-1}$  for  $(\text{P}=\text{N}-\text{X})$  (Table 2). These values are similar to those observed by Corbridge<sup>137</sup> for delocalised  $\text{P}=\text{N}$  systems ( $1260\text{--}1385\text{ cm}^{-1}$ ). This implies that there is some contribution of the ylid form ( $\text{P}^+-\text{N}^-$ ). N.m.r. studies initially gave some problems because compounds such as (212;  $X = p\text{-NO}_2\text{C}_6\text{H}_4-$ ) gave a deformed doublet at  $\tau$ ; 3.1-3.3, (App. II fig. 4). Expansion of this "doublet" showed further splitting, which eliminated the possibility that this resonance was due to the phospholimine ring protons. Two sharp resonances at  $\tau$ ; 2.30 and  $\tau$ ; 2.64 overlie the aromatic region and were assigned to the elusive ring proton resonances. Similar peaks were observed in other phospholimines by analogy to this example and are tabulated (Table 2).

An interesting feature of these phospholimines is that both (212;  $X = -SO_2-C_6H_4CH_3$ ) and (212;  $X = p\text{-NO}_2-C_6H_4-$ ) (App. II Fig. 4 and 5) gave  $A_2B_2$  resonance patterns for the substituent ring protons.

With the phospholimine (212; X=pCH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>) the ring protons gave a broad singlet at relatively high field  $\tau$ ; 3.16 and not

an A<sub>2</sub>B<sub>2</sub> system. This suggests that the electron donating effect of the (-CH<sub>3</sub>) group is balanced equally by that of (P=N).

In N-phenyl-2,5-di-t-butyl-1-phenylphospholimine (212; R=-C(CH<sub>3</sub>)<sub>3</sub>) the imine ring protons (=N-Ph) were observed as a multiplet and double irradiation was required to identify which resonances were due to the phospholimine ring protons. In all cases the o-protons of the phenyl group on phosphorus (Ph-P=N-X) are further down field than the normal aromatic position. This is especially clear with (212; X=-SO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>) where these protons appear as an octet with  $J_{PH} = 12$  Hz,  $J_{HoHm} = 8$  Hz,  $J_{HoHp} = 2$  Hz. These observations support the suggestion of a contribution from the ylid form ( $\overset{+}{P}=\overset{-}{N}$ ).

The relative ease of formation of these phospholimines (212) is evidence of the availability of the phosphorus lone pair. It also highlights the dominance of the chemistry of phosphorus over any heteroaromatic properties the system may have.

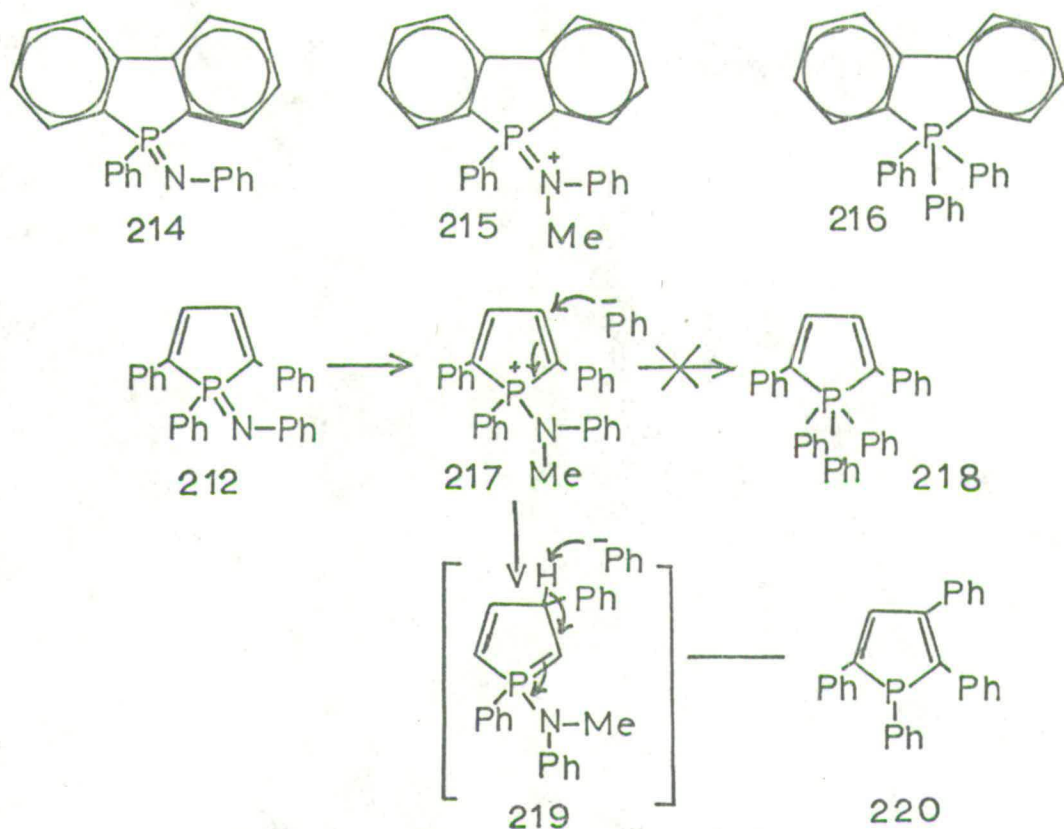
The crystalline phospholimines all have intense colouration varying from yellow ochre (212; X=-CO<sub>2</sub>Et) to burgundy red (212; X=p-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-). This variation is not as distinct in the U.V. and visible spectra where a very similar envelope is observed. The peaks at 405-380 nm have a fairly high extinction coefficient ( $\epsilon$ ; 18,000 to 25,000), but is absent in (212; R=t-butyl, X=Ph). The variation in position and intensity of this peak with substituents implies that it is due to conjugation of the group (P=N-) with the two phenyl rings, while the others at higher energy are more likely due to the (P-Ph) or phosphole ring.

Reaction of Phospholimines: An attempt to form the N-p-azidophenyl derivative from (212; X=pNO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-) by reduction to N-p-aminophenyl-1,2,5-triphenylphospholimine (212; X=p NH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-) was unsuccessful. The standard iron and hydrochloric acid reduction of nitro groups was used, but gave only 1,2,5-triphenylphosphole oxide. The phospholimine had behaved as an ylid and hydrolysed in acid conditions.

To date the only simple phospholes reported with penta-valent phosphorus have undergone several structural reappraisals, some of which have been discussed in the Introduction. Wittig and Kochendorfer<sup>138</sup> have prepared a fused ring phosphole with penta-valent phosphorus (216). The reaction involved N-phenyl-1-phenyldibenzophospholimine (214). This compound was methylated and then reacted with phenyl lithium to displace the methylphenyl-amino group. The suggested structure for the intermediate salt (215) curiously suggested that a +ve charge was localised on nitrogen, when it is much more likely to reside almost entirely on phosphorus.

