# SOME RING EXPANSION

# AND

# RELATED REACTIONS

# OF

# THE PHOSPHOLE SYSTEM

BY

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A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
THE DEGREE OF MASTER OF SCIENCE

Lakehead University
Thunder Bay, Ontario, Canada

JULY, 1970

Canadian Theses on Microfilm No. 10867

## ABSTRACT

The chemistry of simple phosphole derivatives is comprehensively reviewed to the early part of 1970.

Using 1,2,5-triphenylphosphole and some of its derivatives as starting materials, several ring expansion and related reactions of the phosphole system have been studied. Thus, pyrolysis and photolysis of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide and certain pyrazolino derivatives of 1,2,5-triphenylphosphole oxide lead to the formation of compounds of formula $C_{46}H_{36}O_2P_2$ and $C_{46}H_{34}O_2P_2$ respectively. These compounds are shown to be derivatives of the 4,4'-diphosphabi(cyclohexa-1,5-dienyl) and 4,4'-diphosphabi-(cyclohexa-2,5-dienylidene) systems respectively and possible mechanisms for the formation of these compounds are discussed. Furthermore, the first of these compounds may be converted into the second in an unusual reaction in which lithium aluminium hydride acts as an oxidizing agent.

The alkaline hydrolysis of 1-iodomethyl-1,2,5-triphenylphospholium iodide is discussed as a possible route to unsymmetrically substituted phosphorins. The hydrolysis is shown to follow an unexpected reaction path to give 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide. Two possible mechanisms for the reaction are discussed and the actual mechanism has been established by isolation and identification of the predicted intermediate.

Other reactions which could possibly lead to ring expansion of the phosphole system have been explored. These approaches involve the reaction of the phosphafulvene system with dimethyl acetylenedicarboxylate and treatment of 1-allyl-1,2,5-triphenylphospholium bromide with base. Although several interesting reactions occur, no ring expansion reactions of these systems were observed.

Several new organophosphorus compounds are reported and, for the most part, are fully characterized.

Details are also reported of a high resolution mass spectrometric investigation of ethyl 1,2,5-triphenyl-1-phosphacyclohexa-2,5-diene-3-carboxylate.

# ACKNOWLEDGEMENTS

The author wishes to express his thanks to Dr. A. N. Hughes who directed this research. He is also indebted to Dr. D. Orr for his valuable mechanistic suggestions and to Dr. T. Griffith for mass spectrometric and other instrumental measurements. Finally, the author is most grateful to the National Research Council of Canada and The Ontario Department of University Affairs for generous financial support.

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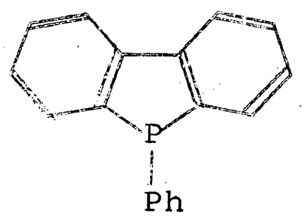
# INTRODUCTION

## THE CHEMISTRY OF DERIVATIVES OF PHOSPHOLE

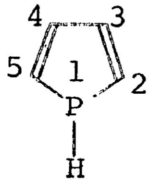
Most of the known phosphorus-carbon heterocycles, covering a wide variety of ring systems, have been synthesized and investigated during the last fifteen years and brief surveys of such heterocycles have been published by Märkl[1] and Hudson[2]. In these recent investigations, unsaturated five and six-membered ring phosphorus heterocycles have been the most extensively studied. Derivatives of fully unsaturated five-membered ring phosphorus heterocycles (known as phospholes) had not been reviewed in detail until very recently and the following discussion is a total survey of the chemistry of simple phosphole derivatives. However, it should be mentioned here that while this survey was being completed, Berlin[3] published a review of phosphorus-carbon heterocycles in which phosphole chemistry is covered to 1967.

The first phosphole derivative, 9-phenyl-9-phosphafluorene (I), was prepared in 1953 by Wittig and Geissler[4] from pentaphenylphosphorane ($Ph_5P$) and by other means. Despite the fact that phospholes were not investigated until so recently, studies of the chemistry of phosphole derivatives have played a significant role in organophosphorus chemistry. Thus, during the past ten years, almost one hundred papers on various aspects of phosphole chemistry have appeared.

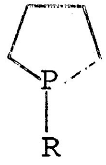
The main interest of the phosphole system (II) arises from the fact that it is the phosphorus analogue of the well-known heterocyclopentadienes, furan, pyrrole and thiophene. Since the last three are known to possess aromatic character - at least to a certain extent - it would be logical to ask whether the phosphole system is a potentially aromatic compound and how its aromatic character, if any, compares with that of the more common heterocyclopentadienes. Apart from the possible aromatic character, phospholes may also behave as dienoid compounds as well as tertiary phosphines. Furthermore, the chemistry and stereochemistry of phosphole derivatives containing pentacovalent and six-coordinate phosphorus are also of interest. Reduced phosphole derivatives such as phospholanes (III)



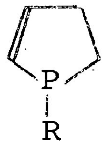
I



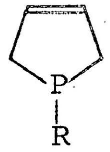
II



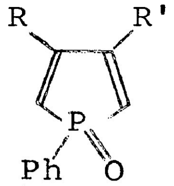
III



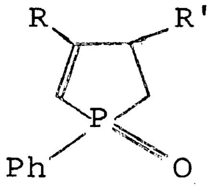
IV



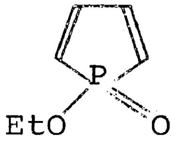
V



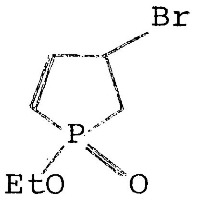
VI a) R = R' = H
b) R = H, R' = Me



VII a) R = R' = H
b) R = H, R' = Me



VIII



IX

and phospholenes (IV and V) are also known[1,3,5] but are outside the scope of this discussion except that in some cases, they may be used as starting materials for the synthesis of phospholes.

## Synthesis of Simple Phosphole Derivatives

Simple phosphole derivatives are those phospholes without additional fused rings. Phosphole itself (II) has not been reported and all phospholes prepared so far carry at least one substituent. The first syntheses of simple phosphole derivatives were reported almost simultaneously, but independently, in 1959 by three different groups of workers.[6,7,8] Since these first reports, synthetic techniques have been gradually improved to the extent that a wide variety of simple phospholes with different substituents has been synthesized. However, very few of these syntheses can be counted as general.

Simple phosphole derivatives have so far been synthesized by four major routes. The first of these is the dehydrohalogenation of halogen derivatives of phospholanes (III), 2-phospholenes (IV) and 3-phospholenes (V). By the application of this technique, phosphole oxides (VI) have been synthesized by Howard and

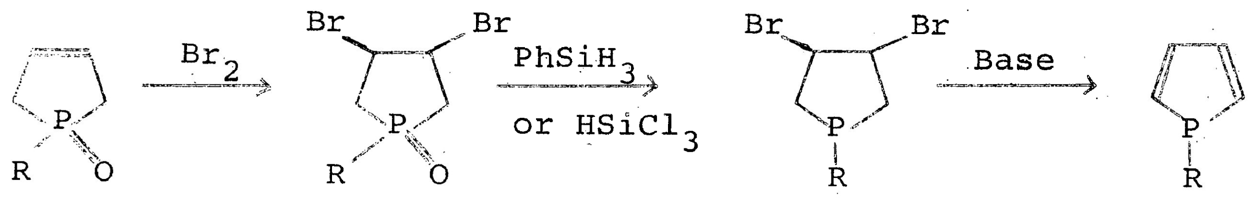
Donadio[6,9] by dehydrobromination of the bromine adducts of 2-phospholene oxides (VII) with organic bases. Similarly, Westheimer[10] obtained 1-ethoxyphosphole oxide (VIII) by the dehydrobromination of the allyl bromide IX or by conversion of IX into the corresponding 3-trimethylammonium iodide by treatment with dimethylamine and methyl iodide followed by Hofmann degradation. Unfortunately, the yield of VIII was not recorded as the compound is highly reactive and tends to dimerize. The presence of VIII was, however, confirmed by ultra-violet (UV) spectrophotometry and by trapping it as a Diels-Alder adduct with cyclopentadiene. The more stable phosphole derivatives 1-phenylphosphole and 1-methylphosphole have been synthesized by Märkl[11] and Quin[12,13] respectively, by a related approach. The syntheses were accomplished as shown in the sequence X → XIII. The starting 3-phospholene oxides (X) were prepared by methods similar to those of McCormack.[14] Addition of bromine across the carbon-carbon double bond followed by reduction with phenylsilane[11] or trichlorosilane[12,13] gives the dibromophospholanes XII which can be dehydrobrominated by organic bases to give the desired phospholes XIII. Reduction of the oxides XI prior to dehydrobromination is necessary so as to avoid dimerization of the phosphole oxides under the dehydrobromination conditions.

Campbell and her colleagues[15,16] demonstrated the formation of simple phosphole derivatives in a single step by heating phenyldichlorophosphine with 1,4-diphenylbutadiene or 1,2,3,4-tetraphenylbutadiene at 214 - 217°. The reaction is believed to proceed *via* the intermediate 3-phospholene XIV (possibly followed by migration of the halogen) with thermal dehydrochlorination to give the corresponding phosphole (XV) in high yield. The suggestion that the intermediate XIV is formed by a Diels-Alder type of reaction is reasonable as phenyldichlorophosphine oxide [PhP(O)$Cl_2$], which possesses no lone-pair electrons on the phosphorus atom, fails to react with the diene under similar conditions.[16] Moreover, McCormack[14] has shown that additions of this type can occur under different conditions.

Although this type of synthesis seems to be very simple, the scope of the reaction is strictly limited and only two phosphole derivatives (XV) have so far been successfully synthesized by this method.

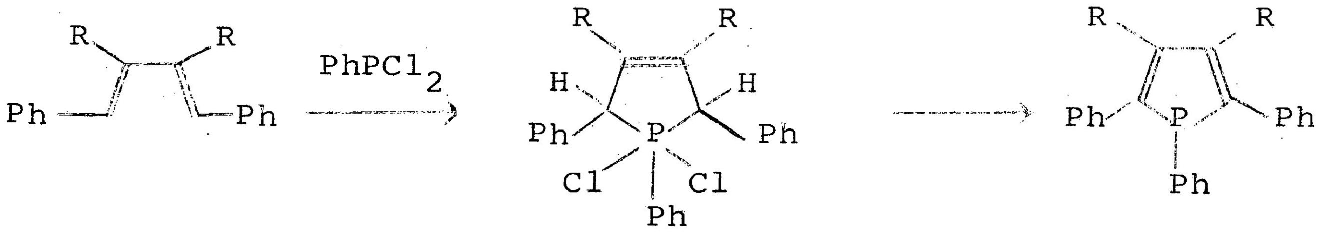
A very closely related single-step synthesis of simple phosphole derivatives is that of Mathey[17] in which phenyldibromophosphine is treated with dienes (XVI) in the presence of an organic base (1,5-diazabicyclo[5.4.0]undec-5-ene). Again, the reaction probably proceeds *via* a Diels-Alder type of mechanism followed by migration of the halogen and dehydrobromination *in situ* to give the corresponding phosphole (XVII).

The second synthetic approach to simple phosphole derivatives involves the reaction of dihalogenophosphines with 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (XVIII)[7,18,19] which is readily obtainable by the dimerization of diphenylacetylene (tolan) in the presence of metallic lithium.[20] The reaction is usually carried out by direct treatment of the dilithio compound XVIII with the appropriate dihalogenophosphine[7,18,19] or, alternatively, the dilithio compound is first converted into the 1,4-diiodo compound XIX followed by treatment with a suitable metal phosphide such as disodium phenylphosphide ($PhPNa_2$)[19] to give a high yield of the desired phosphole (XX). Dihalogenophosphine oxides react with 1,4-dilithio-1,2,3,4-tetraphenylbutadiene[18] in a similar manner but the products are the corresponding phosphole oxides. In contrast, phenyldichlorophosphine sulphide reacts[18] with the dilithio compound to give mainly the phosphole with traces of the phosphole sulphide.



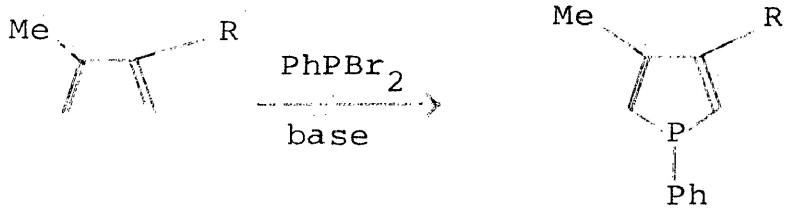
X XI XII XIII

R = Me or Ph



XIV a) R = H
b) R = Ph

XV a) R = H
b) R = Ph



XVI a) R = H
b) R = Me

XVII a) R = H
b) R = Me

The third approach is the reaction of dihalogenophosphines with the iron carbonyl-diphenylacetylene complex XXI,[8,19a] which can be easily obtained by the reaction of iron dodecacarbonyl $[Fe(CO)_4]_3$ with tolan.[21] This method is related to the second in principle and the iron carbonyl-tolan complex, which contains a *cis*-butadienoid system bonded to an iron atom, reacts with dihalogenophosphines in a similar fashion to that of XVIII.

The fourth, probably the most general, synthesis of simple phosphole derivatives starts from 1,3-butadiyne derivatives.[22] The reaction, which is closely related to syntheses of pyrroles[23] and thiophenes,[24] was introduced by Märkl who found that butadiynes react smoothly with both bis(hydroxymethyl)phenylphosphine in pyridine and phenylphosphine in benzene containing a catalytic quantity of phenyllithium to give a high yield of the corresponding phosphole (XXII).

It is worth noting that the synthetic approaches to simple phosphole derivatives described so far are characterized by intermolecular cyclization. There is, however, an isolated report on the synthesis of simple phosphole derivatives by Perveev and Rikhter[25] who claim that certain acetylenic phosphines such as XXIII undergo intramolecular cyclization when treated at 150° with an organic base containing traces of water to give products to which the general structure XXIV was assigned. The structure assignment was made mainly on the basis of the infrared (IR) spectrum which shows absorption suggestive of a five-membered cyclic conjugated diene. Oxidation of the compound assumed to be XXIVb with hydrogen peroxide gives a dubious view of the proposed biphosphine structure XXIV as both phosphorus atoms apparently still remain in the oxidized product which is inconsistent with previous observations that P-P bonds are normally cleaved by treatment with hydrogen peroxide.[2] Satisfactory analytical figures for the proposed biphosphine structure were not obtained and it should, therefore, be concluded that the structure of the compound assumed to be XXIV is in doubt.

## Reactions of Simple Phosphole Derivatives

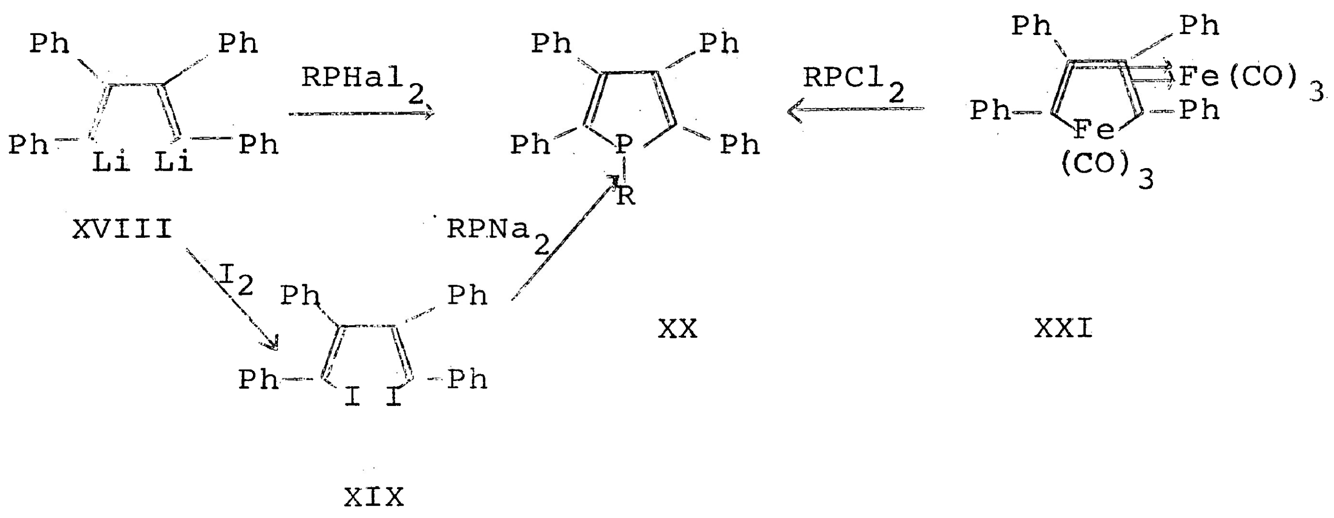
It will be seen that most simple phosphole derivatives apparently show little aromatic character in the chemical sense as compared with other heterocyclopentadienes and benzene, although this will be discussed in detail later. In contrast to pyrroles which show little basic or dienoid character, phospholes behave very much like tertiary phosphines as well as conjugated dienes. The reactions of simple phosphole derivatives can take place either at the phosphorus atom or on the ring carbon atoms and these reaction types will be discussed separately.

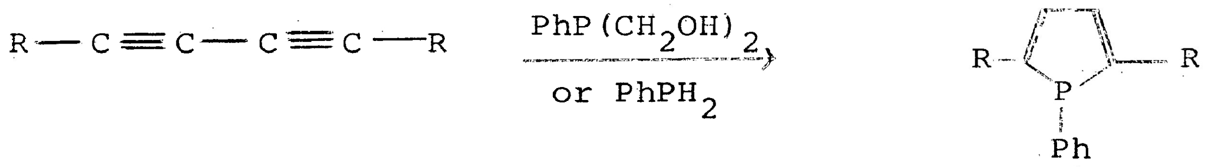
The normal reactions of simple phosphole derivatives which occur at the phosphorus atom are typical tertiary phosphine reactions. The tertiary phosphine character of simple phosphole derivatives is shown by the easy formation of oxides, sulfides, selenides, phosphine dihalides, quaternary salts, phosphonium ylids and inorganic complexes. These reactions reveal that the nonbonding electron pair on the phosphorus atom is readily available for combination and, consequently, the possible aromatic character of simple phosphole derivatives is at first sight in doubt.