A similar methylation step was observed for N-phenyl-1,2,5-triphenylphospholimine (212) and 1(methylamino)-1,2,5-triphenylphospholium iodide (217) was isolated. The coupling constant for phosphorus with phospholimine ring protons has increased  $J_{PH}$  45 Hz. This suggested that either the +ve charge causes more efficient coupling or that there had been a change in dihedral angle to approach closer to 180°, where maximum coupling occurs. The phospholium iodide (217) was allowed to react with phenyl lithium but no clear products were isolated. Column chromatography gave a little oil that speculation on spectral data of an impure

sample suggested that 1,2,3,5-tetraphenylphosphole (220) had been formed, but no 1,1,2,3,5-pentaphenylphosphole (218) was detected.



Since 1,2,5-triphenylphosphole is a relatively stable system an attempt was made to photolyse N-phenyl-1,2,5-triphenylphospholimine (212), reform the phosphole and produce a phenyl nitrene. A similar reaction of N-*t*-butyltriphenylphosphinimine (221) was reported by Zimmer and Jugawant<sup>141</sup>. These workers found a complex mixture of products that included *t*-butylamine, a product of double hydrogen abstraction by the nitrene. In a photolysis reaction of the phospholimine in diethylamine a reaction was indicated by the change in colour of the solution, but neither aniline nor 2-diethyl-3H-azepine, products of nitrene formation, were observed. This route to phenyl nitrene had therefore failed.

III D. THE REACTION OF PHOSPHOLE AND PYRROLE DERIVATIVES WITH  
DIMETHYL ACETYLENEDICARBOXYLATE.

The possible use of a retro Diels-Alder reaction as a source of reactive intermediates has been briefly reviewed in the Introduction. Braye et al.<sup>33</sup> and Campbell et al.<sup>42</sup> considered the reaction of phosphole derivatives with dimethyl acetylenedicarboxylate. Both groups of workers were unable to isolate a bridged Diels-Alder adduct (222) and only found the corresponding phthalate (224) following aromatisation and extrusion of a phosphorus fragment. Schmidt et al.<sup>93</sup> considered this reaction when looking for another route to the phosphorus reactive intermediate phenylphosphidene ( $\text{Ph}\ddot{\text{P}}$ ) which they claimed to have formed previously<sup>139</sup>. These workers attempted to obtain the bridged adduct (222) by the standard chlorosilane deoxygenation of the corresponding oxide (223) prepared by a circuitous route. These workers only obtained the phthalate (224) and did not report a search for the extruded phosphorus fragment.

Diels-Alder Reaction of Phospholimines: The present study considered the Diels-Alder reaction of phospholimines and other related derivatives, where the larger substituents on phosphorus could stabilise a reactive intermediate and facilitate its identification.

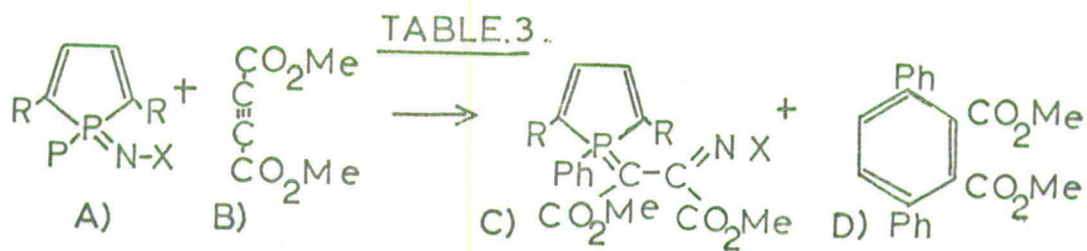
Thus N-tolyl-1,2,5-triphenylphospholimine (226;  $\text{X}=\text{pCH}_3\text{-C}_6\text{H}_4\text{-}$ ) was reacted with dimethyl acetylenedicarboxylate at 105° with t-butylbenzene as solvent. The product was shown by analysis and mass spectral data to be a 1:1 adduct, but the i.r. spectrum included peaks at 1660 (C=N) and 1350 (P=C)  $\text{cm}^{-1}$ , besides those expected for the phosphole moiety. The n.m.r. spectrum showed two distinct resonances for the methoxyl protons, which could not be



due to coupling with phosphorus or another proton (App.II.fig. 6). Moreover, the singlet originally observed for the phospholimine ring protons now resonated as a distinct  $A_2B_2$  system. This demonstrated that the environment of this ring had changed considerably. All the reasonable structures for the compound ( $X=\underline{p}CH_3-C_6H_4$ ) are represented in the scheme opposite. If the expected bridge-head adducts (225) had been isolated, the observed data would require a 50:50 mixture of two conformations (225a and 225b). The different methoxyl resonances would then be explained by an involvement of the imine double bond with those of the ring. If, however, the imine bond altered the environment of the methoxyl protons, a similar alteration would have been observed for the vinyl protons. This was not observed and since the difference in resonance position for the methoxyl protons would probably be too large, this explanation was rejected. The phosphorane structure (231) would certainly satisfy the different methoxyl resonances. The observed doublet overlying the aromatic region in the n.m.r. spectra (App.II fig. 6.) could be due to a single proton, but since no bridge-head proton resonance was observed, this isomer was also rejected.

The true explanation lies in the formation of isomer (230) by two consecutive four-centre reactions depicted in the scheme opposite. Phosphorus derivatives are known to react readily by this path because phosphorus to carbon bonds are longer than normal carbon-carbon bonds and normal steric considerations are not so important. It was therefore decided to investigate this reaction and test if intermediate (228) was involved by altering the substituents on nitrogen.

A similar reaction has been reported of phosphinimines



R	X	Solvent	Temp. °C	Ratio A:B	Yield		Analysis
					C%	D%	
Ph	-tolyl	<u>t</u> -butyl benzene	105	1:1	40.2	-	cryst.
"	"	"	105	1:1	63.8	4.1	col.
Ph	Ph	<u>t</u> -butyl benzene	105	1:1	10.0	10.0	cryst.
"	"	"	105	1:1	5.6	6.0	col.
Ph	<u>p</u> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<u>t</u> -butyl benzene	105	1:1	8.0	3.0	cryst.
"	"	"	160	1:1	-	70.8	col.
Ph	-CO <sub>2</sub> Et	<u>t</u> -butyl benzene	105	1:1	-	34.0	cryst.
"	"	"	130	1:1	-	57.0	col.
Ph	-tosyl	<u>t</u> -butyl benzene	105	1:1	-	-	-
"	"	"	160	excess B	-	100.0	cryst. & col.
"	"	<u>p</u> -dimethoxy benzene	160	1:1	-	23.0	col.
<u>t</u> -butyl	Ph	<u>t</u> -butyl benzene	105	1:1	30.0*	-	col.
1,2,5-triphenyl-phosphole oxide		<u>t</u> -butyl benzene	105	1:1	-	87.0	cryst.
"		cyclohexene	95	1:1	-	33.0	cryst. & distill.