Simple phosphole derivatives readily form oxides when treated with oxidizing agents (*e.g.* hydrogen peroxide).[8,11,15,16,19a] Oxidation of phospholes bearing aryl substituents on the phosphorus atom to give the corresponding phosphole oxides is usually carried out by treatment of solutions of phospholes in acetone[11] or ethyl acetate-ethanol mixtures[15,16] with hydrogen peroxide. As would be expected, phospholes having alkyl substituents (*e.g.* methyl or benzyl) instead of aryl substituents on the phosphorus atom are more susceptible to oxidation because of the electron donating nature of the alkyl group compared with the electron accepting nature of aryl groups and, consequently, the lone-pair electrons are more readily available for oxidation. In fact, phospholes having alkyl substituents on the phosphorus atom may oxidize spontaneously in air,[19a] particularly when kept in solution.

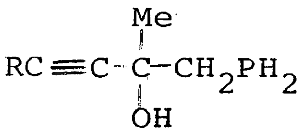
Phosphole sulfides and selenides are formed in a similar fashion by heating simple phosphole derivatives with sulfur or selenium in a suitable solvent such as benzene[11,16,19a] or xylene.[16] Phosphole sulfides may also be prepared by heating a solution of a simple phosphole derivative under reflux in 2-ethoxyethanol with sodium polysulfide.[8,19a]

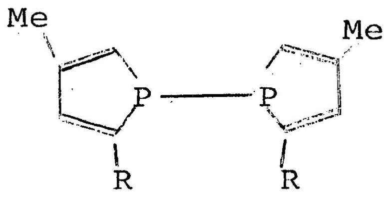
It is well known that cyclopentadiene and thiophene-1,1-dioxide dimerize readily. Phosphole oxides and sulfides behave similarly. For example, 1,2,5-triphenylphosphole oxide readily forms a photodimer upon irradiation with UV light.[16] 1,2,5-Triphenylphosphole sulfide also shows some tendency to dimerize on exposure to daylight.[16] Phosphole oxides and sulfides with no aryl substituents on the ring are less stable and dimerize much more rapidly[6,10,11] - perhaps because these compounds are less sterically hindered

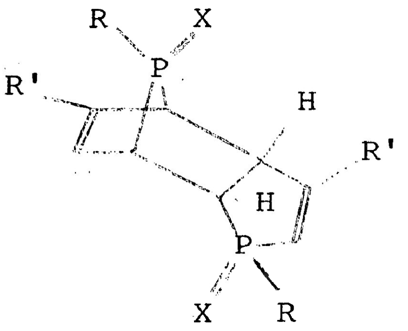




XXII R = Me, Ph, *p*-tolyl
*p* - bromophenyl
or 2-naphthyl


$RC\equiv C-\overset{\displaystyle Me}{\underset{\displaystyle OH}{C}}-CH_2PH_2$





XXIII a) R = Me
b) R = Bu

XXIV a) R = Me
b) R = Bu

XXV R = Ph or OEt
R' = H or Me
X = O or S

and stabilization by conjugation with aryl substituents is not present. 1-Ethoxyphosphole oxide,[10] as mentioned previously, is highly reactive and dimerizes so rapidly that its presence can only be detected by UV spectrophotometry and by trapping it as a Diels-Alder adduct with cyclopentadiene.

The dimerization of phosphole oxides and sulfides is believed to proceed *via* a Diels-Alder reaction and the products, in most cases, are assumed to be the normal Diels-Alder adduct XXV without confirmatory structure elucidation. The structure of the Diels-Alder dimer of 1-ethoxylphosphole oxide has, however, received considerable attention[26] and molecular and crystal structure studies confirm the structure as XXV (R=OEt, R'=H and X=O). In addition, the configuration at the ring junction was shown to be *endo*, the stereochemistry of the oxygen atoms and ethoxy groups at the phosphorus atoms has been established, and the unit cell is orthorhombic containing four molecules.

Attempts to brominate 1,2,5-triphenylphosphole (XVa) with bromine in carbon tetrachloride[16] led to the formation of the corresponding phosphole P-dibromide exclusively without attack of bromine on the ring carbon atoms. The red solid, which was assumed to be a simple phosphole P-dibromide, decomposes rapidly on exposure to air to give a quantitative yield of the corresponding phosphole oxide. Attempts to brominate 1,2,5-triphenylphosphole oxide under a variety of conditions were also unsuccessful.[16]

Protonation and quaternization reactions of simple phosphole derivatives give rise to two apparently conflicting views regarding the possible aromatic character of the phosphole ring system. 1-Methylphosphole[12,13] (XIII, R=Me) is not extracted from *n*-pentane even by 2*N* hydrochloric acid. This suggests an unusually low basicity for a tertiary phosphine and may indicate some degree of aromatic character. Like simple pyrrole derivatives, however, 1-methylphosphole undergoes protonation when treated with stronger acid (6*N*), and, upon neutralization, an unidentified brown polymeric material is formed.

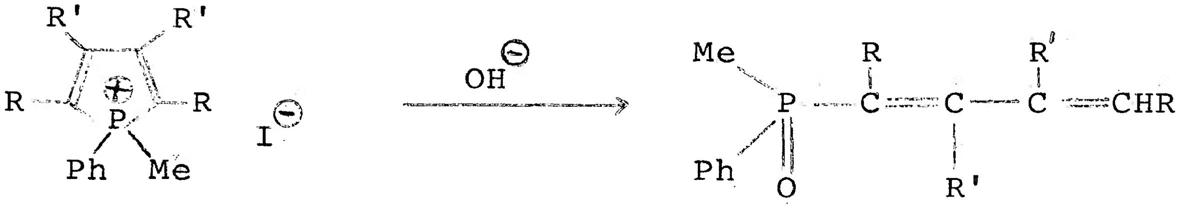
The site of protonation of the phosphole ring has not been established and since it is well known that carbon, rather than nitrogen, is protonated in simple pyrrole derivatives,[29] Quin[13] suggested that it would be of interest to consider this point in relation to phosphole chemistry.

Quaternization of simple phosphole derivatives proceeds with ease. Phosphole methiodides[12,13,16,28] form readily under standard conditions. Alkaline decomposition of the methiodides (XXVI) of 1,2,5-triphenyl and 1,2,3,4,5-pentaphenylphosphole[28] (XVa and XVb) has been found to follow second-order kinetics (first-order in phosphonium ion and first-order in hydroxide ion) and the decompositions result in cleavage of the five-membered rings, rather than the P-Ph linkage, to give exclusively the corresponding open chain phosphine oxide XXVII.

The mode of the decomposition was attributed to the much greater resonance stabilization of the intermediate carbanion formed by P-C ring cleavage. Activation energy calculations give a similar conclusion. The activation energies for the ring opening decomposition of 11-12 kcal./mole are relatively low compared with those for quaternary phosphonium salts where phenyl is the leaving group[29] (*i.e.* 35 kcal./mole).

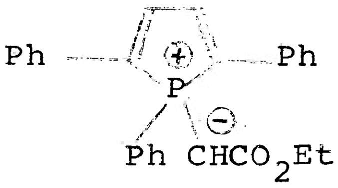
In connection with the formation of phosphonium salts, the phosphonium ylid[16,30] XXVIII can be obtained in good yield by treatment of the phosphonium salt XXIX, derived from 1,2,5-triphenylphosphole and ethyl bromoacetate, with aqueous sodium hydroxide. The phosphonium ylid XXVIII ( a phosphafulvene derivative) was originally reported to be stable[16] under normal Wittig reaction conditions. However, Hocking[30] demonstrated that under drastic conditions (*e.g.* in a sealed tube at 170° for 10 hours), the ylid XXVIII does undergo the Wittig reaction with cyclohexanone and a number of other carbonyl compounds. Both the reactivity and stereoselectivity of the ylid XXVIII are, in general, less than those of the corresponding open-chain ylid carbethoxymethylenetriphenylphosphorane ($Ph_3\overset{+}{P}-\overset{-}{C}HCO_2Et$) and these properties, as has been pointed out by Hocking, may be of some advantage in Wittig reactions with molecules containing two or more carbonyl groups of different reactivity, *e.g.* ketoaldehydes.

In contrast to pyrroles, simple phosphole derivatives show the ready availability of the phosphorus lone-pair electrons for formation of complexes with metal carbonyls[8,19a,31,32] and metal halides.[33] 1,2,3,4,5-Pentaphenylphosphole (XVb)[8,19a] reacts with $Fe(CO)_5$ to give the phosphole-iron carbonyl complex XXX in quantitative yield. Reaction of XVb with $Fe_3(CO)_{12}$, however gives a mixture of three complexes identified as XXX, XXXI and XXXII. Thus, Braye[19a] concluded that reactions between 1,2,3,4,5-pentaphenylphosphole and iron carbonyls show characteristics of both tertiary phosphines and conjugated dienes.

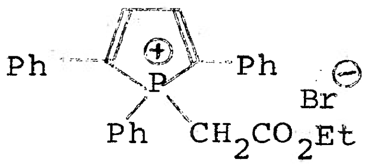


XXVI a) R = Ph, R' = H
b) R = R' = Ph

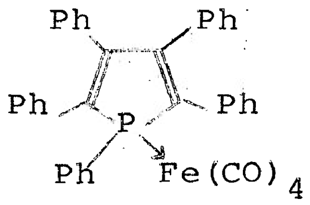
XXVII a) R = Ph, R' = H
b) R = R' = Ph



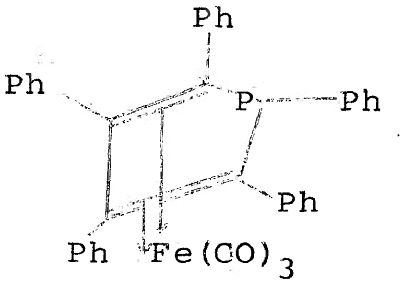
XXVIII



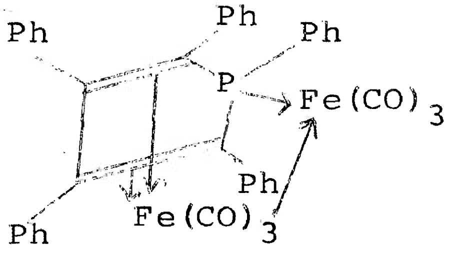
XXIX



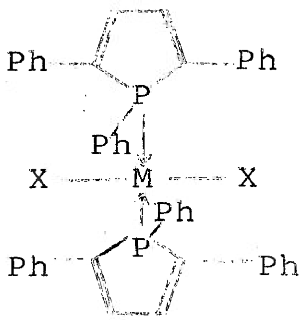
XXX



XXXI



XXXII



XXXIII M = Pd or Pt
X = Cl or Br

Braye[8,19a] has also demonstrated that 1,2,3,4,5-pentaphenylphosphole oxide undergoes similar complex formation with $Fe(CO)_5$ to give exclusively the P-oxide of the complex XXXI. In contrast, treatment of the corresponding phosphole sulfide with iron carbonyls gives only the complex XXX in which the sulfur is removed.

Cookson and his co-workers[31] described complex formation between 1,2,5-triphenylphosphole (XVa) and various metal carbonyls such as $Fe(CO)_5$, $Fe_2(CO)_9$, $Ni(CO)_4$ $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, and some bis-morpholine-metal tetracarbonyl complexes together with $\pi$-toluenemolybdenum tricarbonyl. Unlike XVb, the phosphole XVa undergoes complex formation with $Fe(CO)_5$ to give a $\pi$-complex analogous to XXXI whereas reaction of XVa with $Fe_2(CO)_9$ and $Ni(CO)_4$ gives the normal phosphine $\sigma$-complexes (phosphole)$Fe(CO)_4$ and (phosphole)$Ni(CO)_3$, respectively. Similar monosubstituted $\sigma$-complexes of the type (phosphole)$M(CO)_5$ (M=Cr, Mo and W) are also obtained from the reactions of the phosphole XVa with hexacarbonyls of Cr, Mo and W.

Reactions of 1,2,5-triphenylphosphole oxide with several metal carbonyls have also been investigated[31] but only with $Fe(CO)_5$ was a $\pi$-complex analogous to XXXI isolated.

"Mixed-ligand" complexes (morpholine)(phosphole) $M(CO)_4$ (M=Mo and W)[31] are formed when the phosphole XVa reacts with bis-morpholine-metal tetracarbonyls. In addition to the "mixed-ligand" complexes, $(Phosphole)_3\ M(CO)_4$ (M=Mo and W) are also formed by further displacement of the morpholine ligands. The products, even though analyzed for $(phosphole)_3M(CO)_4$ (M=Mo and W), *e.g.* 7-coordination, show carbonyl stretching frequency patterns typical of 6-coordinate $L_2M(CO)_4$ complexes. Repeated recrystallization retained the ligand-metal carbonyl ratio. On this evidence, Cookson[31] suggested that one molecule of phosphole is not directly coordinated to the metal atom.

Reaction of 1,2,5-triphenylphosphole (XVa) with $\pi$-toluenemolybdenum tricarbonyl results in the formation of a more common 6-coordinate $(phosphole)_2Mo(CO)_4$ complex.

Cobalt carbonyl complexes of phosphole and phospholene derivatives are of synthetic value. These complexes have been used as catalysts[32] in syntheses of aldehydes and/or alcohols by the hydroformylation reactions of alkenes. The reactions are usually carried out by heating a mixture of the alkene, carbon monoxide and hydrogen at 150 - 210° under 27.2 -

81.6 atm. in the presence of catalytic amounts of the complex. The advantage of these five-membered ring phosphine complexes over ordinary phosphine complexes arises from the observation that these catalysts enhance the reaction rate as well as the percentage of alcohol formed and reduce the amount of undesired saturated hydrocarbon formed.

Apart from the zero-valent metal complexes mentioned above, metal halide complexes of 1,2,5-triphenylphosphole (XVa) are also known. Thus, Walton[33] found that reactions of XVa with halides of Pd(II), Pt(II), Hg(II) and Rh(III) afford unrecorded yields of complexes of the types (phosphole)$_2$ $MX_2$(M=Pd or Pt; X=Cl or Br), (phosphole)$HgX_2$ (X=Cl or Br) and (phosphole)$RhCl_3$.

Unlike metal carbonyl complexes, metal halide complexes of 1,2,5-triphenylphosphole (XVa) are all normal phosphine $\sigma$-complexes in which the lone-pair electrons on the phosphorus atom in the phosphole ligand are bonded to the metal. $\pi$-Complexes are not isolated. From the stoichiometry of the complexes, the structure of the complexes (phosphole)$_2MX_2$(M=Pd or Pt; X=Cl or Br) were suggested to be monomers (XXXIII), whereas (phosphole)$HgX_2$(X=Cl or Br) are probably halogen-bridged dimers (XXXIV). IR spectro scopic evidence confirms that the phosphole ligand is not bonded as a diene since the phenyl and phosphole C=C stretching vibrations, which occur as weak bands at 1592 and 1568 $cm^{-1}$ in the free ligand, are virtually unmodified by complex formation. Metal-halogen stretching vibrations were also assigned.

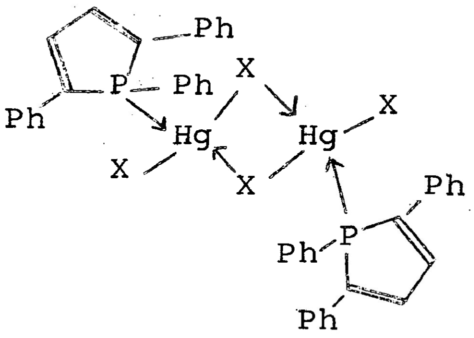
In the case of the (phosphole)$RhCl_3$ complex, no reduced product is formed even though rhodium (III) chloride is known[34] to react with an excess of triphenylphosphine ($Ph_3P$) to give the reduced complex $(Ph_3P)_3RhCl$.

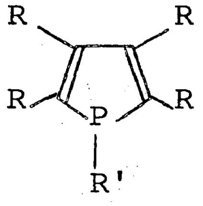
It should be included here that the reactions of 1,2,5-triphenylphosphole (XVa), its oxide, sulfide and selenide with halides of Nb, Ta, Th and U are at present under investigation in our laboratories.[35]

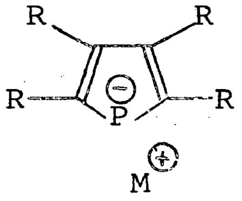
Another reaction which illustrates the ready availability of the lone-pair electrons on the phosphorus atom in simple phosphole derivatives is that reported by Hughes[36] who found that 1,2,5-triphenylphosphole (XVa) reacts as a weak nucleophile with dimethyl acetylenedicarboxylate. As the product is a phosphole derivative containing pentacovalent phosphorus, this will be discussed in detail later.

Prior to surveying reactions on ring carbon atoms of simple phosphole derivatives, reactions of phospholes with alkali metals[37,38] should be mentioned as these reactions may be of synthetic value. As with the reactions of pyrroles and arsoles with alkali metals, the substitutent on the phosphorus atom in phospholes XXXV can be removed by alkali metals to give the corresponding alkali metal derivatives XXXVI and, upon treatment of XXXVI with water, phospholes without a substituent at the phosphorus atom (XXXVII) are obtained. Since phospholes with substituents only at the phosphorus atom are now known,[11,12,13,22] this may lead to the synthesis of the as yet unknown parent phosphole (II).

Reactions of phospholes on the ring carbon atoms are also known. The $\pi$-complex formation of simple phosphole derivatives and the dimerizations of phosphole oxides and sulfides, which have already been discussed, are typically dienoid. The dienoid character of simple phosphole derivatives is further illustrated by the Diels-Alder type reactions of 1,2,3,4,5-pentaphenylphosphole (XVb) with dimethyl acetylenedicarboxylate and maleic anhydride.[8,19a] However, there is a marked difference in the products of these two reactions. Under similar reaction conditions,







XXXV

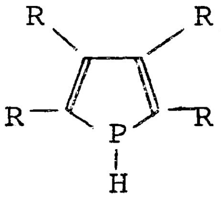
XXXVI

XXXIV     X = Cl or Br

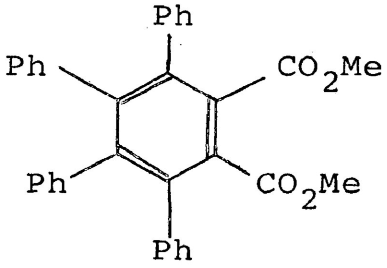
M = K or Li

R = H or Hydrocarbon

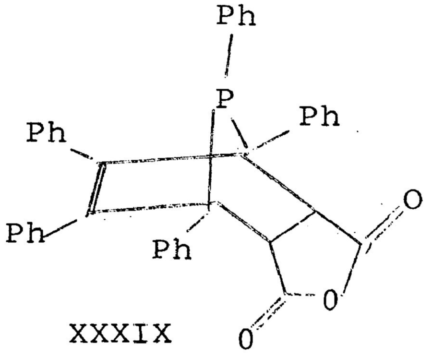
R' = Ph, $CH_2Ph$ or $CH_2CO_2H$



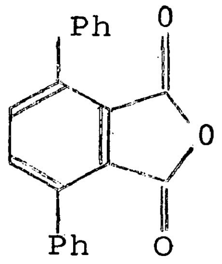
XXXVII



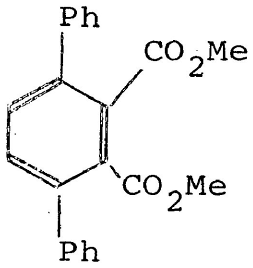
XXXVIII



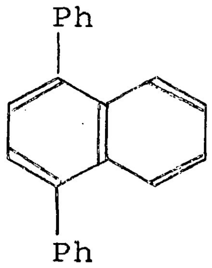
XXXIX



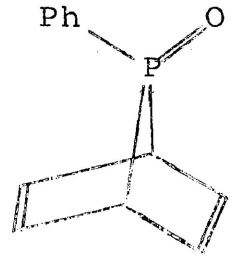
XL



XLI



XLII



XLIII

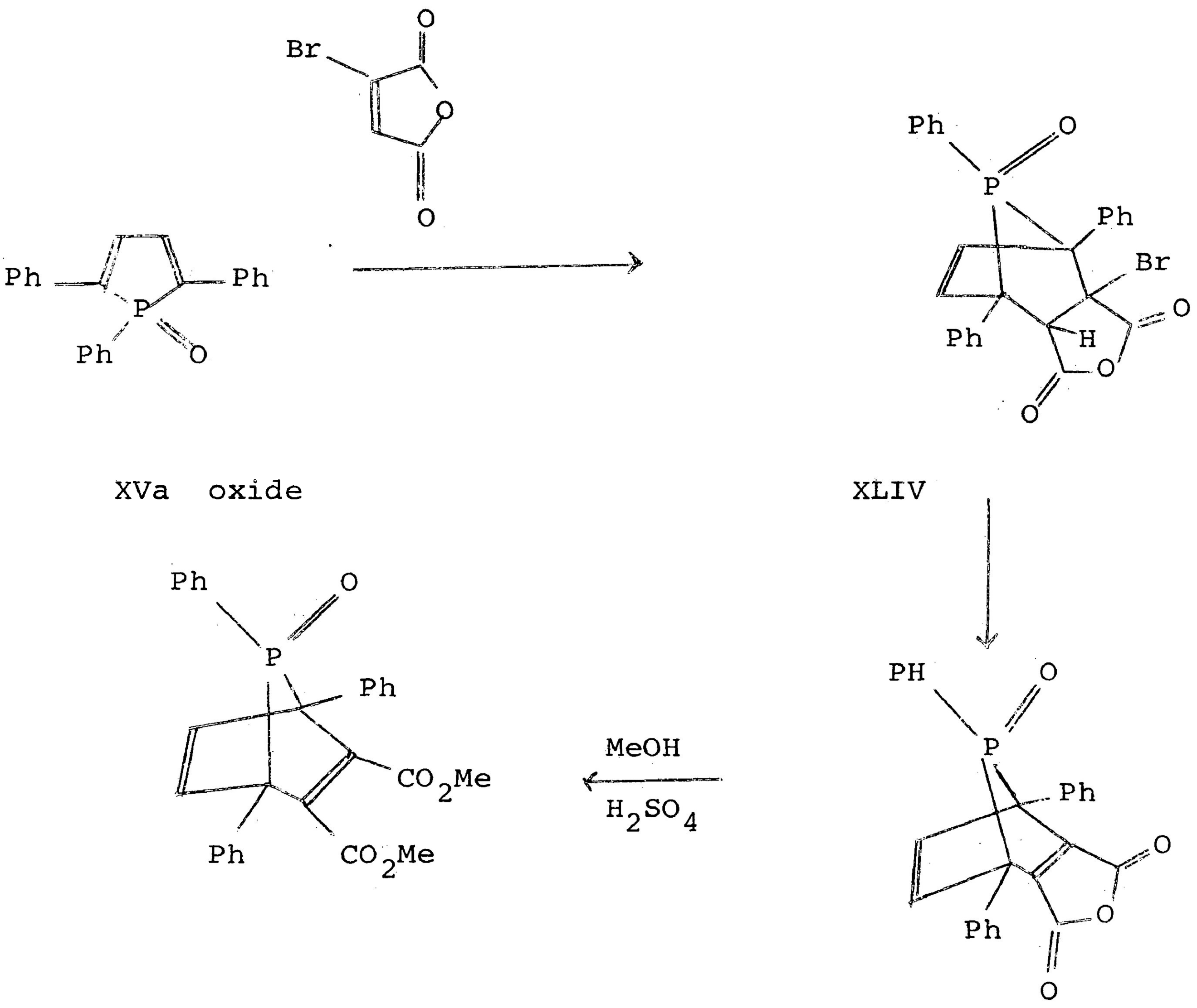
the reaction of XVb with dimethyl acetylenedicarboxylate gives the adduct XXXVIII in which the phosphorus-phenyl bridge has been eliminated whereas the reaction of XVb with maleic anhydride results in the formation of the normal Diels-Alder adduct XXXIX for which the stereochemistry still remains unestablished. 1,2,5-Triphenylphosphole (XVa) reacts similarly[16] except that in the case of maleic anhydride, the phosphorus-phenyl bridge is eliminated under the severe reaction conditions and the product is the fully aromatic compound XL.

Phosphole oxides undergo Diels-Alder reactions much more readily. 1-Ethoxyphosphole oxide has been trapped[10] as a Diels-Alder adduct with cyclopentadiene. 1,2,5-Triphenylphosphole oxide reacts in hot benzene with maleic anhydride[16] and acrylonitrile[16,31] to give the normal adducts in which the phosphorus-phenyl bridge is retained. However, under similarly mild reaction conditions 1,2,5-triphenylphosphole oxide reacts with dimethyl acetylenedicarboxylate[16] and benzyne[39] to give respectively the adducts XLI and XLII, *i.e.*, the phosphorus-phenyl bridge is eliminated.

It is worth noting that 7-phosphabicyclo[2.2.1]heptadiene-7-oxides (XLIII)(the type of intermediate expected to form in Diels-Alder reactions of phosphole oxides with acetylenic dienophiles[8,16,19a,39]) tend to aromatize under the reaction conditions by elimination of the phosphorus-phenyl bridge. In contrast, Diels-Alder reactions of phosphole oxides (and phospholes) with ethylenic linkages[8,16,19a,31] usually occur with retention of the phosphorus-phenyl bridge unless the reaction conditions are drastic. A Diels-Alder adduct of the type XLIII not previously isolated has however, been successfully synthesized[39] by an alternative route as shown in the sequence; oxide of XVa → XLIV → XLV → XLVI. Rapid elimination of the phosphorus-phenyl bridge under reducing conditions inhibits the conversion of the phosphine oxide XLVI to the corresponding phosphine.

Although 1,2,5-triphenylphosphole (XVa) undergoes photodimerization as does its oxide, the paths of the two reactions are completely different. As mentioned earlier, 1,2,5-triphenylphosphole oxide readily forms a photodimer[16] probably *via* the Diels-Alder type of mechanism. 1,2,5-Triphenylphosphole (XVa) undergoes photodimerization[40] to give a different type of dimer which was identified as a "2 + 2" dimer (XLVII). The structure assignment of XLVII was made on the basis of elemental analyses, the mass spectrum and the nuclear magnetic resonance (NMR) spectrum. This evidence, however, does not necessitate a "head-to-tail" dimer nor does it specify the stereochemistry of the cyclobutane ring.

1,2,5-Triphenylphosphole (XVa) or, better, its oxide reacts[16] with methyl (or ethyl) diazoacetate and diazomethane to give a variety of products depending upon the reaction conditions. Thus, at room temperature in either dioxan or without solvent, 1,3-dipolar addition of methyl diazoacetate to one double bond of the phosphole results in the formation of the pyrazoline XLVIII to which the hydrazone type structure XLVIII was assigned in preference to the tautomeric azo-structure XLIX. This assignment was made on the basis of the IR spectrum which shows a fairly strong absorption due to the N-H stretching frequency at 3130 $cm.^{-1}$ Heating of the pyrazoline XLVIII under reflux in diglyme containing traces of copper powder results in the elimination of nitrogen and leads to the formation of a nitrogen-free compound to which the structure L was assigned although the alternative bicyclic structure LIa has not yet been completely excluded. The same nitrogen-free compound L can be obtained directly by heating under reflux a mixture of the phosphole and methyl diazoacetate in dioxan.

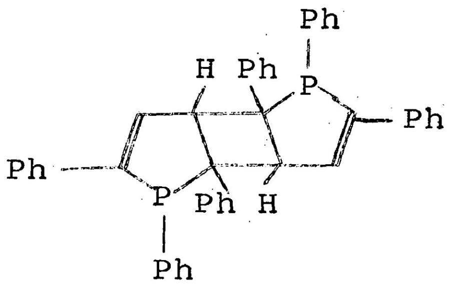


XVa oxide

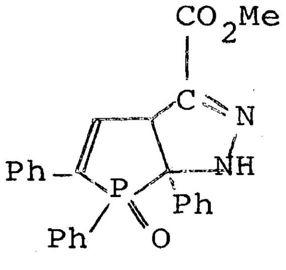
XLIV

XLVI

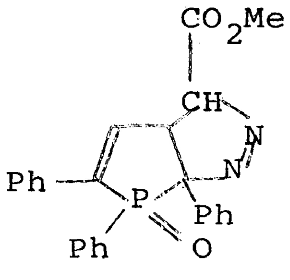
XLV



XLVII



XLVIII



XLIX

In the presence of catalytic amounts of copper, the reaction of 1,2,5-triphenylphosphole (XVa) with methyl diazoacetate in boiling dioxan gives rise to the dihydrophthalic ester LII. The reaction probably occurs by the initial decomposition of the diazo ester to give dimethyl fumarate which then reacts with the phosphole in a Diels-Alder type of reaction with the loss of the phosphorus-phenyl bridge to give the observed dihydrophthalic ester LII.

1,3-Dipolar addition of diazomethane to one double bond of the phosphole oxide provides similar results. Thus, at -15° in dioxan-ether mixture, 1,2,5-triphenylphosphole oxide reacts with diazomethane over a period of several days to give the pyrazoline LIII in high yield. Thermal decomposition by treatment with traces of copper in boiling diglyme converts the pyrazoline LIII into LIb. The same cyclopropane derivative LIb is formed directly from the photochemical reaction of the phosphole oxide and diazomethane.[16] Pyrolytic and photochemical reactions of this cyclopropane derivative LIb are of some interest and these reactions will be considered in the results and discussion section of this thesis.

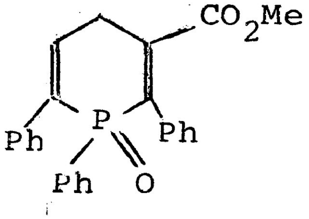
## Aromatic Character of Simple Phosphole Derivatives

In order for the phosphole ring to have aromatic properties, the lone-pair electrons on the phosphorus atom in the phosphole ring system (II) must interact with the *cis*-butadiene portion of the molecule to form an aromatic sextet of 6π-electrons. Phosphole (II), superficially, meets this requirements as it is structurally and electronically similar to pyrrole which is believed to possess extensive delocalization of the hetero-atom lone-pair electrons. However, ever since the phosphole ring system (II) was discovered, the possible aromatic character of this type of compound has been the subject of considerable discussion. Thus, from the chemical point of view it may be concluded that the phosphole ring system (II) has little aromatic character as the behaviour of simple phosphole derivatives in certain reactions does not match that of the common heterocyclopentadienes (particularly pyrrole) and benzene. As mentioned earlier, the ready formation of oxides, sulfides, selenides, P-dihalides, quaternary salts, phosphonium ylids, inorganic complexes and Diels-Alder adducts illustrate not aromatic character but the tertiary phosphine and dienoid character of simple phosphole derivatives. However, Brown[41] has pointed out that this apparently non-aromatic chemical behaviour may be misleading since the ease of formation of oxides and quaternary salts is determined in part by the energy difference in changing from the original planar aromatic model to a tetrahedral arrangement about the hetero atom, and the difference in energy between the two arrangements is very much greater for a nitrogen atom than for phosphorus.

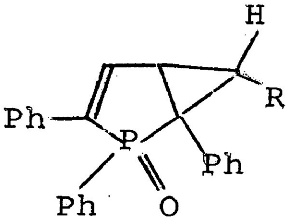
It has also been argued[13] that these reactions have been studied qualitatively and a quantitative study may show diminished phosphine character and point to considerable stabilization by delocalization in the phosphole ring system (II). Chemical evidence supporting this argument is provided by Quin[12,13] who found that the general behaviour of 1-methylphosphole (XIII, R=Me) is similar to that of simple pyrrole derivatives. It is an exceptionally weak base, highly unstable in strong acid solution and not susceptible to the formation of certain phosphine complexes. The $pK_a$ value of XIII (R=Me) was found to be 0.5 which is very much less that that of normal tertiary phosphines ($pK_a$ = 7 - 8) and also lower than the value ($pK_a$ = 5.2) calculated[13] for divinylphosphines.

Resonance energy estimates suggest some aromatic character for the phosphole ring system (II). Thus, molecular-orbital calculations made by Brown[41] indicate that the planar configuration of phosphole (II) possesses a substantial resonance energy comparable to that of pyrrole. In support of this, Millar[42] has measured heats of combustion and calculated the dissociation energies for the P=O bond of some crystalline phosphine oxides. The results suggest that the difference of 39 ± 13 kcal./mole between the dissociation energy (100.4 ± 9.5 kcal./mole) for the P = O bond of 1,2,3,4,5-pentaphenylphosphole oxide and those for other phosphine oxides (*e.g.* triphenylphosphine oxide[43] = 128.4 ± 5.5 kcal./mole; trimethylphosphine oxide[44] = 139.3 ± 3.0 kcal./mole) might be taken as an estimate of the resonance energy of 1,2,3,4,5-pentaphenylphosphole relative to its oxide.

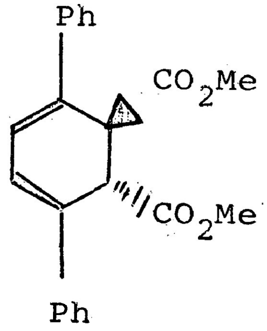
Evidence pointing to some degree of aromatic character in the phosphole ring system (II) is also provided by spectroscopic studies. The NMR spectrum of 2,5-dimethyl-1-phenylphosphole[22] (XXII, R = Me) shows chemical shifts of the phosphole ring protons and of the methyl groups in the same regions as those for 2,5-dimethylfuran, 1,2,5-trimethylpyrrole and 2,5-



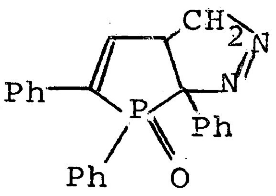
L



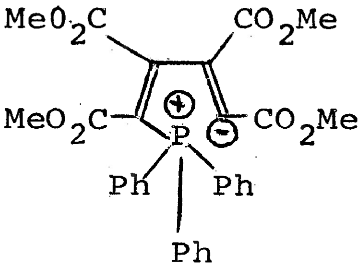
LI a) R = $CO_2Me$
b) R = H



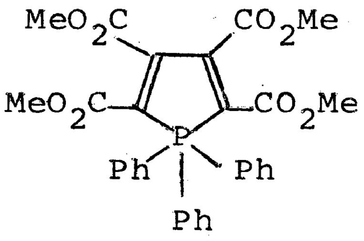
LII



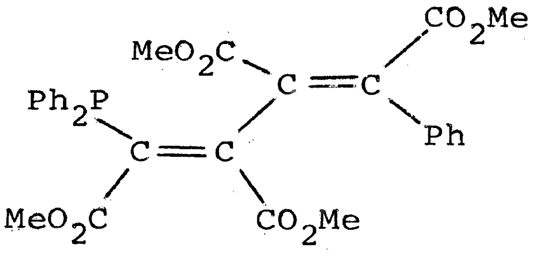
LIII



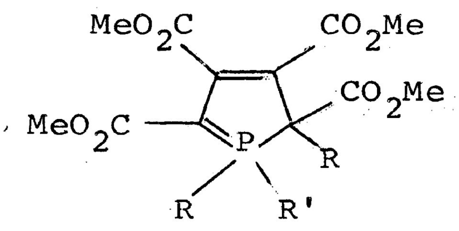
LIV



LV



LVI



LVII a) R = R' = Ph
b) R = R' = *p*-tolyl
c) R = Ph, R' = cyclopropyl

dimethylthiophene which are regarded as aromatic compounds. Studies of the NMR spectrum of 1-phenylphosphole[11] lead to similar conclusions - the phosphole ring protons appear in the normal aromatic region and the spectrum is very similar to that of N-phenylpyrrole. According to Quin,[12,13] this potentially aromatic character of the phosphole ring system (II) is confirmed. Comparison of the chemical shifts of the ring protons and of the methyl groups in 1-methylphosphole (XIII, R = Me) with those in thiophene and 2-methylthiophene suggests an extra deshielding of the ring portons and of the methyl group in XIII (R = Me), *i.e.* a "ring-current" effect. The low field $^{31}P$ chemical shift (+ 8.7 ± 0.1 p.p.m. relative to external 85% $H_3PO_4$) compared with other unsaturated tertiary phosphines also suggests some delocalization of the lone-pair electrons of the phosphorus atom in 1-methylphosphole (XIII, R=Me). UV and mass spectral studies indicate a pyrrole-type electronic structure.

It would be of great interest if 2-methylphosphole could be synthesized so that Elvidge's method[45] could be used to estimate the relative aromatic character in the 2-methyl derivatives of phosphole, furan, pyrrole and thiophene.

In connection with the aromatic character of phospholes, other useful techniques are dipole moment and X-ray crystallographic studies. Both of these techniques are currently being applied to 1,2,5-triphenylphosphole (XVa) in our laboratories.[46] Dipole moment studies of the phosphole XVa give values of 1.45D and 1.08D in *p*-xylene and dioxan respectively. These values, which are very close to that of triphenylphosphine (1.40D in benzene),[47] are inconclusive and comparisons between P-alkylphospholes and alkylphosphines would be more useful. Preliminary X-ray studies show that the crystal structure of the phosphole XVa is monoclinic and the unit cell is large. Hopefully, a complete crystal structure of XVa will be determined.