\* The structure of this 1:1 adduct is discussed in Ch. III sect. D.

cryst. = fractional crystallisation.

col. = column chromatography on alumina.

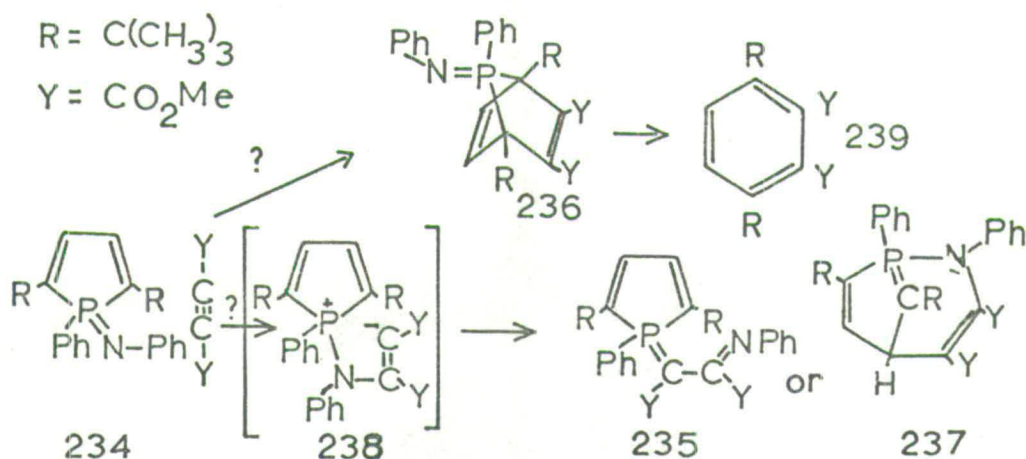
(232) with dimethyl acetylenedicarboxylate by Brown et al.<sup>140</sup> These workers found that an ethylphosphinidene (233) had been formed and suggested that a four-centre reaction had occurred. They found that substituents with increased electron withdrawing power reduced the yield of ethylphosphinidene (233). This implies that nucleophilic attack by nitrogen on the relatively electron deficient acetylenic ester is the first step.

A series of phospholimines were therefore allowed to react with the alkyne to test the mechanism of the first step. The reactions were normally analysed by both fractional crystallisation and column chromatography and the results are summarised in Table 3 opposite.

It was found that with 1,2,5-triphenylphospholimines (226) only the N-tolyl case ( $X = \text{pCH}_2\text{C}_6\text{H}_4$ ) predominantly formed the ethylphospholidene (230). It appeared that the N-phenyl substituent of the phospholimines (226; X=Ph) represented the turning point because low yields of both possible products (224 and 230) were observed. With substituents on nitrogen of high electron withdrawing power (226; X=tosyl; X= $-\text{CO}_2\text{Et}$ ), no ethyl phospholidenes (230) were observed. Brown et al.<sup>140</sup> found that these substituents also failed to give the corresponding phosphinidenes (233), but that N-p-nitrophenyltriphenylphosphinimine (232) did. They found that two nitro groups were required on the imine ring of their phosphinimines before the reaction failed. This suggests that, in the compounds studied here, the phosphole ring reduces the nucleophilicity of the (-P=N-) group more than the three phenyl groups of the phosphinimines studied by Brown or, which is more likely, presents an easier alternative reaction path. The low solubility of some of

the more polar phospholimines (226; X=tosyl) in the solvent (t-butylbenzene) meant that higher temperatures had to be used for a realistic concentration of reactant.

It has been conclusively shown that electron withdrawing groups on nitrogen reduce the yields of phospholidenes (230) in the reactions studied. This indicated that the reaction of the phospholimines (226) probably proceeds by nucleophilic attack by the nitrogen group on the alkyne to form (228) rather than electrophilic attack by an ylid form of the phospholimine to give (227). The intermediate is, however, involved after both initiation steps and is almost certainly present.



The reaction of N-phenyl-di-t-butylphospholimine (234) with dimethyl acetylenedicarboxylate was not as straightforward. The product obtained was proved to be a 1:1 adduct by mass spectroscopy but the n.m.r. spectrum contained some anomalies. The methoxyl resonance appeared as a broad singlet with some fine structure and a doublet. A similar complexity of three peaks was also observed for the t-butyl resonance. This implies that the phospholidene isomer (235) can only be present if it is one component of a

mixture. The alternative isomers (236) would also only give single resonances for the t-butyl groups. Thus isomer (237) must be considered as a possibility. This requires that attack by the intermediate has occurred (238) on the 3 position of the phosphorus ring rather than on phosphorus itself. The very different environment for the t-butyl and methoxyl protons would certainly cause two sets of doublets.

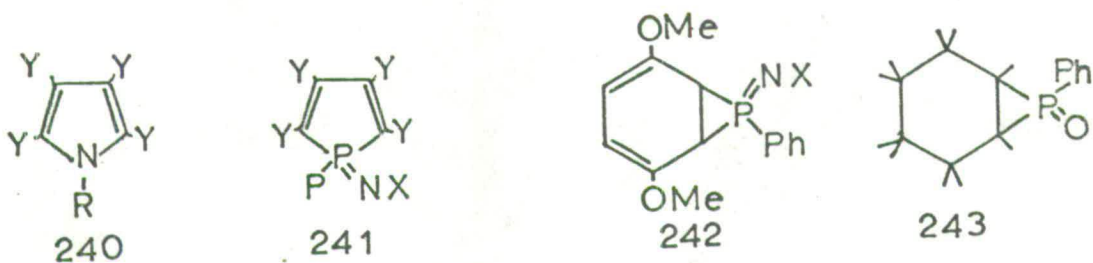
None of the proposed isomers however, explains the observation of other resonances. This implies that a mixture of compounds is present, which is unexpected because the compound was isolated from an alumina column by chromatography. It is unlikely that dimethyl di-t-butylphthalate (239) would have the same retention time as the bicyclo- substance (237) and is therefore ruled out as a component. It is possible that the phthalate (239) might be a product of a reaction on the alumina column, which is then eluted by the solvent causing the reaction, but this is an unlikely explanation. Thus the probable explanation is that, either the compound isolated was a mixture of isomer (237) and one other, or none of these.