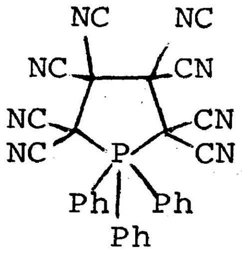
## Simple Phospholes Containing Pentacovalent Phosphorus

Simple phosphole derivatives containing pentacovalent phosphorus are rare and this is, at least in part, due to their unstable nature. Although several compounds[36,48,49,50] of this type have been reported, recent structure revisions[51,52] have diminished the number of such systems to two and only one of these is stable at room temperature while the other may have considerable zwitterionic character and is highly unstable.

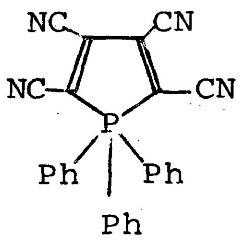
Johnson and Tebby[48] found that triphenylphosphine reacts with dimethyl acetylenedicarboxylate in ether at -50° under nitrogen to give a yellow, unstable 1:2 phosphine-ester adduct for which the zwitterionic structure LIV was provisionally proposed although the phosphole type structure LV was not completely excluded. Later investigation by Hendrickson[49] suggested that the adduct is in fact LV. Evidence given for the structure of LV comes from NMR studies on very fresh samples of the adduct which show only two methoxy signals rather than the three or four required by LIV although this conclusion should be treated with caution since molecular geometry and pseudorotational processes were apparently not considered. The adduct LV (or LIV) undergoes rearrangement,[48,49] rapidly when exposed to air at room temperature to give a stable and methanol-insoluble yellow adduct of unchanged stoichiometry. Since the oxidation of the rearranged adduct with hydrogen peroxide in acetic acid gives diphenylphosphinic acid and benzoic acid, the structure of the rearrangement adduct was incorrectly given[49] as the open chain structure LVI. Very recently, the correct structure has been shown[51] to be a cyclic system (LVIIa) and since this is a 2*H*-phosph(V)ole derivative, the discussion is best deferred to the next section of this survey.

It should also be included here that the rearrangement of LV (or LIV) gives in fact two products,[51] one of which is methanol soluble while the other is methanol insoluble. The methanol soluble product is reported to be under investigation.[51]

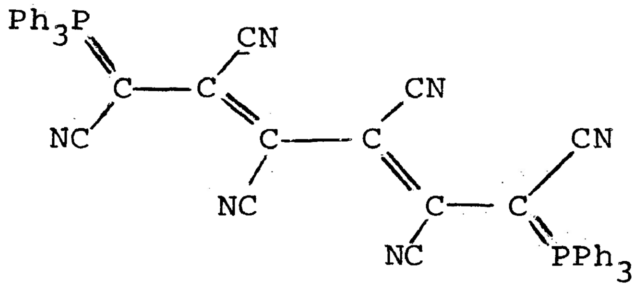
Following Johnson's report,[48] Reddy and Weis[50] found that triphenylphosphine reacts with tetracyanoethylene and dicyanoacetylene to give unusually stable products for which structures were again incorrectly assigned as LVIII and LIX, respectively. Since recent studies[53] suggest that a phosphorus atom with five covalent P-C bonds normally shows the $^{31}P$ chemical shift in the region of +80 to +100 p.p.m. relative to 85% $H_3PO_4$, Tebby[52] pointed out that the triphenylphosphine-tetracyanoethylene adduct, which shows the $^{31}P$ chemical shift at -22 p.p.m. (relative to 85% $H_3PO_4$), is unlikely to have the structure originally proposed. Consequently, Tebby[52] reassigned the structure of the triphenylphosphine-dicyanoacetylene adduct as the open chain adduct LX on the basis of both spectroscopic and chemical evidence.



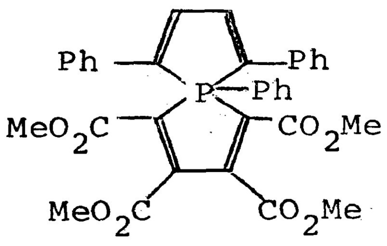
LVIII



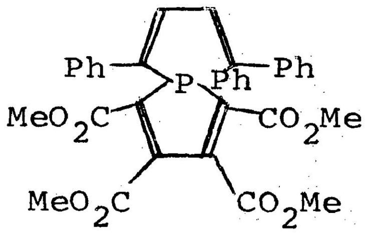
LIX



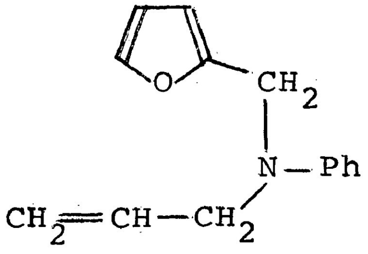
LX



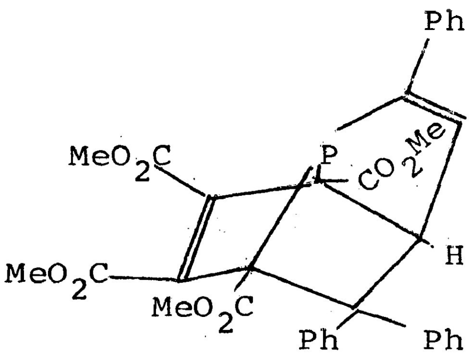
LXI



LXII



LXIII



LXIV

The dual dienophilic and electrophilic properties of dimethyl acetylenedicarboxylate together with the reports on the reaction of triphenylphosphine with acetylenic compounds led Hughes and Uaboonkul[36] to investigate the diene and tertiary phosphine character of 1,2,5-triphenylphosphole (XVa) by treating the phosphole XVa with undiluted dimethyl acetylenedicarboxylate. Under mild reaction conditions, the phosphole XVa reacts with a large excess of the ester to give, in addition to dimethyl 3,6-diphenylphthalate which is presumably formed *via* a Diels-Alder reaction followed by elimination of the phosphorus-phenyl bridge, a yellow 1:2 phosphole-ester adduct as the major product (37% yield). An unidentified 1:4 phosphole-ester adduct was also formed in 2.5% yield. The 1:2 phosphole-ester adduct, for which the spiran structure LXI has been postulated, is of some interest since it is the first stable spirobiphosphole derivative reported which contains no benzene rings fused to the phosphole system. However, the structure assignment is not fully satisfactory as it was achieved mainly by elimination of several other possible structures on spectroscopic and chemical evidence without directly confirming the present of a pentacovalent phosphorus atom by $^{31}P$ NMR studies.

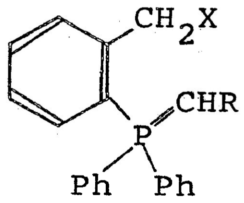
The spirobiphosphole derivative LXI is stable for long periods at room temperature. However, rearrangement occurs on warming in chloroform. The rearrangement of LXI is probably initiated by phenyl migration similar to that suggested by Johnson[48] and Hendrickson[49] to give the phosphole derivative LXII as a transient intermediate which then undergoes intramolecular Diels-Alder addition in the same fashion as the furan LXIII[54] to give the observed product LXIV. The structure assignment of LXIV was made on the basis of spectroscopic and chemical evidence.

## Simple 2*H*- and 3*H*- Phosph(V)oles

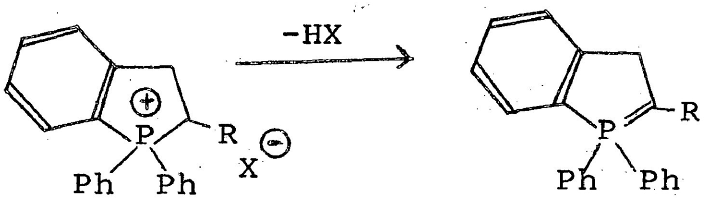
Simple 2*H*- and 3*H*-phosph(V)ole derivatives (which are also unsaturated five-membered ring phosphonium ylids) are rare and have only been investigated recently. The first such report came from Märkl[55] who found that intramolecular nucleophilic attack of the phosphonium ylid portion on the side-chain alkyl halide portion in LXV followed by dehydrohalogenation of the so-formed cyclic phosphonium salt LXVI with potassium *tert*-butoxide leads to the formation of a 3*H*-phosph(V)ole derivative LXVII. The main interest of LXVII arises from the fact that it is the only benzophosphole derivative so far characterized.

More recently, Hughes and Davies[56] investigated the reaction of diphenylvinylphosphine with dimethyl acetylenedicarboxylate and found that several products are formed depending upon the order of addition of the reactants. If the reaction is carried out in the presence of an excess of the ester, the phosphine oxide LXVIII is isolated. The course of the reaction was postulated as the initial formation of the 3*H*-phosph(V)ole derivative LXIX as a transient intermediate which then reacts further with the excess of ester to give the bicyclic ylid LXX. Subsequent hydrolysis of LXX gives the observed phosphine oxide LXVIII.

On the other hand, if the reaction is carried out in such a way that unreacted phosphine is always present, the formation of the highly reactive 3*H*-phosph(V)ole LXIX and/or its more stable but still highly reactive tautomer LXXI is postulated. However, since hydrolysis occurs during the work-up process; the final product is therefore the open-chain phosphine oxide LXXII which is obviously formed from the more stable 2*H*-phosph(V)ole tautomer LXXI. The ylid



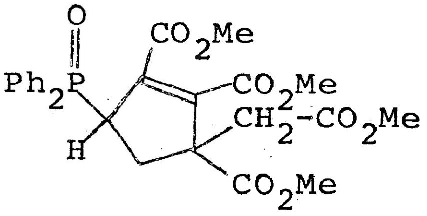
LXV



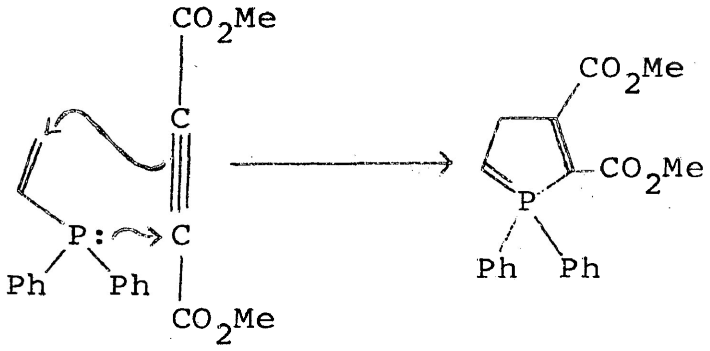
LXVI

LXVII

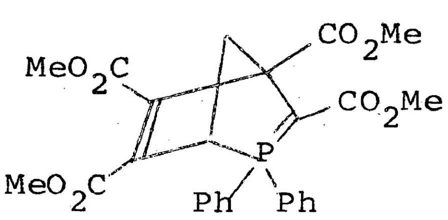
R = H, Ph or $CO_2Me$; X = Br or I



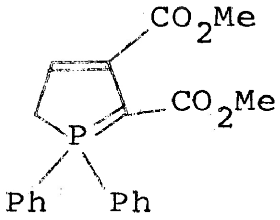
LXVIII



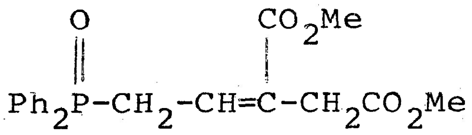
LXIX



LXX



LXXI



$\overset{O}{\overset{\|}{Ph_2P}}-CH_2-CH=\overset{CO_2Me}{\overset{|}{C}}-CH_2CO_2Me$

LXXII

LXXI has also been trapped[57] with *p*-nitrobenzaldehyde in a Wittig reaction.

As mentioned in the preceding section, Tebby[51] has reconsidered the structure of the methanol insoluble rearrangement product of the unstable triphenylphosphine-dimethyl acetylenedicarboxylate adduct LV (or LIV). The rearrangement is usually effected by keeping an ethereal solution of LV (or LIV) at room temperature for a few days and the product is in fact the stable 2*H*-phosph(V)ole LVIIa rather than the open-chain phosphine LVI. The formation of the stable 2*H*-phosph(V)ole LVIIa can also be achieved by brief heating of LV (orLIV) in a solvent as well as by direct treatment of triphenylphosphine with dimethyl acetylenedicarboxylate in ether under reflux. The structure assignment of LVIIa was made on the basis of both spectroscopic and chemical evidence. The 2*H*-phosph(V)ole derivatives LVIIb[51] and LVIIc[57] have also been reported to form in reactions of tri-*p*-tolylphosphine and cyclopropyldiphenylphosphine with dimethyl acetylenedicarboxylate, respectively.

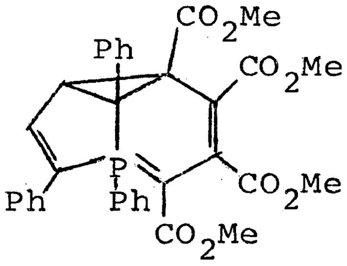
The preceding survey has been published in an expanded form which also covers phospholes containing additional fused rings.[58]

## CONCLUSION

It can be seen from this survey that relatively few reactions of simple phosphole systems have been studied in any detail, particularly reactions at the ring carbon atoms. Therefore, the next section of this thesis will present the results of an investigation of some of these reactions with particular emphasis on possible ring expansion reactions.

## Note Added in Proof

Since this introduction was prepared, Tebby[84] has shown that the structure LXI is incorrect. The structure of the adduct is, in fact, the tricyclic system shown below:



Further evidence for the aromatic character of the phosphole ring system (II) has been provided by Egan's observation[85] that the energy barrier to inversion at the phosphorus atom in 1-isopropyl-2-methyl-5-phenylphosphole is unusually low compared to that of open-chain tertiary phosphines.

# RESULTS AND DISCUSSION

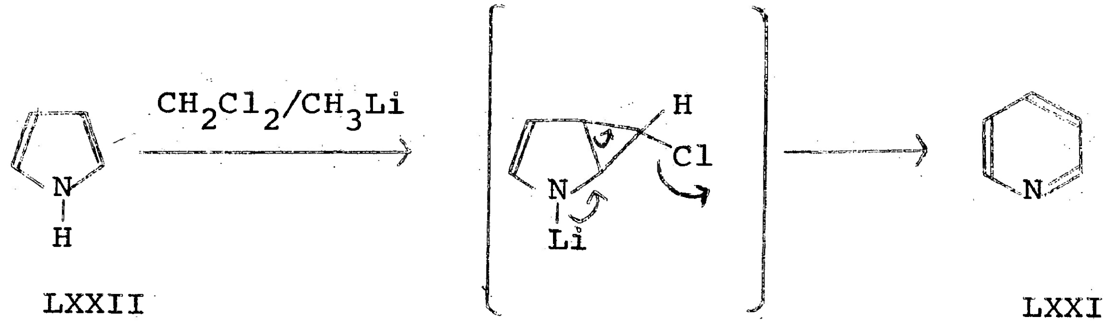
## Introduction

Since phospholes are structurally and electronically similar to pyrroles, chemical reactions entered into by phospholes are best investigated in such a manner that the reactivity of the phosphole system can be compared with that of pyrrole derivatives. It was therefore decided to investigate possible ring expansion and other reactions of phosphole derivatives at the ring carbon atoms as part of a general investigation of the chemistry of the phosphole system.

It is well known[59,60,61] that pyrrole derivatives will undergo ring expansion reactions. Thus, treatment of pyrrole (LXXIII) with methylene chloride and methyllithium[61] results in the formation of pyridine (LXXIV) in 32% yield. Phospholes should also in principle undergo ring expansion reactions although not necessarily of the same mechanistic type. Furthermore, ring expansion reactions of phosphole derivatives are of some interest as they might lead to the synthesis of six-membered ring unsaturated phosphorus heterocycles - possibly with unsymmetrical substitution.

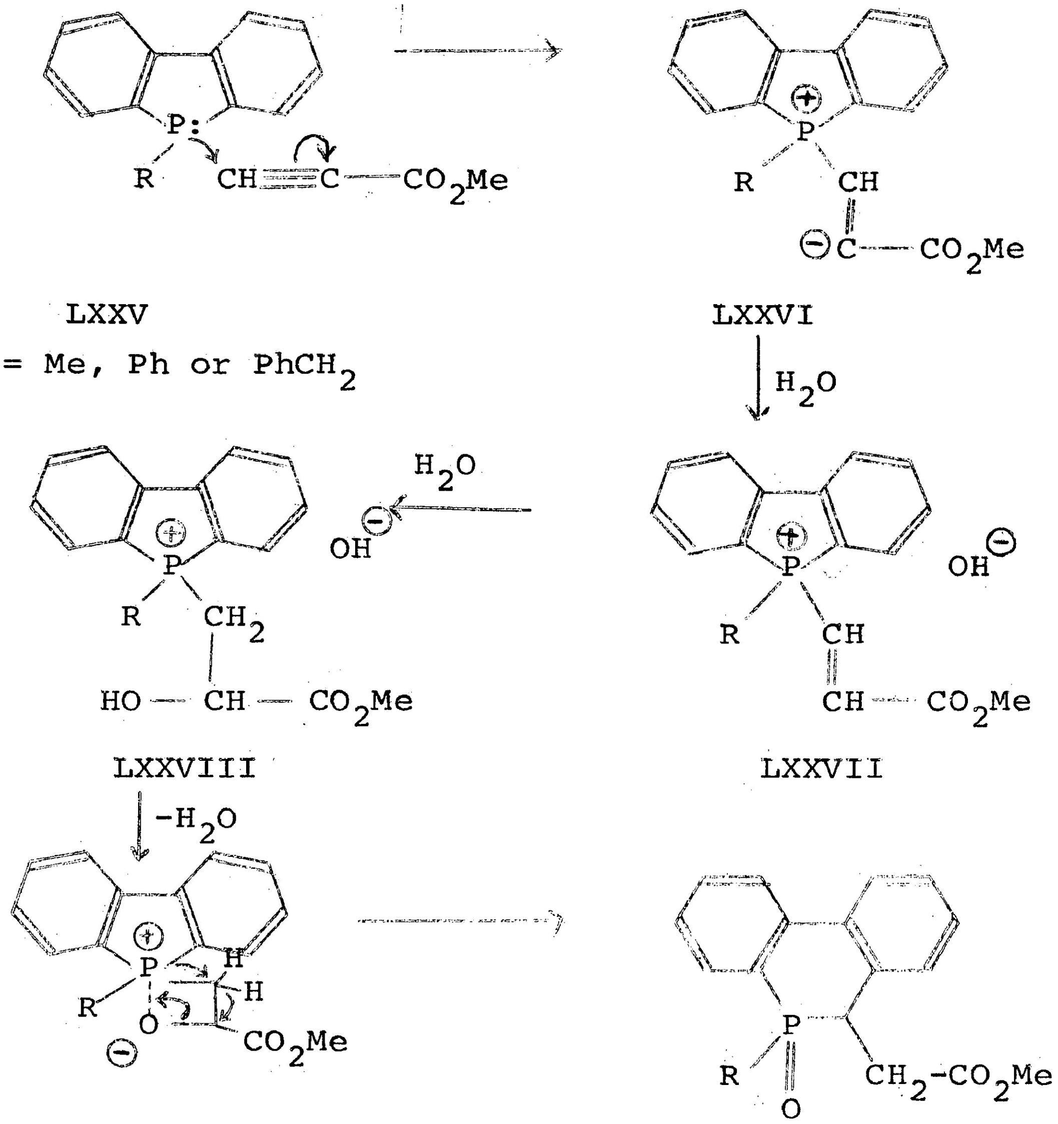
As already mentioned in the introduction to this thesis, ring expansion reactions of phosphole derivatives have been previously investigated very briefly. Thus, Campbell[16] found that 1,2,5-triphenylphosphole (XVa) reacts with methyl diazoacetate in boiling dioxan without a catalyst to give the ring expanded product L although the alternative bicyclic structure LIa has not been completely excluded. 9-Substituted 9-phosphafluorene derivatives such as LXXV have also been shown to undergo ring expansion reactions. Treatment of LXXV (R = Me, Ph or $-CH_2Ph$) with methyl propiolate and water[62] gives rise to the formation of 9,10-dihydro-9-phosphaphenanthrene-9-oxides (LXXX where R = Me, Ph or $-CH_2Ph$) probably as shown in the sequence LXXV → LXXVI → LXXVII → LXXVIII → LXXIX → LXXX.[63] Quaternization of LXXV (R = Me or Ph) with methylene iodide followed by alkaline hydrolysis[64] gives similar ring expanded products LXXXI (R = Me or Ph).

These reports, together with the ready availability of several simple phosphole derivatives as starting materials, led us to try with some success, several approaches to ring expansion of the phosphole system which are outlined in the following discussion.



LXXII

LXXIV



LXXV

R = Me, Ph or $PhCH_2$

LXXVI

LXXVIII

LXXVII

LXXIX

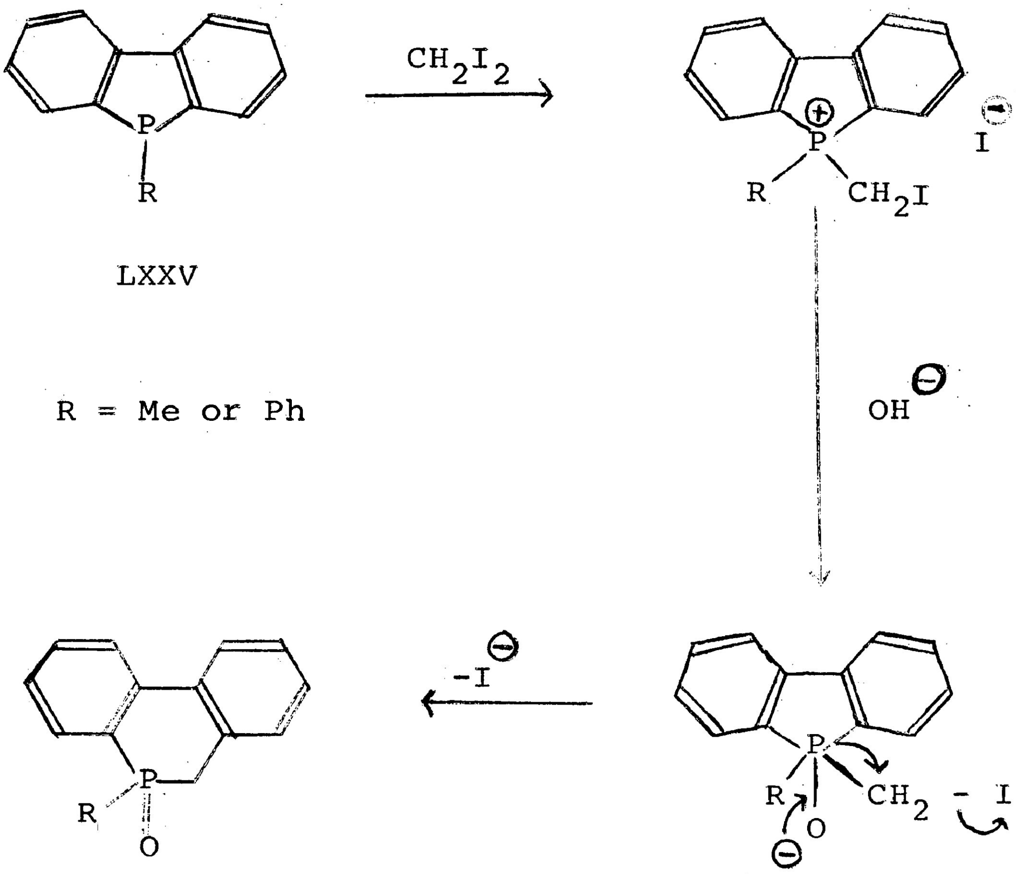
LXXX

## Pyrolysis of 2,3,-Cyclopropano and 2,3-Pyrazolino Derivatives of 1,2,5-Triphenylphosphole Oxide

The first approach was a more detailed investigation of the reactions of the phosphole oxide with diazo compounds reported by Campbell.[16] In particular, Campbell observed that 3,4,5-triphenyl-4-phosphabicyclo [3.1.0]hex-2-ene-4-oxide (LIb) resolidifies above its melting point to give a high melting product which was not further investigated at that time.

In order to commence the investigation, the following starting materials were prepared by the methods described by Campbell[16]: 1,2,5-triphenylphosphole (XVa), 1,2,5-triphenylphosphole oxide, adduct of 1,2,5-triphenylphosphole oxide with diazomethane (the pyrazoline LIII), adduct of 1,2,5-triphenylphosphole oxide with ethyl diazoacetate (the pyrazoline XLVIII with Me replaced by Et), 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (the cyclopropane LIb), ethyl 1,2,6-triphenyl-1-phosphacyclohexa-2,5-diene-3-carboxylate-1-oxide (L, Me replaced by Et) and the free acid of L. Since trichlorosilane ($HSiCl_3$) is known to reduce phosphine oxides to the corresponding phosphines in good yield,[13] the above compounds were treated with this reagent in attempts to prepare the phosphines from the corresponding phosphine oxides. These reductions led to the formation of the reduced pyrazoline LXXXII, m.p. 211 - 212°, and the phosphine derived from LIb, m.p. 134 - 135°. These are new compounds for which satisfactory elemental analyses were obtained. In contrast, the pyrazoline ester XLVIII (Me replaced by Et) is not affected by trichlorosilane.

It was reported by Campbell[16] that the pyrazoline ester XLVIII exists as the imine structure XLVIII rather than the azo-form XLIX since the N-H link is indicated by a fairly strong IR band at 3130 $cm.^{-1}$ Structure XLVIII, which has a C=N double bond in conjugation with the ester group, might be expected to be more stable than XLIX which contains an isolated N=N double bond in the pyrazoline portion of the molecule. On the other hand, Campbell[16] proposed the azo-structure LIII for the 1,2,5-triphenylphosphole oxide/diazomethane adduct which shows a weak band at $\lambda_{max}$ (log $\varepsilon$) = 365 m$\mu$ (1.88) indicating an azo-group and no N-H absorption in the IR region. However, it is worth noting that reduction of the pyrazoline LIII with trichlorosilane to give the reduced pyrazoline (LXXXII) is accompanied by a prototropic shift. Evidence supporting structure LXXXII is provided by the IR spectrum which shows a fairly strong N-H stretching band at 3280 $cm^{-1}$ and

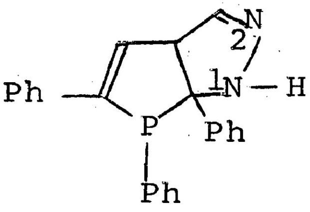


LXXV

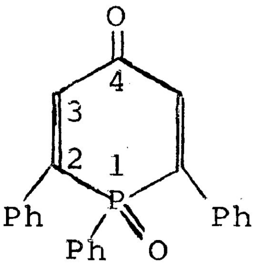
R = Me or Ph

LXXXI

R = Me or Ph



LXXXII



LXXXIII

also by the UV spectrum which shows $\lambda_{max}$ at 224 mμ and 250 mμ indicating the absence of an azo-group. Since hydrogen chloride is generated as a by-product in the reduction of the pyrazoline LIII with trichlorosilane and it is well known that 1-pyrazolines tend to isomerize to the more stable 2-pyrazolines with a trace of acid,[65] the structural change is not unexpected. However, several other effects such as the stereochemistry at the ring junction (which is still unknown) and the strong electron withdrawing effects of the P=O and $CO_2Me$ groups may be important in determining the imine or azo-structures in the pyrazolines XLVIII, LIII, and LXXXII.

It should also be noted that repetition of the photochemical reaction between 1,2,5-triphenylphosphole oxide and diazomethane gave a mixture of the cyclopropane LIb and the pyrazoline LIII rather than the cyclopropane alone as reported by Campbell.[16] This is possibly due to minor differences in reaction conditions and in the type of photochemical reactor.

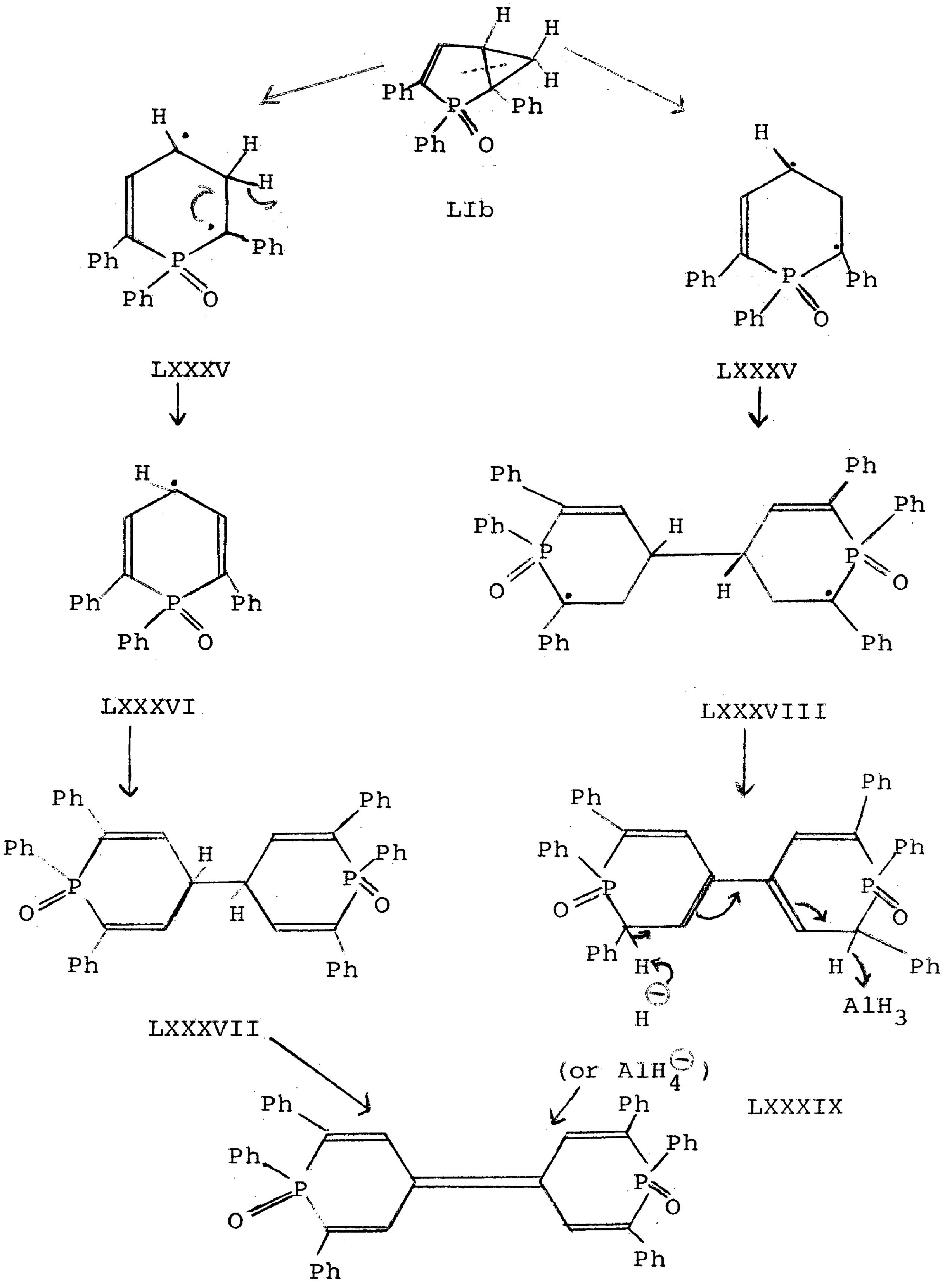
The cyclopropane LIb was carefully pyrolysed in a woods metal bath at 238° until gas evolution ceased and the material turned dark brown and resolidified. The crude product which is rather oily was washed with diethyl ether followed by ethanol and the reddish yellow solid left was recrystallized from chloroform/ethanol mixture. The product was obtained in 47% yield, m.p. 386 - 387°. Pyrolysis of LIb under vacuum (*ca.* 1 torr) under similar conditions gave a slightly better yield (51%) of the same product. The high melting point and low solubility of this pyrolysed product indicate a higher molecular weight than the starting material. Elemental analyses and the high melting point suggest the formulae $C_{46}H_{38}O_2P_2$ or $C_{46}H_{36}O_2P_2$ or $C_{46}H_{34}O_2P_2$, *i.e.* a dimer of the starting material $C_{23}H_{19}OP$, a dimer minus $H_2$ or a dimer minus $2H_2$.

Pyrolysis of LIb under vacuum ($<4 \times 10^{-7}$ torr) followed by mass spectrometric analysis of the gas given off shows that hydrogen is evolved in the reaction. This suggests that thermal dimerization of LIb occurs with elimination of hydrogen. Consequently, the molecular formula $C_{46}H_{38}O_2P_2$ can be tentatively ruled out. Since the pyrolysis product itself is too involatile even under high vacuum ($<$ 4 X $10^{-7}$ torr) at 300°, its molecular weight could not be confirmed by mass spectrometry.

A compound of molecular formula $C_{46}H_{34}O_2P_2$ containing two unsaturated phosphorus-containing six-membered rings has been previously prepared by Märkl.[66] Treatment of 1,2,6-triphenyl-1-phosphacyclohexa-2,5-diene-4-one-1-oxide (LXXXIII) with triethyl phosphite at 80 - 100° gives a quantitative yield of 3,3',4,4',5,5'-hexaphenyl-4,4'-diphosphabi-(2,5-cyclohexadienylidene)-4,4'-dioxide (LXXXIV), m.p. 425 - 428°, $\lambda_{max}$ = 324.5 and 437 mμ.

Superficially the pyrolysis product of the cyclopropane LIb is similar to LXXXIV obtained by Märkl.[66] However, a more detailed investigation shows that the pyrolysis product differs from LXXXIV in its melting point and in its UV spectrum. Also, the NMR spectrum of the pyrolysis product shows the presence of non-aromatic/olefinic protons. The pyrolysis product is therefore not identical to LXXXIV. The UV spectrum (in absolute ethanol) of the pyrolysis product shows $\lambda_{max}$ (log ε) at 315 mμ (4.83) and 408 mμ (4.87). This indicates extensive conjugation in the molecule. The IR spectrum (Nujol) shows a typical P=O stretching band at 1180 $cm.^{-1}$ The NMR spectrum (in trifluoroacetic acid) shows a ratio of 17 aromatic and olefinic protons (complex multiplet at $\tau$ = 2.01 - 3.13) to one tertiary proton (very broad unresolved hump at $\tau$ = 6.11) which suggests a molecular formula of $C_{46}H_{36}O_2P_2$ for the pyrolysis product.

It is known[67] that vinylcyclopropane derivatives undergo thermal rearrangement to give the corresponding cyclopentene derivatives but this type of thermal rearrangement would perhaps not be expected in compound LIb because of the rigid nature of the bicyclic system. Furthermore, such rearrangements would lead to products containing little conjugation although further rearrangements could possibly occur. Since mechanistic studies of the pyrolysis of LIb were not carried out in this investigation, it is not known whether the reaction is homolytic or heterolytic although a homolytic mechanism might be expected bearing in mind the high temperature at which the reaction occurs and the fact that molecular hydrogen is eliminated during the reaction. These observations together with the NMR evidence suggest that one of the two principal modes of reaction shown in the sequences LIb → LXXXV → LXXXVI → LXXXVII and LIb → LXXXV → LXXXVIII → LXXXIX may be possible, although the intermediate LXXXVIII is somewhat unlikely. Structure LXXXVII is consistent with the NMR evidence but seems to be ruled out on the basis of UV evidence which shows a strong absorption band at $\lambda_{max}$ (log $\varepsilon$) = 408 mμ (4.87) indicating extensive conjugation in the molecule whereas LXXXVII would be expected to be colourless since it is very similar to the ring enlarged ester L which is colourless. The pyrolysis product is, in fact, deep red and structure LXXXVII is therefore eliminated. This leaves LXXXIX as the most likely structure since it fits all of the evidence available at this point. It should, however, be mentioned that other reactions leading to products containing conjugated chromophores can be postulated, but, in the opinion of the author, these are most unlikely since they involve breaking one of the bonds of the cyclopropane ring in LIb other than the bond forming the junction of the two rings. The structure of the pyrolysis product will be considered further in the next section of this discussion.



LIb

LXXXV

LXXXV

LXXXVI

LXXXVIII

LXXXVII

LXXXIX

LXXXIV

Pyrolysis of the 1,2,5-triphenylphosphole oxide-diazomethane adduct (LIII) under vacuum (*ca.* 1 torr) at 238° gives the same product (LXXXIX) in good yield (55%) whereas pyrolysis of the 1,2,5-triphenylphosphole oxide-ethyl diazoacetate adduct XLVIII (Me replaced by Et) at 220 - 225° for 20 minutes results only in the formation of Campbell's ring enlarged ester L (Me replaced by Et) without dimerization or loss of $H_2$. Pyrolysis of the reduced pyrazoline (LXXXII) and the reduced cyclopropane obtained by the action of trichlorosilane on LIb gives only general decomposition.