The investigation of the reaction of phospholimines with dimethyl acetylenedicarboxylate was not limited to establishing the mechanism for the formation of phospholidenes. It had been shown by the proportion of products that this reaction competes with the Diels-Alder addition, which formed the intermediate (225). This alternative path operated exclusively with strong electron withdrawing substituents on nitrogen (226;  $X=SO_2C_6H_4CH_3$ ). If the bridge-head intermediate (225) could be isolated, controlled experiments could then be designed to investigate the retro-

Diels-Alder reaction observed by the formation of the phthalate (224), and the nature of the phosphorus fragment extruded. Therefore, the reaction of the N-tosylphospholimine derivative (226; X=tosyl) was attempted at 105° in *t*-butylbenzene, at 100° in dioxan and at 80° in benzene. In all these experiments the phospholimine failed to react. This showed that the system was resistant to this diene reaction. With excess alkyne at 160° in *t*-butylbenzene however, a quantitative yield of dimethyl 3,6-diphenylphthalate (224) was obtained.

Krika and Vernon<sup>84</sup> have suggested that the alkyne acted as a catalyst for deamination in their reaction with isoindoles and propose formation of a pyrrole (240). If this had occurred in the phospholimine reaction reported here, the phosphole tetraester (241) would have been formed, but this phosphole might also react with the alkyne. Moreover in other experiments equimolar alkyne and phospholimine gave good yields of the phthalate. (Table 3)

The nature of the phosphorus fragment is of course critical. If it supposed that a species similar to a nitrene was generated, it could be considered as an electron deficient analogue. An attempt was therefore made to trap such an intermediate with *p*-dimethoxybenzene, which might form the bicyclo-intermediate.(242).

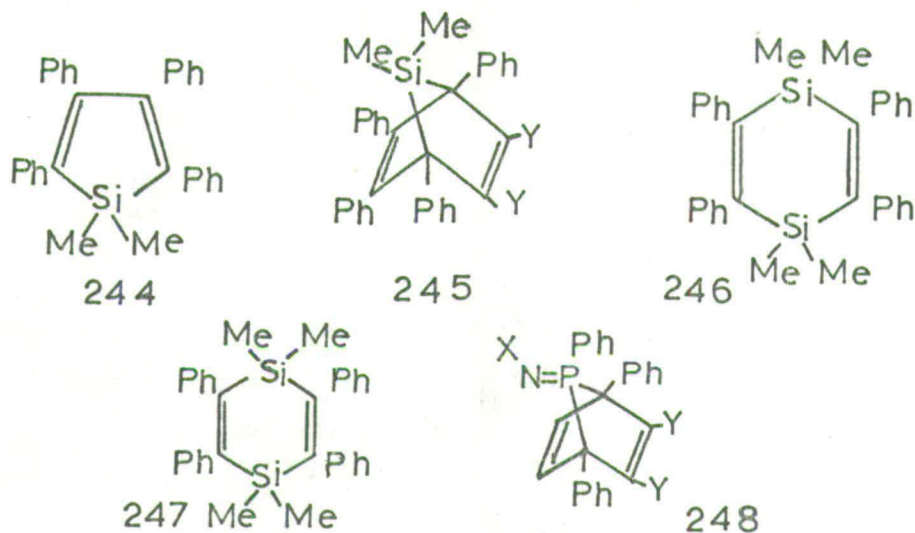


G.l.c. and spectral studies during this reaction and of the solvent after distillation failed to observe any species accountable to the phosphorus fragment. Column chromatography gave solvent, the phthalate and some very polar buff solids. These solids were similar to those obtained in several other reactions of phospholimines with this alkyne and were eluted from the column by methanol. These solids gave a positive ammonium molybdate phosphorus test and the mass spectrum of one gave peaks representing a mass greater than 800. This result conflicted with a molecular weight determination using vapour pressure osmometry. This latter technique is, however, normally restricted to organic solvents without hydroxyl groups, and it is possible that some technical difficulty caused the low readings that were observed.

Several experiments were performed on 1,2,5-triphenylphosphole oxide, since there can be no competing reaction. The results are included in Table 3. A normal Diels-Alder reaction was observed, as reported by Campbell et al.<sup>42</sup> in *t*-butylbenzene at 105° with an 87% yield of dimethyl 3,6-diphenylphthalate. The reaction in boiling cyclohexene gave only a low yield of the phthalate and no sign of the bicyclo-analogue (243), corresponding to a carbene addition to cyclohexene. In *p*-dimethoxybenzene at 110° the phthalate was obtained and some buff solids, similar to those observed for phospholimines, which had similarly confusing mass data.

When Mann<sup>45</sup> reviewed this type of retro Diels-Alder reaction, reported earlier<sup>33, 42</sup>, he speculated that polyphenylphosphorus polymers had been formed by the extruded fragment. This suggestion is supported by the analogous reaction of a silicon bridged adduct (245) obtained by Gilman<sup>96</sup>. These workers found

that silicon polymers were found and were able to trap the silicon fragment by diphenylethyne to form (246). Further investigation by Gilman et al.<sup>96</sup> of the reaction of the silicon heterocycle (244) with dimethyl acetylenedicarboxylate formed a 1:1 adduct (245).



When the adduct (245) was heated in diphenylethyne none of the expected 1,4-disilacyclohexadiene (247) was isolated. Moreover, the adduct (245) appeared to react with ethanol to give a yellow compound. This substance denied attempts to characterise it and decomposed to dimethyl tetraphenylphthalate. This observation might be a clue to the retro Diels-Alder reaction of phospholimines reported here. In all the reactions, analysed via crystallisation, the solvent used was ethanol. It was observed that rapid formation of white needles of phthalate from the black tarry reaction mixture occurred, even in the cold. The mother liquors from these crystallisations were very contaminated, gave no sensible t.l.c. chromatograms, and were evaporated to brown tars. In experiments where the reaction mixture was analysed by column chromatography the phthalate was eluted by ether and not a mixture of ether and petrol

(50:50). It is possible that the ether causes a bridged adduct such as (248) to decompose on the adsorbant (alumina) but that this adduct was not eluted from the columns. In a control experiment pure dimethyl 3,6-diphenylphthalate was eluted only by ether and this decomposition theory is therefore unlikely. If a bridged phosphole adduct is to be obtained, some other milder reaction conditions and work up must be found or a different dienophile employed.

These results have shown that polar phospholimines reluctantly undergo a Diels-Alder addition. The adduct formed however, readily aromatises by a retro Diels-Alder step. The extruded phosphorus fragment possibly forms polyphenylphosphorus polymers, analogous to the corresponding silicon case, but this has not been conclusively proved.