## Photolysis of 2,3-Cyclopropano and 2,3-Pyrazolino Derivatives of 1,2,5-Triphenylphosphole Oxide

Photolysis of the cyclopropane LIb in dry, peroxide-free tetrahydrofuran under dry, oxygen-free nitrogen with a medium pressure mercury lamp (100 watt) through pyrex for 8 days gives a compound (m.p. 439 - 440°) in 44% yield similar, but not identical to, the pyrolysis product. Increasing the reaction time gives no improvement in yield since the product absorbs UV radiation so strongly that it effectively screens the remaining starting material. Photolysis of the pyrazoline LIII under similar conditions gives the same product in 14% yield. The reaction possibly proceeds *via* the cyclopropane

LIb as a transient intermediate since the same cyclopropane LIb has been previously isolated[16] from the photochemical reaction between 1,2,5-triphenylphosphole oxide and diazomethane under milder reaction conditions. Moreover, photolysis of simple pyrazolines is known to give cyclopropane derivatives.[68]

Elemental analyses of the photolysis product are in excellent agreement with $C_{46}H_{34}O_2P_2$. The UV spectrum shows $\lambda_{max}$ (log $\varepsilon$) at 325 mμ (4.53) and 438 mμ (4.91) which indicates extensive conjugation in the molecule. The IR spectrum shows a typical P=O stretching vibration at 1169 $cm^{-1}$ and the NMR spectrum shows only aromatic and olefinic protons as a multiplet at $\tau$ = 2.22 - 2.96. Both the melting point and the UV spectrum of the photolysis product are very similar to those of Märkl's compound LXXXIV[66] although the extinction coefficients of the UV absorptions were not given in Märkl's report. The NMR spectrum of the photolysis product agrees well with structure LXXXIV. It therefore seems likely that the photolysis product has structure LXXXIV. Photolysis of the pyrazoline and cyclopropane obtained by reduction of the P=O bonds of LIII and LIb respectively with trichlorosilane gave no result.

Very recently, Cooke[69] found that vinylcyclopropane (XC) undergoes photochemical rearrangement to give the corresponding cyclopentene XCI by a concerted mechanism. However this type of mechanism seems unlikely in the photolysis of LIb for the reasons already outlined for the pyrolytic reaction. As with the pyrolysis, the photolysis of LIb has not been investigated mechanistically but one possible mechanism for the formation of LXXXIV is that shown in the sequence LIb → LXXXV → LXXXVI → LXXXVII → LXXXIV.

Further pyrolysis of the original pyrolysis product, tentatively assumed to be LXXXIX at much higher temperature (385 - 390°) under vacuum ( *ca.* 1 torr) produced more hydrogen as detected by mass spectrometry but only the original pyrolysis product LXXXIX was isolated with no apparent conversion into the photolysis product LXXXIV observed. However, substantial thermal decomposition occurs and this probably accounts for the evolution of hydrogen gas.

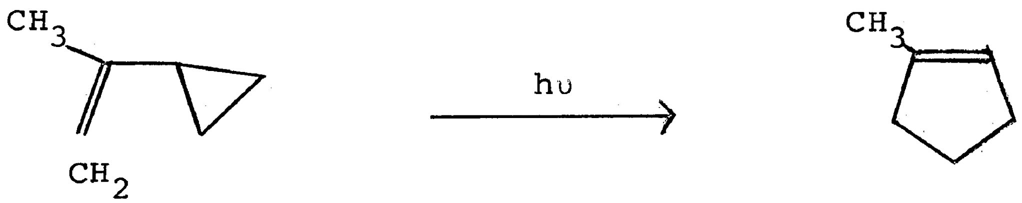
Prolonged irradiation (10 days) of the pyrolysis product thought to be LXXXIX with UV radiation also gives no conversion into the photolysis product LXXXIV and only a quantitative amount of starting material is isolated with no decomposition observed. Thus, it seems likely that the pyrolysis product is not an intermediate in the formation of the photolysis product.

Attempts to reduce both the photolysis and pyrolysis products (LXXXIV and LXXXIX ?) with trichlorosilane under a variety of conditions were unsuccessful. The two compounds are highly stable and reduction with trichlorosilane, even under forcing conditions in a sealed tube under pressure at 100°, is ineffective. The stability of both the photolysis and pyrolysis products towards trichlorosilane is not unexpected since Märkl[66] has previously observed that silanes leave unsaturated six-membered ring phosphorus heterocycles such as LXXXIII untouched.

Treatment of the photolysis product LXXXIV with a large excess of phosphorus pentachloride at 120 - 130° results in the formation of an unisolated, deep red compound assumed (by analogy with Märkl's observations[66]) to be the P,P,P',P' -tetrachloro compound. Sublimation leads to removal of the excess of phosphorus pentachloride. Subsequent treatment of the deep red residue with lithium aluminium hydride in ether leads to formation of the corresponding phosphine, m.p. 338 - 340°, in good yield. The IR spectrum of the reduced photolysis product shows no P=O stretching vibration and the mass spectrum indicates a molecular weight of 648 (*i.e.* $C_{46}H_{34}P_2$) with traces of compounds with molecular ions at *m/e* 664 (monoxide) and 680 (dioxide). The appearance of peaks at *m/e* 664 and 680 is probably due to oxygen scavenging in the mass spectrometer rather than impurities since the dioxide itself is not volatile under the same conditions. The UV spectrum and melting point are virtually identical with those of Märkl's reduction product (XCIIa) and the structure of the reduced photolysis product and the photolysis product itself are therefore confirmed.

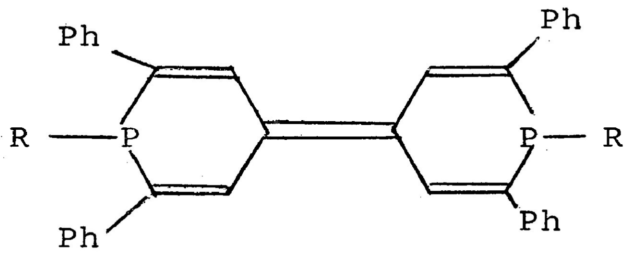
The UV spectrum of XCIIa deserves some comment since Märkl reports $\lambda_{max}$ at 337 mμ and 467 mμ (log ε not given by Märkl). The reduction product XCIIa obtained from LXXXIV in the experiments described in this section shows $\lambda_{max}$ (log ε) at 339 mμ (3.88) and 468 mμ (4.64). These minor differences in UV spectra are probably due to instrumental errors since the values for $\lambda_{max}$ reported here are corrected values obtained by instrument calibration using a holmium filter.

Turning again to the pyrolysis product assumed to by LXXXIX, the first attempt at reduction with phosphorus pentachloride and lithium aluminium hydride surprisingly gave rise to formation of the photolysis product LXXXIV, *i.e.* reduction of the P=O link did not occur. The quantity of phosphorus pentachloride used in this trial experiment was small and formation of the P,P,P',P'-tetrachloro compound had probably not occurred when the hydride was added. The transformation might therefore



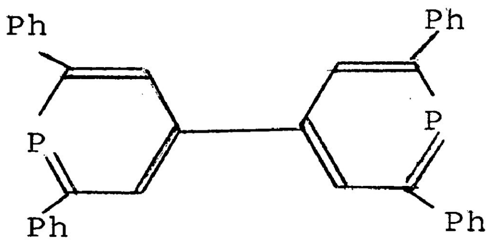
XC

XCI

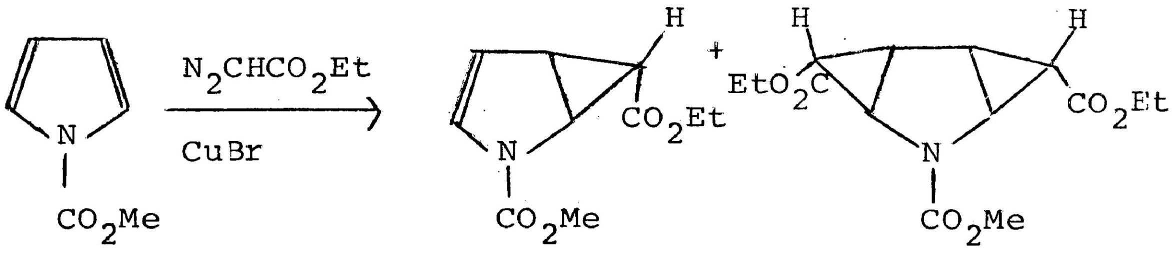


XCII a) R = Ph

b) R = $PhCH_2$-



XCIII



XCIV

XCV

XCVI

occur by the action of lithium aluminium hydride alone upon the pyrolysis product LXXXIX. This proved to be the case since the same transformation occurs when the pyrolysis product is treated with lithium aluminium hydride alone. Conversion of the pyrolysis product into the photolysis product LXXXIV also occurs with sodium hydride but not with other strong bases such as sodium hydroxide, potassium *tert*-butoxide or *n*-butyllithium. This confirms the six-membered ring nature of the pyrolysis product.

The behaviour of the pyrolysis product with lithium aluminium hydride and with sodium hydride is not inconsistent with the proposed structure LXXXIX because the tertiary protons would be expected to be fairly acidic as they are adjacent to strongly electron withdrawing groups. The mechanism could be as shown in the scheme LXXXIX → LXXXIV, *i.e.* an unusual reaction in which lithium aluminium hydride acts as an oxidizing agent.

Improvement of the reduction technique by treatment of the pyrolysis product (LXXXIX) with a large excess of phosphorus pentachloride at 120-130° followed by sublimation of the excess of phosphorus pentachloride prior to reduction with lithium aluminium hydride leads to formation of the reduced pyrolysis product which is identical to the reduced photolysis product LXIIa in all respects. Thus, the structures of the pyrolysis and photolysis products derived from the cyclopropane LIb have been proved beyond any doubt.

Compound XCII has been shown to be of some synthetic value. Thus, Märkl[70] found that heating of XCIIb under nitrogen at 350° results in the formation of the biphosphorinyl derivative XCIII in 51% yield. Since the mass spectrum (recorded at 300°) of XCIIa shows no significant peak corresponding to XCIII at *m/e* = 494, pyrolysis of XCIIa was not further investigated. Conversion of XCIIa into XCIII by this method is not very likely because the phenyl group is known to be a poor leaving group compared with the benzyl group.

## Attempted Reactions of 1,2,5-Triphenylphosphole and its Oxide with Dichlorocarbene and Dibromocarbene

In view of the numerous reports[59,60,61] on reactions of pyrrole derivatives with halogenated carbenes, it was decided to investigate reactions of 1,2,5-triphenylphosphole (XVa) and its oxide with dichlorocarbene and dibromocarbene in attempts to produce other cyclopropano derivatives of the phosphole similar to LI. However, under a variety of reaction conditions and with halogenated carbenes generated by several methods, the reactions led either to no detectable reaction or greyish, insoluble, high-melting compounds in small quantities which were not further investigated. In general, halogenated carbenes were generated *in situ* by either thermal decomposition of the sodium salt of trichloroacetic acid[71] or alkaline decomposition of haloforms.[72]

## The Reaction of 1,2,5-Triphenylphosphole Oxide and Ethyl Diazoacetate - The Nature of the Product.

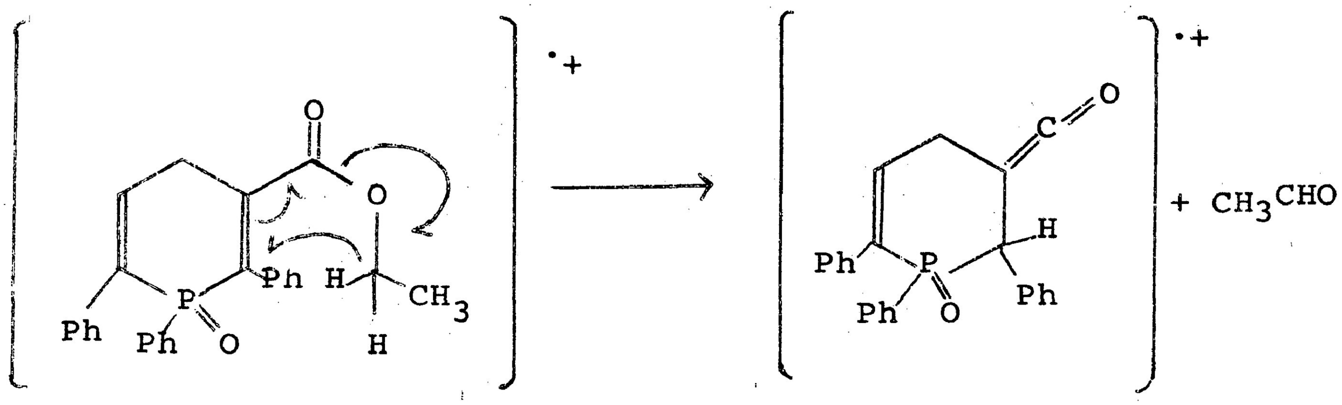
Pyrrole derivatives such as *N*-methoxycarbonylpyrrole (XCIV) have been shown to react with ethyl diazoacetate in the presence of cuprous bromide to give a mixture of mono and bis-adducts (XCV and XCVI).[73] In contrast, Campbell[16] found that 1,2,5-triphenylphosphole oxide reacts slowly with methyldiazoacetate at room temperature to give exclusively the pyrazoline ester (XLVIII) which eliminates nitrogen on treatment with copper in diglyme under reflux to give a product which is almost certainly the ring enlarged ester L. The same ester L is obtained directly by heating a mixture of 1,2,5-triphenylphosphole oxide and methyl diazoacetate in dioxan. Similar results were obtained from reactions of 1,2,5-triphenylphosphole oxide with ethyl diazoacetate and the products are the corresponding ethyl esters XLVIII (Me replaced by Et) and L (Me replaced by Et).

The ring enlarged ester L (Me replaced by Et) is of interest for two reasons. First, if the ester group is absent is is found that a bicyclic compound rather than a ring enlarged compound is formed. Thus, thermal decomposition of the 1,2,5-triphenylphosphole oxide/diazo methane adduct (LIII) yields not a ring enlarged product but a cyclopropane derivative LIb. Since an ester group is known to be a strongly electron withdrawing group, the presence of such a group would probably weaken the C-C bond at the ring junction in the bicyclic compound LIa which may exist as a transient intermediate in the reaction of 1,2,5-triphenylphosphole oxide and methyl diazoacetate.

Second, ring enlargement of the cyclopropane LIb, both pyrolytically and photochemically, could conceivably go through a transient intermediate of similar structure to L which, under the conditions of the reaction, reacts further or oxidizes with traces of oxygen in the nitrogen atmosphere or oxygen derived from the P=O bond to give the observed photolysis and pyrolysis products (LXXXIV and LXXXIX). In particular, two of the three ring protons in the ring enlarged ester L (Me replaced by Et) are double allylic and might be unusually reactive. However, treatment of the ring enlarged ester L (Me replaced by Et) with either neutral or alkaline potassium permanganate or hydrogen peroxide left the starting material untouched. Similarly, pyrolysis of the ester L (Me replaced by Et) or the corresponding free acid of L at 290 - 300° gives no reaction. Furthermore, the ester L (Me replaced by Et) remains unchanged upon irradiation through quartz under nitrogen with a medium pressure 100 watt mercury lamp.

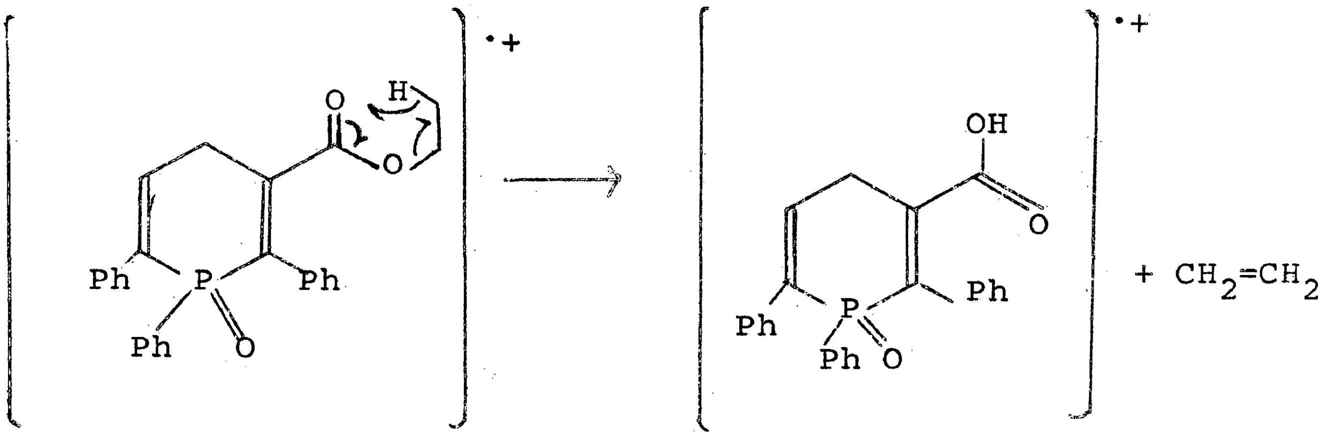
It should also be mentioned that hydrolysis of the ester L (Me replaced by Et) by heating under reflux with methanol containing sodium methoxide gave, on one occasion, two different crystal forms (snowy white plates and colourless needles) of the free acid which were at first thought to be two different compounds. However, both of the two crystal modifications showed the same m.p. (288 - 289°), UV, NMR and mass spectra with some differences in the IR spectra (Nujol mull) and X-ray powder patterns.

Although there is virtually no doubt that the structure of the ring enlarged ester L (Me replaced by Et) is as proposed, it was thought that the structure could be definitely confirmed by using mass spectrometry. The mass spectrum of L (Me replaced by Et) should show peaks at *m/e* 386 and 370 corresponding to McLafferty rearrangements[74] on electron impact of the types shown in sequences L (Me replaced by Et) → XCVII and L (Me



L (Me replaced by Et) XCVII

*m/e* = 414 *m/e* = 370



L (Me replaced by Et) XCVIII

*m/e* = 414 *m/e* = 386

replaced by Et) → XCVIII, respectively. This would give very strong evidence for the unsaturated six-membered ring structure of the ester L (Me replaced by Et) because the alternative bicyclic structure LIa should show only one McLafferty rearrangement on electron impact of the type shown in sequence L (replaced Me by Et) → XCVIII assuming that ring opening and/or rearrangement does not occur. In fact, peaks are observed at *m/e* 386 and 370 (25% and 15% of the molecular ion peak at *m/e* 414, respectively) but high resolution mass spectrometric investigation of L (Me replaced by Et) shows that the precise masses of the two peaks are in fact at *m/e* 386.14350 and 370.14896 indicating that these peaks correspond to ions of composition $C_{25}H_{23}O_2P$ and $C_{25}H_{23}OP$, respectively. This means that the peaks are due to elimination of CO and $CO_2$, respectively. The reasons for this fragmentation are obscure. Details of the precise mass spectrum of L (Me replaced by Et) are as follows and the atomic compositions for each ion were found by complete element mapping.

The molecule ion is at *m/e* 414.13914 $C_{26}H_{23}O_3P$.

The peak at *m/e* 386 is a doublet in the ratio of 1:30 at

*m/e* 386.10312 $\equiv C_{23}{}^{13}C_1H_{18}O_3P$

and *m/e* 386.14350 $\equiv C_{25}H_{23}O_2P$ (molecular ion - CO)

The peak at *m/e* 370 is also a doublet in the ratio of 1:2 at

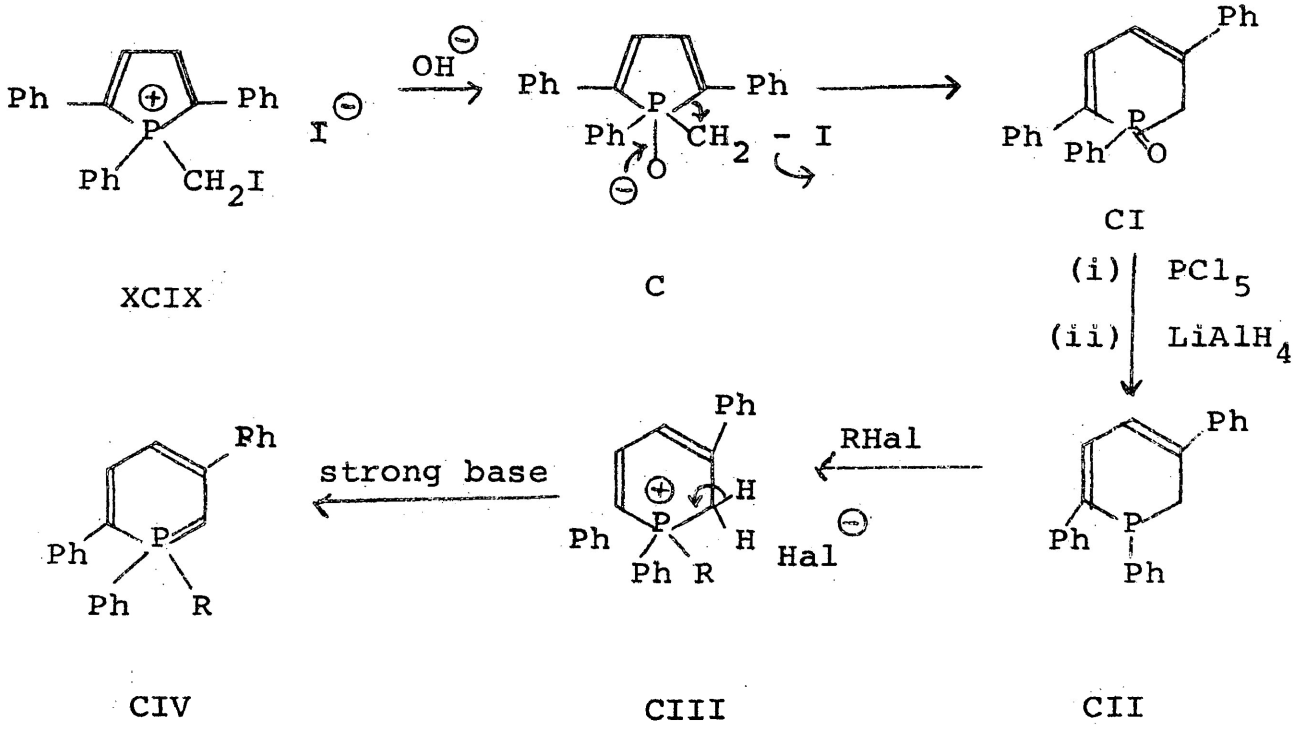
*m/e* 370.10768 $\equiv C_{23}{}^{13}C_1H_{18}O_2P$

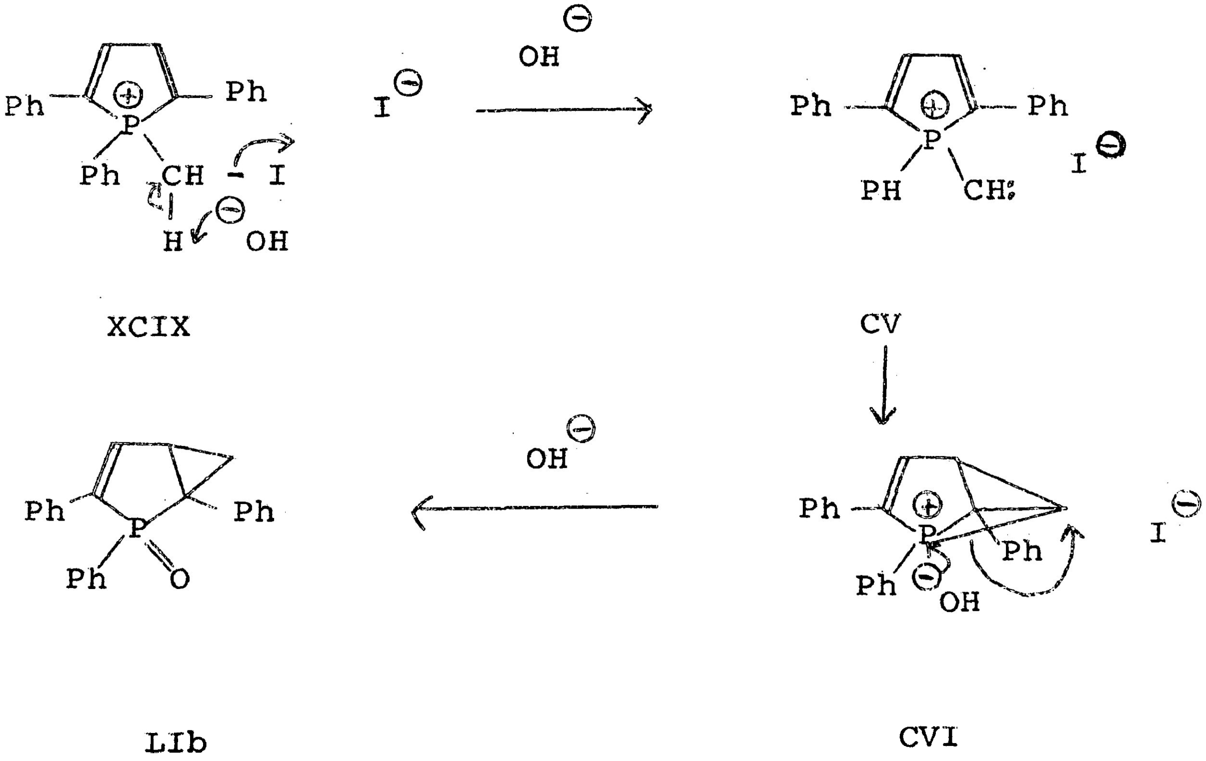
and *m/e* 370.14896 $\equiv C_{25}H_{23}OP$ (molecular ion - $CO_2$)

## Treatment of 1-Iodomethyl-1,2,5-Triphenylphospholium Iodide with Aqueous Base

As already mentioned, Millar[64] found that ring enlargement of methylene iodide quaternary salts of 9-substituted-9-phosphafluorenes (LXXV) occurs readily in the presence of hydroxide ion to give the corresponding ring enlarged products LXXXI in moderate yield. A similar reaction might be expected to occur with the methylene iodide quaternary salt of 1,2,5-triphenylphosphole (XVa) and the product could be used in the synthesis of unsymmetrically substituted phosphabenzene derivatives which are still unknown. The expected reaction scheme is outlined in the sequence XCIX → C → CI → CII → CIII → CIV. Alkaline hydrolysis of XCIX does not, however, proceed as expected and a very unusual type of reaction occurs.

1,2,5-Triphenylphosphole (XVa) reacts very slowly with methylene iodide over a period of 4 1/2 days in a pressure bottle at 80 - 85° to give a quantitative yield of the corresponding methylene iodide quaternary salt (XCIX) which is a new compound and for which satisfactory elemental analyses were obtained. The NMR spectrum (in trifluoroacetic acid) of XCIX shows a ratio of 17 aromatic and olefinic protons (multiplet at $\tau = 1.75 - 2.76$) to 2 methylene protons (doublet centered at $\tau =$


XCIX
OH⁻
C
CI
(i) PCl5
(ii) LiAlH4
CII
RHal
CIII
strong base
CIV
Hal⁻
I⁻

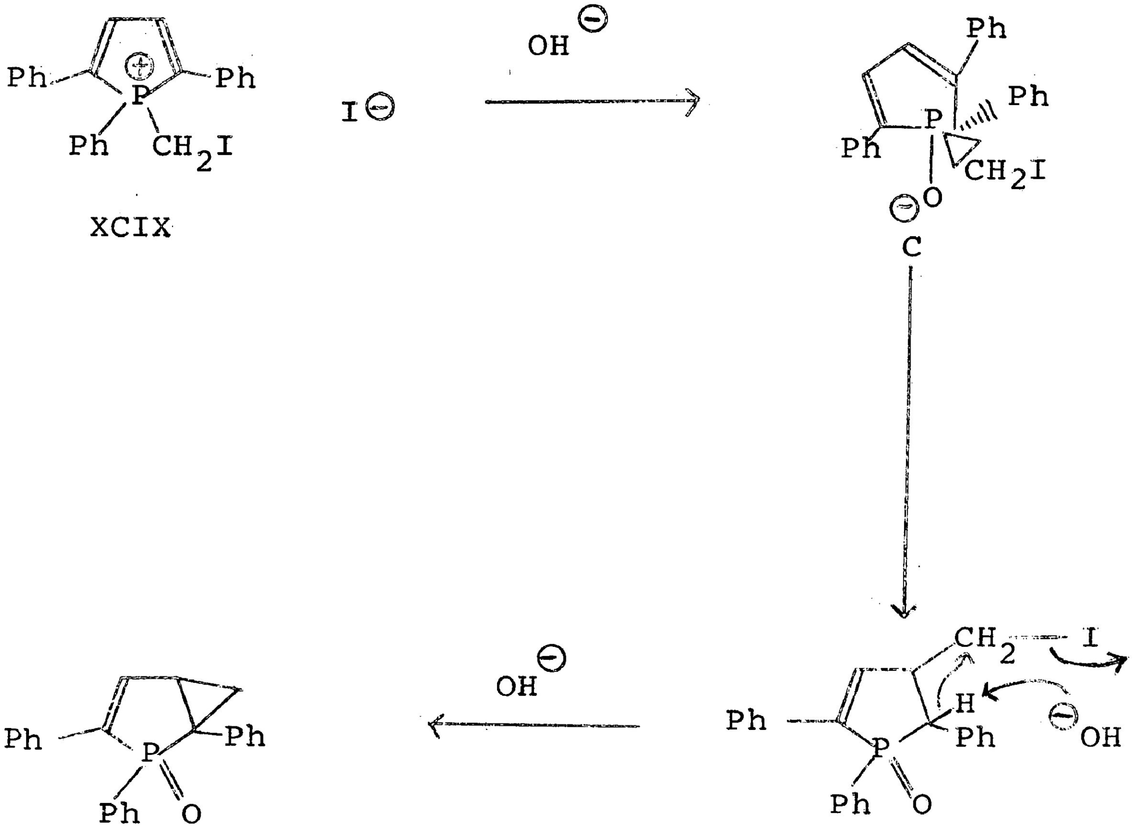

XCIX
OH⁻
CV
CVI
OH⁻
LIb
I⁻

5.68, $J_{HP}$ = 8Hz). The UV spectrum (in ethanol) shows $\lambda_{max}$ (log $\varepsilon$) at 225 mμ (4.58), 275 mμ (3.71) and 411 mμ (4.19). Hydrolysis of XCIX with sodium hydroxide in aqueous methanol under reflux conditions for 24 hours surprisingly gives a good yield of the cyclopropane LIb for which the melting point and IR, UV and NMR spectra are identical to those of an authentic sample in all respects. Furthermore, reduction, pyrolysis and photolysis of the product obtained from alkaline hydrolysis of XCIX gives exactly the same results as authentic LIb.

There are two possible mechanisms for the formation of LIb from XCIX. The first of these is a carbene type of mechanism. Abstraction of a proton on the methylene group followed by α-elimination of iodide ion may give a carbene which adds to one of the ring double bonds to give a highly strained tricyclic intermediate. Ring opening by hydroxide ion could give the observed cyclopropane LIb as shown in the reaction scheme XCIX → CV → CVI → LIb. The proposed formation of the carbene CV as a transient intermediate is very similar to the generation of dihalocarbenes from haloforms by the action of base.[72] On the other hand, the positively charged phosphorus atom in XCIX might be expected to be a better leaving group than the iodine atom.

Another possible mechanism is as shown in the scheme XCIX → C → CVII → LIb. Attack of hydroxide ion on the positively charged phosphorus atom of XCIX could occur to give the pentacovalent phosphorus intermediate C or, at least, a transition state approximating to this type of structure. Rearrangement by migration of the methylene iodide group could give CVII which under the reaction conditions could cyclize by elimination of hydrogen iodide in the presence of base to give the cyclopropane LIb. By analogy with Millar's[64] and Trippett's[75] observations regarding alkaline hydrolysis of quaternary salts of phosphafluorenes and phosphetanes, the stereochemistry of the intermediate C should be similar to that shown in C *i.e.*, the five-membered ring should occupy an equatorial-apical position. If this is the case, it is not easy to see how migration of the $-CH_2I$ group to position three of the phosphole ring occurs.

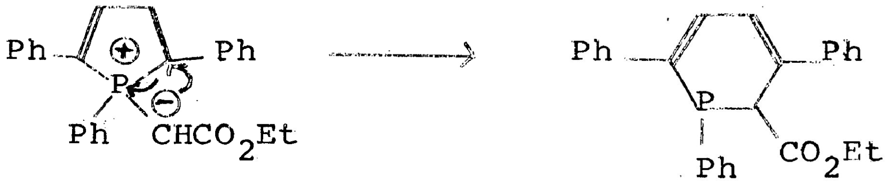
It should be possible to distinguish between the two postulated mechanisms if the appropriate intermediate can be isolated. In order to determine the mechanism, alkaline hydrolysis of XCIX was carried out under milder conditions at room temperature for a much shorter reaction time (2 hours). The product, m.p. 199 - 200°, was shown by elemental analyses to be $C_{23}H_{20}OPI$ and the mass spectrum confirms the molecular weight of 470. The IR



XCIX

LIb

CVII



XXVIII

CVIII

spectrum shows a typical P=O stretching vibration at 1180 $cm^{-1}$ and the UV spectrum shows $\lambda_{max}$ (log $\epsilon$) at 220 mμ (4.33) and 261 mμ (4.07) indicating considerable loss of conjugation. The NMR spectrum shows a ratio of 16 aromatic and olefinic protons (complex multiplet at $\tau$ = 2.19 - 3.16) to 2 methine protons (multiplet at $\tau$ = 5.52 - 6.08) to 2 methylene protons (multiplet at $\tau$ = 6.65 - 7.02). All of this evidence is consistent with the structure CVII proposed for the compound $C_{23}H_{20}OPI$.

It is worth noting that the side-chain methylene group of CVII appears as a multiplet of at least five peaks rather than a doublet in the NMR spectrum. This is probably because the two protons are non-equivalent due to the adjacent asymmetric center. Such a case is similar to that of the diastereomeric methylene protons of 1,2-dichloropropane.[76] The location of the signal which appears at $\tau$ = 6.65 - 7.02 is characteristic of methylene protons attached to an iodine atom as in the NMR spectrum of ethyl iodide.[77]

Further treatment of CVII with sodium hydroxide in aqueous methanol under reflux for 24 hours gives an almost quantitative yield of the cyclopropane LIb. This suggests that CVII is formed as a stable intermediate in the complete alkaline hydrolysis of XCIX and that the reaction follows the second of the postulated mechanisms rather than the first. However, treatment of CVII with a non-aqueous base such as *n*-butyllithium leaves CVII untouched.

Reduction of CVII with trichlorosilane gives no detectable amount of the corresponding phosphine. Neither pyrolysis (at 220° for 10 minutes) nor irradiation (with a 100 watt medium pressure mercury lamp through quartz for 3 days) of CVII gives any identifiable product.

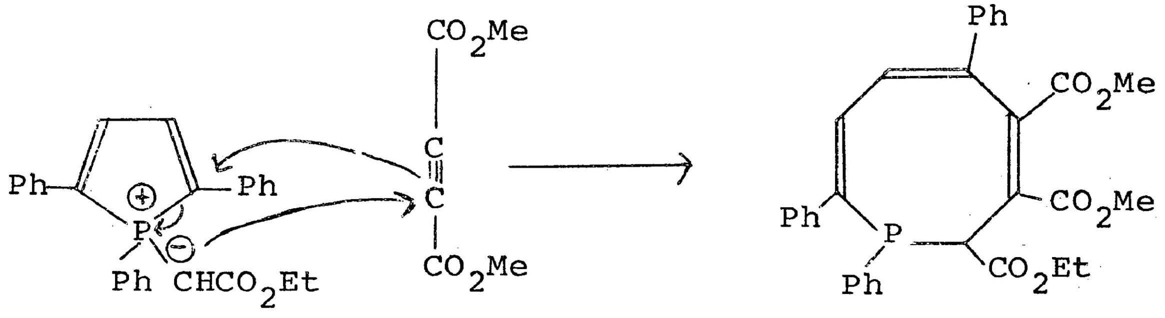
In order to confirm the presence of the side-chain methylene iodide group, the compound CVII was reduced by lithium aluminium hydride but only resinous materials could be isolated.