Diene Reactions of some Pyrroles: Since the bridged phosphorus intermediate (248) very readily aromatises to form the phthalate, an attempt to form the analogous nitrogen system was made. None of the reactions reported in the literature<sup>81</sup> had utilised the possible formation of highly delocalised products. Thus 1,2,5-triphenylpyrrole was allowed to react with dimethyl acetylenedicarboxylate but failed to give a product at 160° in a solvent (t-butylbenzene). With neat alkyne at 160° a reaction was observed but found to consist mainly of polymers of the alkyne. N-methylpyrrole was found to react by a similar path to that reported by Acheson et al.<sup>82</sup>, and extruded acetylene.

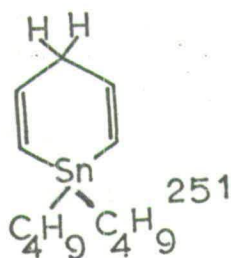
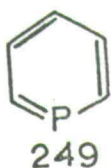
Areas for further Research: During the investigation of the reactions of alkynes with phenylphosphine, several unsaturated phosphorus derivatives were synthesised. The chemical reactivity

of these compounds, which contain two double bonds and a phosphorus atom as reactive centres, is worthy of further investigation.

The study of the chemistry of the phospholimines synthesised was fairly restricted and concentrated on the reaction with a relatively electron deficient dienophile. The limitation of this reagent was that the expected bridged Diels-Alder adduct could not be isolated. This severely hampered the investigation of the interesting reaction in which the phosphorus moiety was extruded. Thus a study of the chemistry of phospholimines and their reaction with other dienophiles could usefully be made.

## APPENDIX I

A communication by Ashe<sup>143</sup>, during the production of this thesis, reported the synthesis of the parent phosphorin (249) and its arsenic analogue (250). The route reported, which complies with the concluding paragraph on the preparation of phosphorins in the Introduction (Ch.I. page 32), utilises the reaction of phosphorus tribromide with 1,4-dihydro-1,1-dibutylstanabenzene (251). The compound (249), which the author calls phosphabenzene, was purified by g.l.c. (A.P.L. at 110°) and is reported to be a colourless, air sensitive liquid. The n.m.r. is interesting in that protons 2 and 6 have  $J_{\text{PH}}$  38 Hz and resonate at low field. The latter is suggested to be due to a ring current effect and not merely the electronic influence of phosphorus. The U.V. spectra of (249) and (250) were compared with pyridine and show some similarities. There has been no report of the chemistry of these compounds.



APPENDIX IIH n.m.r. Spectra at 100 MHz.

- Figure 1. The aromatic, vinyl and methylene region of the main distillate from the reaction of phenylphosphine with trideca-5,8-diyne.
2. The aromatic and vinyl region of the distillate from the reaction of phenylphosphine with butadeca-6,8-diyne.
  3. The aromatic region of N-tolyl-1,2,5-triphenylphospholimine.
  4. The aromatic region of N-pnitrophenyl-1,2,5-triphenylphospholimine.
  5. The aromatic region of N-tosyl-1,2,5-triphenylphospholimine.
  6. The aromatic region of 1,2,5-triphenyl-eth(1',2'-dimethyl carboxylate-2'-N-tolylimine)ylphospholidene.

Figure 1.

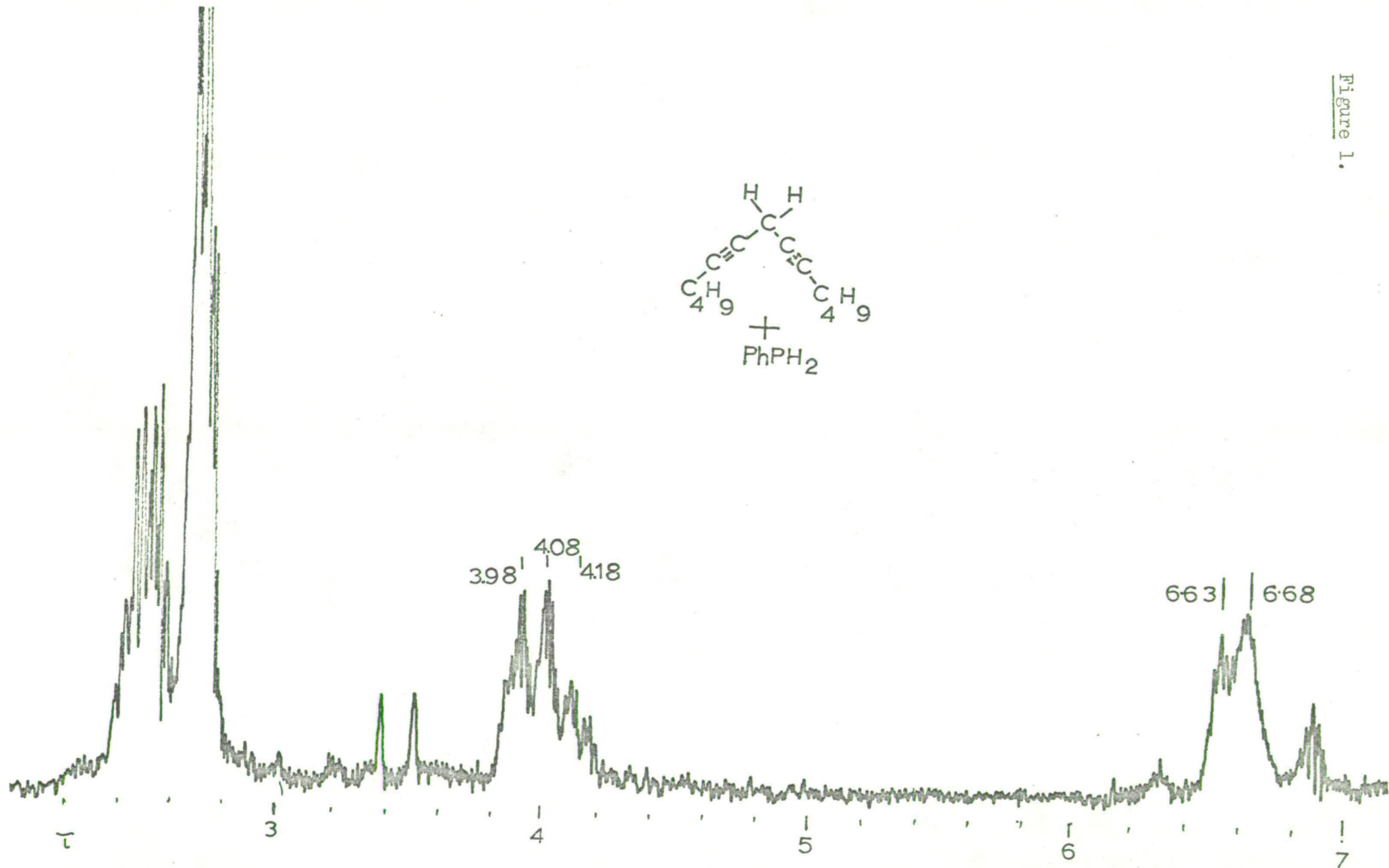


Figure 2.

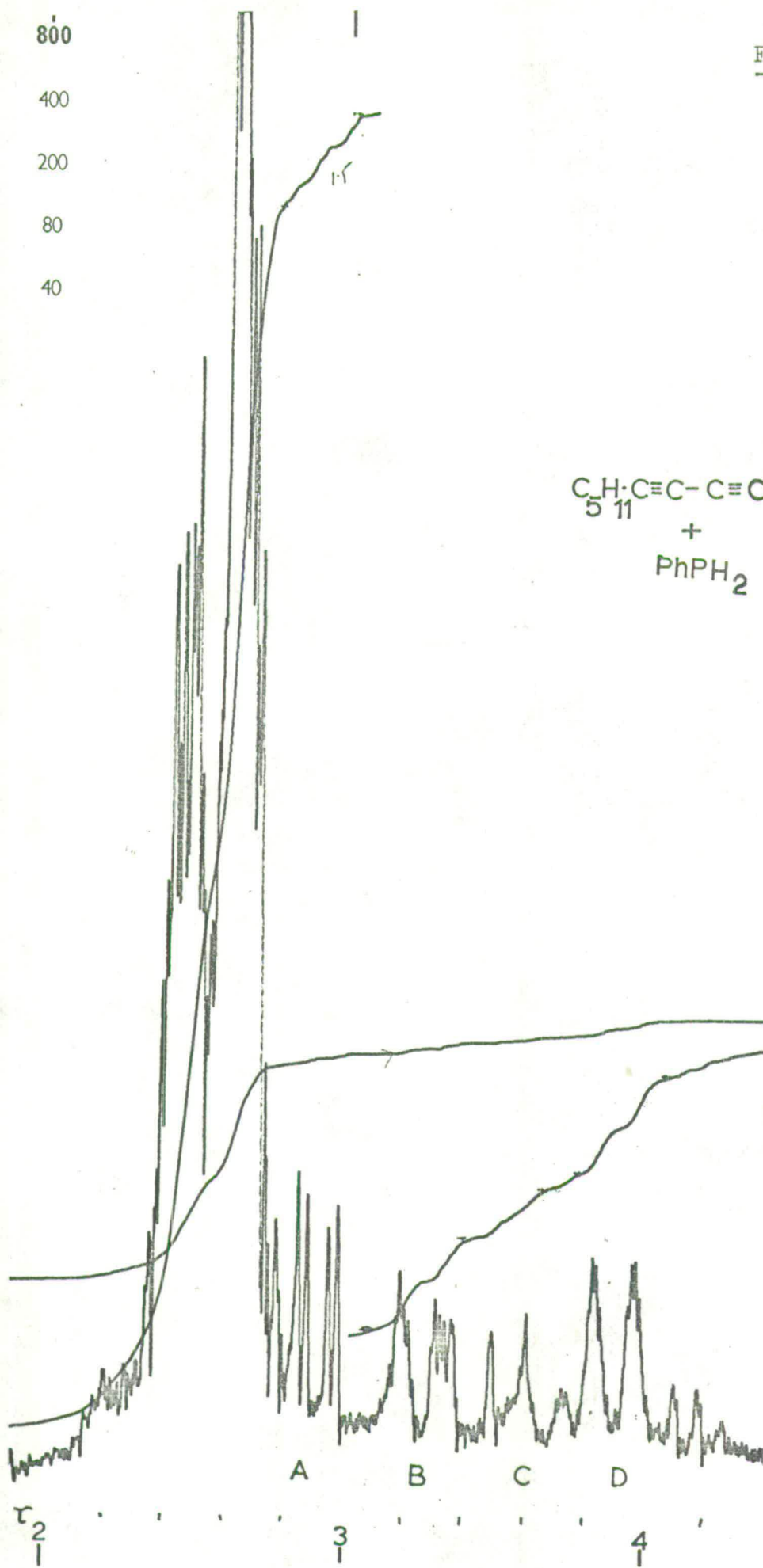


Figure 3.

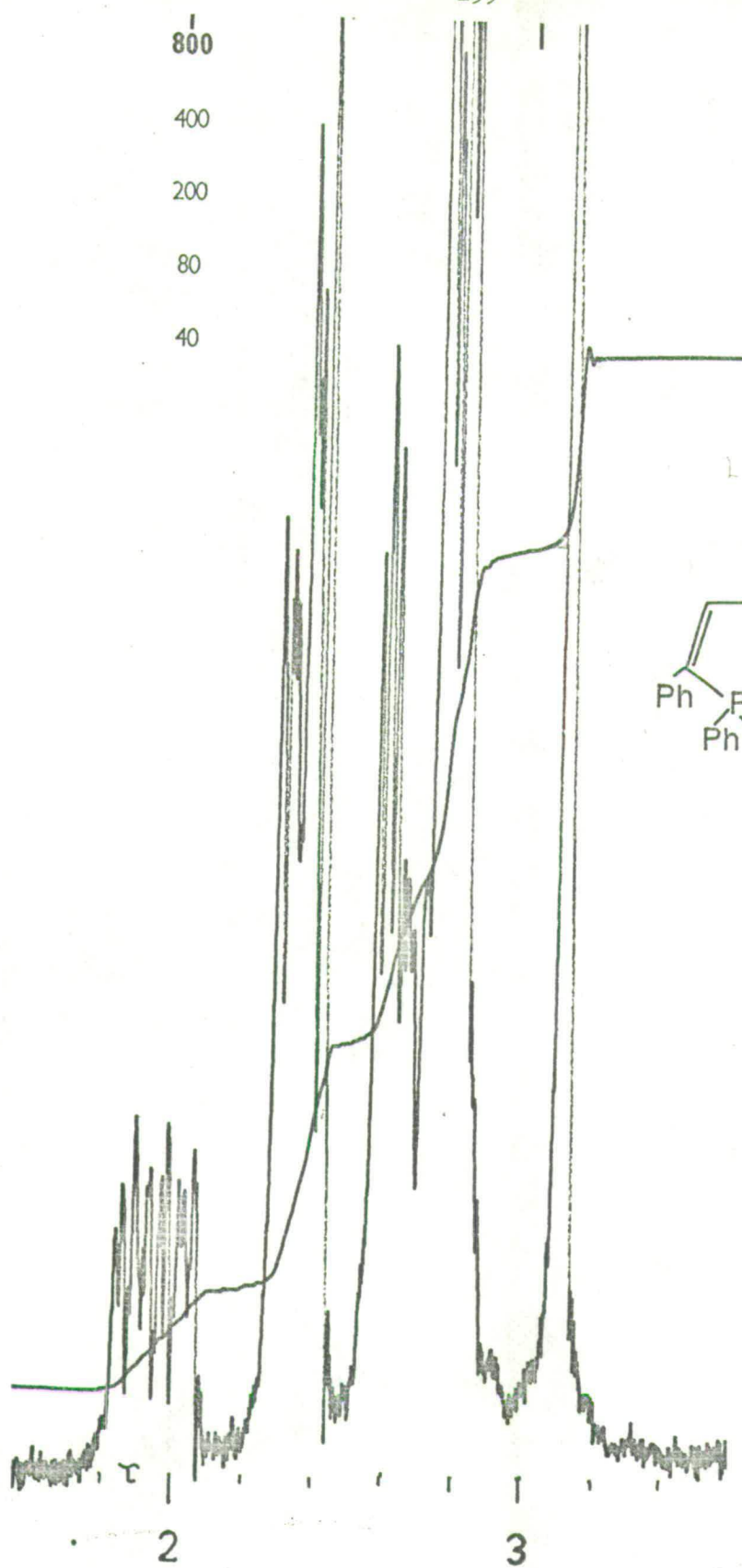
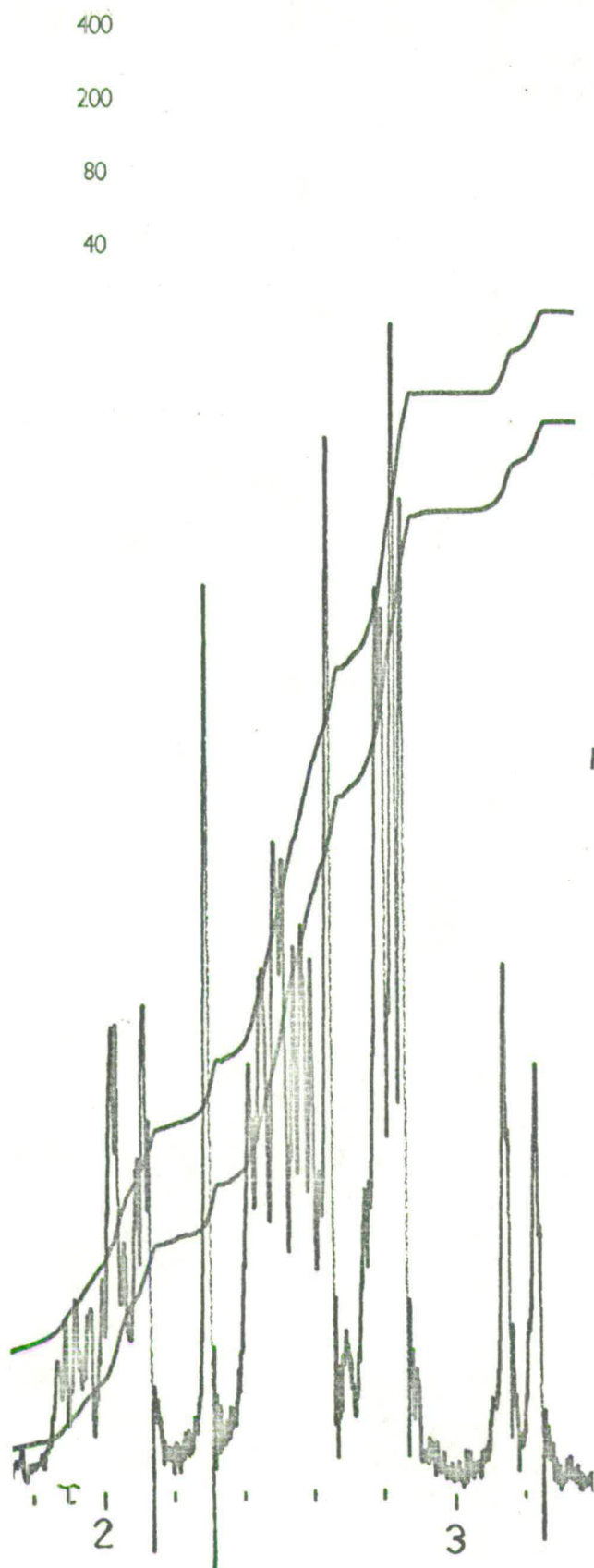


Figure 4.



800

400

200

80

40

Figure 5.

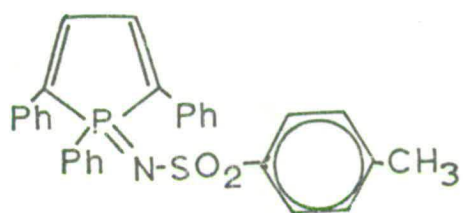
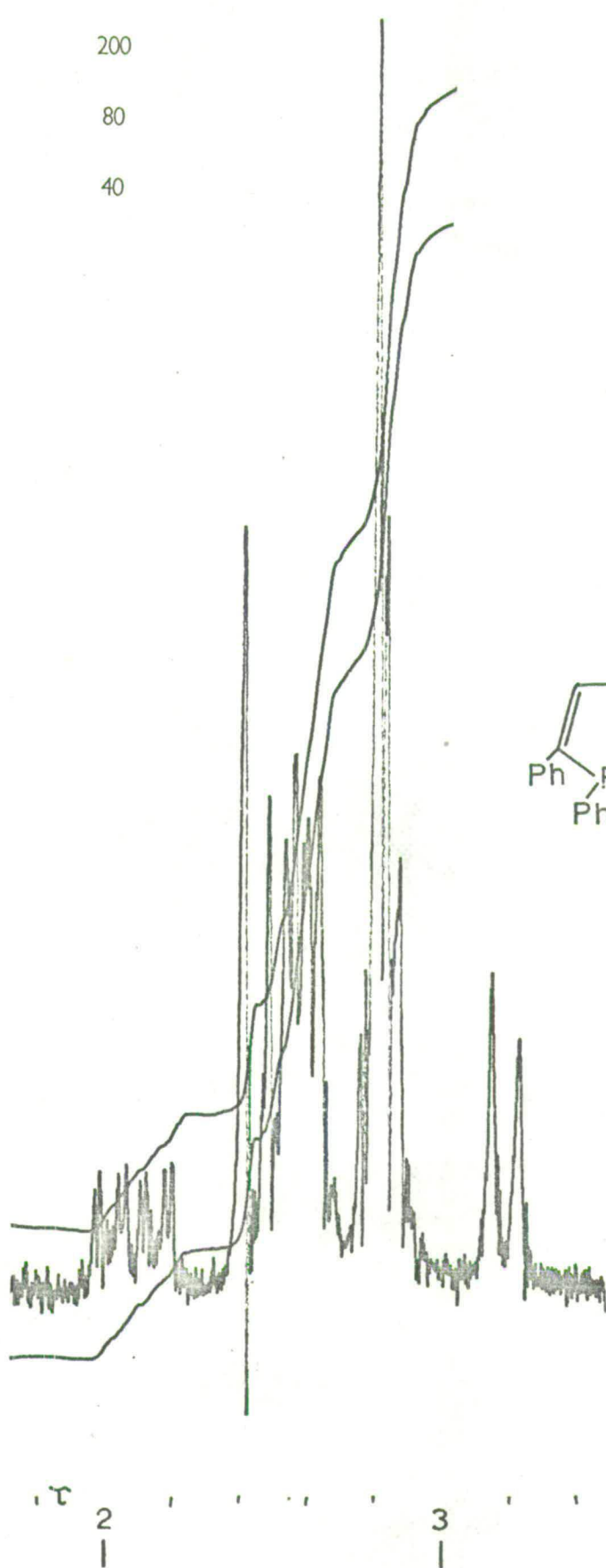
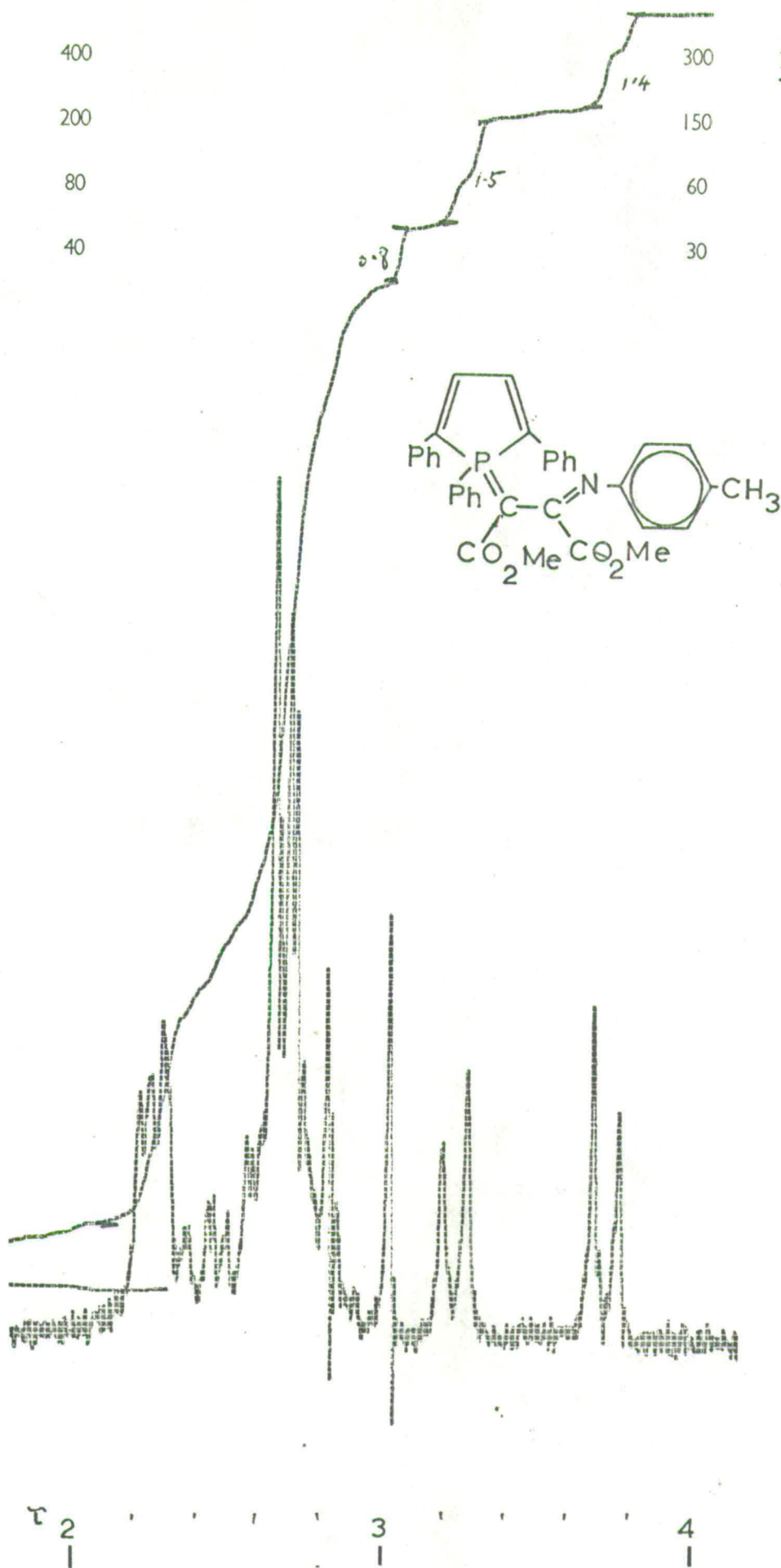


Figure 6.



## APPENDIX III

Nomenclature of Phosphorus Compounds.

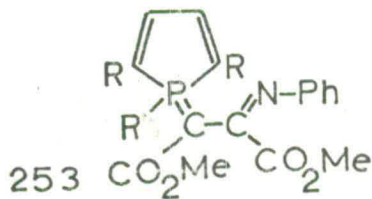
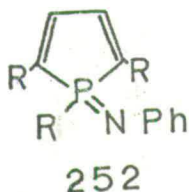
The rules proposed in the J. Chem. soc. 1952, have been used where appropriate for naming all phosphorus compounds and, where no specific rule applies, common usage exemplified by F.G.Mann. With compounds containing a phosphorus heterocyclic ring the name was built round this system. Thus in the structures represented below, rule 4c was applied by replacing the -e of phosphole.

"4c. Bivalent Radicals.

- 1) By adding to the -yl ending the suffix -idene (-imine).
- 2) By dropping the final -o ending and adding the suffix -idene (-imine)."

Thus compound (252) becomes:

N-phenyl-1,2,5-trialkylphenylphospholimine.



Similarly the structure (253), where the sub group on phosphorus is considered to be a bivalent radical derived from an ethyl group, is an ethylphospholidene, but with the substituents shown in the diagram (253), it becomes 1,2,5-trialkyleth(1,2-dimethyl carboxylate -2-N-phenylimine)ylphospholidene.

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