## Other Approaches to Ring Expansion

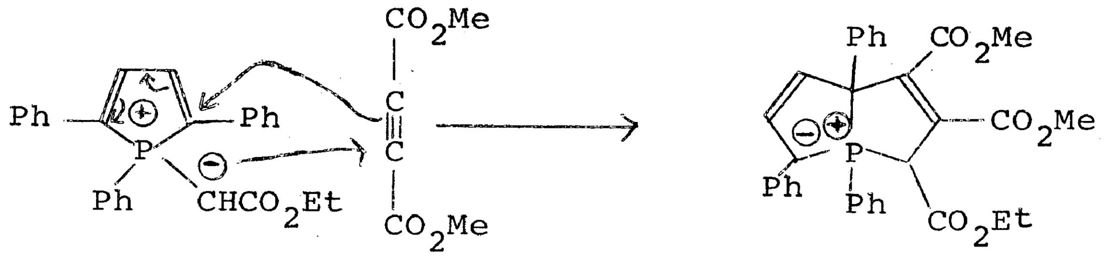
Several other approaches were tried and these were based mainly on the generation of an ylid of the phosphafulvene type. In the first instance, the ylid XXVIII generated by Hocking's method[30] was pyrolysed under vacuum (*ca.* 1 torr) at 170 - 175° for 15 minutes in the hope that it might undergo a ring expansion reaction to give an unsaturated six-membered ring phosphorus heterocycle CVIII. However, only 1,2,5-triphenylphosphole (XVa) was produced in good yield (56%). Thus, the normal reaction that heating ylids leads to dissociation to phosphines and substituted carbenes[78,79] applies.

Irradiation of XXVIII with a 100 watt medium pressure mercury lamp through quartz under nitrogen for 2 weeks was equally unsuccessful and only 1,2,5-triphenylphosphole oxide was isolated.

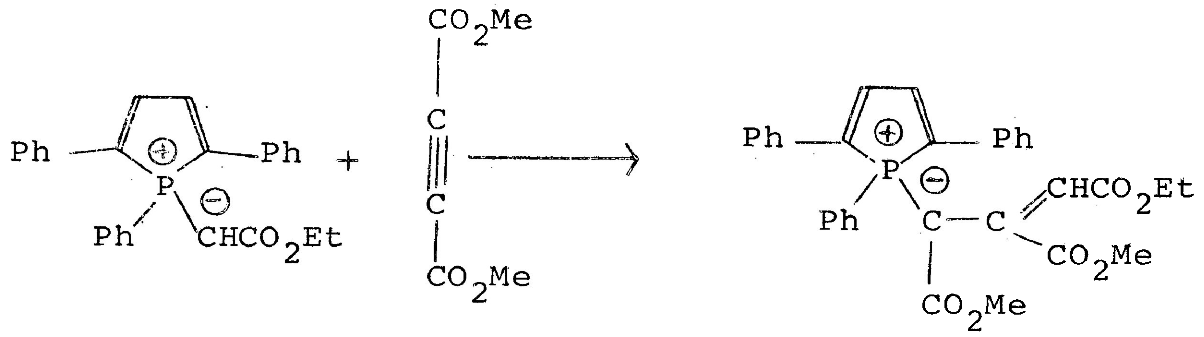
The second approach was to react the ylid XXVIII with dimethyl acetylenedicarboxylate in an attempt to form either CIX, CX, or CXI. The formation of CXI seemed to be the most likely as it would agree with Bestmann's observation[80] that benzhydrylidenetriphenylphosphorane (CXII) reacts with dimethyl acetylenedicarboxylate to afford the rearranged ylid CXIII *via* the four-membered ring transition state CXIV. However, it was found that XXVIII reacts with dimethyl acetylenedicarboxylate in a Diels-Alder type of reaction to give mainly dimethyl 3,6-diphenylphthalate (XLI) in 17% yield. This is unexpected since the carbanion-like center of ylids has been shown to attack the carbon-carbon double bond of the electrophile in all previous experiments.[56] In addition to the formation of XLI, a very small amount of pale yellow crystals (3.7% yield, m.p. 182 - 185°) was also isolated from the reaction of XXVIII with dimethyl acetylenedicarboxylate. The UV spectrum shows $\lambda_{max}$ at 219 mμ and 356 mμ indicating some conjugation. The NMR spectrum (very dilute in $CDCl_3$) shows four main regions of absorption at $\tau$ = 2.33 - 3.15 (complex



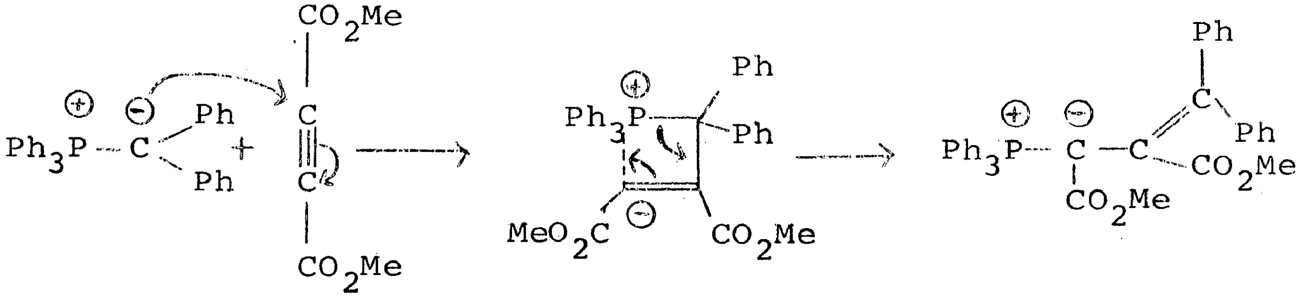
XXVIII CIX



XXVIII CX



XXVIII CXI



CXII CXIV CXIII

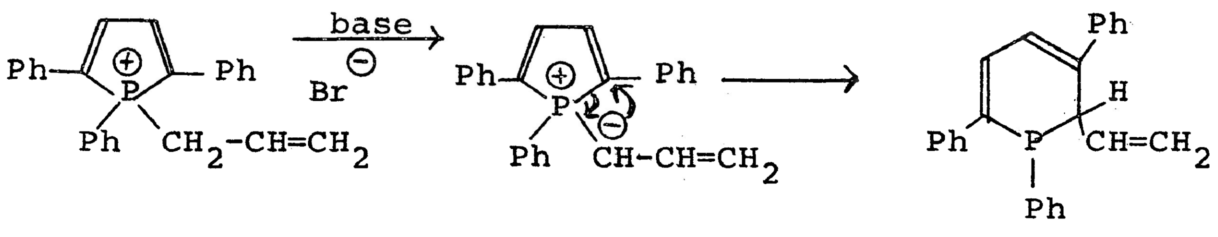
multiplet), 6.01 (quartet), 7.16 (singlet) and 9.04 (triplet) which indicates that the ethyl group has been retained and methoxy groups have been introduced in the reaction. The mass spectrum gives a molecular weight of 540 for the compound and a peak at *m/e* 312 indicates that the 1,2,5-triphenylphosphole fragment remains intact. The evidence, though sparse, is consistent with the structure CXI.

Finally, the quaternary salt CXV was investigated as a possible precursor for ring enlargement reactions. Preparation of CXV can be achieved in quantitative yield by heating 1,2,5-triphenylphosphole (XVa) in dried benzene with allyl bromide under reflux for five days using anhydrous conditions. The quaternary salt CXV (m.p. 202 - 203° with extensive decomposition) is a new compound for which satisfactory elemental analyses were obtained. The UV spectrum of CXV shows $\lambda_{max}$ (log $\varepsilon$) at 212 mμ (4.52), 227 mμ (4.58) and 410 mμ (4.21) which is rather similar to that of the quaternary salt XCIX and indicates considerable conjugation in the molecule. The NMR spectrum of CXV is also similar to that of XCIX and shows a ratio of 20 aromatic and olefinic protons (complex multiplet at $\tau$ = 1.26 - 2.96) to 2 methylene protons (poorly defined quartet centered on $\tau$ = 5.27).

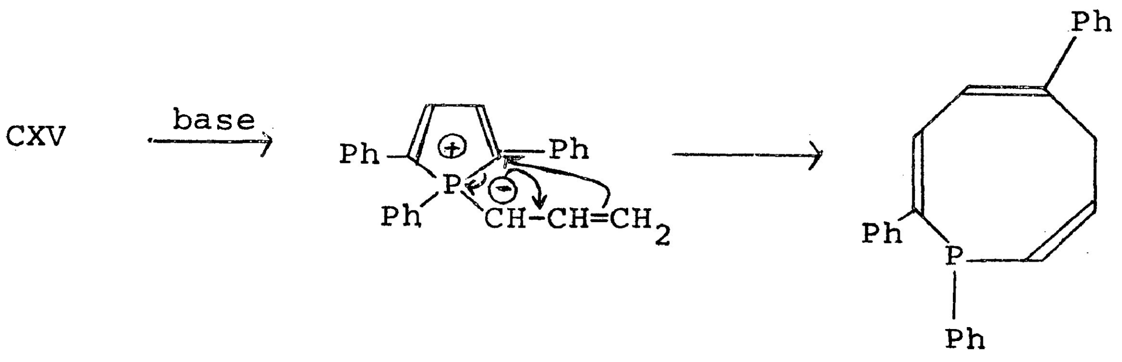
It was thought that alkaline hydrolysis of CXV might proceed to give ring expansion reactions as shown in the schemes CXV → CXVI → CXVII or CXV → CXVI → CXVIII. However, treatment of CXV with *n*-butyllithium in dry benzene under inert atmosphere conditions at room temperature gives mainly unidentifiable oils and traces of *p*-terphenyl (CXIX). Similar results are obtained when the quaternary salt CXV is treated with aqueous sodium hydroxide. The formation of *p*-terphenyl (CXIX) in alkaline hydrolyses of CXV is probably a result of some kind of Diels-Alder reaction of the allyl group across the diene portion of the phosphole system followed by aromatization of the type observed in Diels-Alder reactions of phosphole oxides. However, the detailed mechanism in this case is not clear.

Treatment of the quaternary salt CXV with aqueous methanolic sodium hydroxide at room temperature gives at least two products. The first of these is the original 1,2,5-triphenylphosphole (XVa) *not* its oxide. This suggests a mechanism as shown in the scheme CXV → XVa, *i.e.* the hydroxide ion attacks at the terminal carbon atom of the allyl group and not on the positively charged phosphorus atom as in all previous examples.[28]

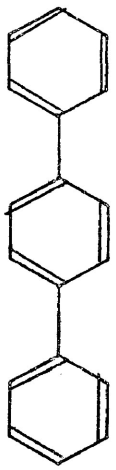
The second product is a colourless compound, m.p. 171 - 172°. The UV spectrum shows $\lambda_{max}$ at 219.5 mμ and 257.5 mμ indicating that the diphenylbutadiene portion is no longer intact and that the molecule contains little



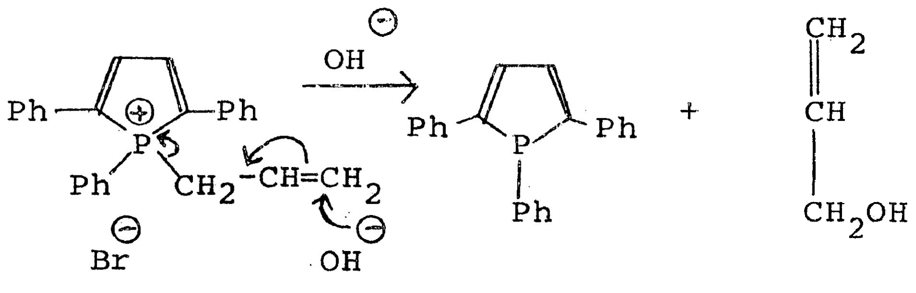
CXV CXVI CXVII



CXVI CXVIII



CXIX



CXV XVa

conjugation other than the benzene rings. The IR spectrum shows a probable P=O absorption and a C-O stretching vibration of the ether type at 1170 $cm^{-1}$ and 1105 $cm^{-1}$ respectively. The NMR spectrum shows 16 aromatic and olefinic protons as a complex multiplet at $\tau$ = 2.15 - 3.14, 3 methoxy protons as a sharp singlet at $\tau$ = 6.97, 5 methylene and methine protons as a complex multiplet at $\tau$ = 5.81 - 7.99 and 3 methyl protons as a distorted triplet (J = 6Hz) at $\tau$ = 8.95. The mass spectrum shows a molecular ion peak at *m/e* = 402. Elemental analyses are in excellent agreement with a molecular formula of $C_{26}H_{27}O_2P$, *i.e.*, an adduct of the phospholium ion CXV ($C_{25}H_{22}P$), hydroxide ion and a methanol molecule. Elemental analyses also show the presence of one methoxy group. Since the methoxy protons appear as a sharp singlet in the NMR spectrum, the methoxy group (MeO) is, therefore, not attached to the phosphorus atom because this would give a doublet due to $^{31}P$ coupling.[81]

Since the substance is available in only very small quantity, further structural investigation was, therefore, not pursued.

Pyrolysis of the quaternary salt CXV under vacuum (*ca.* 1 torr) at 205 - 210 for 10 minutes gives only a small amount of *p*-terphenyl (CXIX) and some unidentifiable oils.

# EXPERIMENTAL

## Introduction

The experimental work described in this section was carried out by the author between September 1968 and May 1970 in the Department of Chemistry at Lakehead University, Ontario, Canada.

All melting points were determined by a high-temperature melting point apparatus (Mel-Temp) and are uncorrected.

IR spectra were recorded on Perkin-Elmer 137 and Beckman IR12 spectrophotometers, the calibration of which was checked for each spectrum against a standard polystyrene film. Unless otherwise stated, spectra were recorded for samples mulled in Nujol using sodium chloride demountable cells.

UV spectra were measured on a Unicam SP800 recording spectrophotometer, usually in absolute ethanol or spectroscopic grade chloroform, using 1 cm. fused silica cells.

NMR spectra were obtained using a Varian model A60-A spectrometer and the samples were dissolved in deuterated chloroform ($CDCl_3$) or trifluoroacetic acid ($CF_3CO_2H$) with tetramethylsilane (TMS) as the internal standard.

Mass spectra were taken on an Hitachi-Perkin Elmer RMU-7 double focussing mass spectrometer using (usually) a direct inlet system. The precise mass measurements were provided by the courtesy of the Perkin-Elmer Corporation, Norwalk, Connecticut.

The X-ray powder diffraction studies reported for the free acid of L were carried out on small quantities of very finely ground material in Lindemann X-ray capillaries. Powder diffraction photographs were recorded using a Debye-Scherrer type powder camera (114.6 mm diameter) with nickel filtered copper-$K_\alpha$ radiation produced by a Phillips PW 1130 3KW X-ray Generator.

Elemental analyses were performed by Dr. Franz Pascher of Bonn.

Column chromatography was carried out using a ratio of not less than twenty parts adsorbent to one part of the sample being chromatographed. Both the neutral alumina and the silica gell used were those supplied by Woelm. Solvents were redistilled before use as eluents. Thin layer chromatographic plates were coated with Kieselgel G Nach Stahl or neutral alumina (Woelm).

Where necessary, solvents were dried as follows:

Diethyl ether was dried by heating under reflux with metallic sodium and was redistilled before use.

Benzene and tetrahydrofuran were dried by heating under reflux with calcium hydride ($CaH_2$) and were redistilled before use.

Chloroform was extracted three times with an equal volume of saturated aqueous calcium chloride to remove ethanol. The ethanol-free chloroform was washed three times with an equal volume of water and dried by distilling from anhydrous calcium chloride.

Nitrogen was dried by passage through two gas washing bottles, the first of which contained sulfuric acid while the second contained sodium hydroxide pellets.

## Starting Materials

The following starting materials were prepared by the methods described by Campbell[16]: 1,2,5-triphenylphosphole (XVa), 1,2,5-triphenylphosphole oxide, adduct of 1,2,5-triphenylphosphole oxide with diazomethane (the pyrazoline LIII), adduct of 1,2,5-triphenylphosphole oxide with ethyl diazoacetate (the pyrazoline XLVIII with Me replaced by Et), 3,4,5-triphenyl-4-phosphabicyclo [3.1.0]hex-2-ene-4-oxide (the cyclopropane LIb), ethyl 1,2,6-triphenyl-1-phosphacyclohexa-2,5-diene-3-carboxylate-1-oxide (L, Me replaced by Et) and the free acid of L. 1,2,5-Triphenyl-1-carbethoxymethylenephosph(V)ole (the ylid XXVIII) was generated by Hocking's method.[30]

## Reduction of the Pyrazoline LIII with Trichlorosilane ($HSiCl_3$)

A solution of the pyrazoline LIII (4.0 g, 10.82 mmole) in dry benzene (200 ml) was treated with a large excess of trichlorosilane (15 g, 110.5 mmole) and the mixture was heated under reflux in a slow stream of dry nitrogen for 2 days. Then, with ice-bath cooling and vigorous stirring, the reaction mixture was treated slowly with 100 ml of water. Considerable evolution of hydrogen chloride occurred and a large quantity of a white solid (probably silica) formed. The mixture was filtered and the benzene layer was separated and washed with water (3 X 50 ml), as was the residue on the funnel. All of the washings were added to the acidic aqueous layer of the filtrate. This solution of the hydrochloride of the reduced pyrazoline LXXXII was neutralized with dilute aqueous sodium hydroxide and saturated with sodium chloride prior to extraction with chloroform (3 X 50 ml). The chloroform extracts were combined, dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. The crude solid was recrystallized from hot ethanol to give colourless long needles (2.3 g, 60% yield) of the reduced pyrazoline LXXXII, m.p. 211 - 212° (dec).

(Found: C, 77.11; H, 5.37; N, 7.84; P, 8.90. $C_{23}H_{19}N_2P$ requires: C, 77.95, H, 5.36, N, 7.91; P, 8.77%).

The IR spectrum shows $\upsilon_{max}$ at 3280 (N-H stretching), 1596, 1490, 1466, 1443, 1431, 1391, 1329, 1300, 1201, 1119, 1084, 1065, 1040, 1024, 1019, 998, 946, 910, 899, 880, 850, 814, 758, 740, 690 $cm.^{-1}$ The UV spectrum in absolute ethanol shows $\lambda_{max}$ at 224 mμ and 250 mμ and the NMR spectrum in deuterated chloroform shows a ratio of 16 aromatic and olefinic protons at $\tau$ = 2.32 - 3.06 (complex multiplet) to 1 amino proton at $\tau$ = 3.39 to 2 methine protons at $\tau$ = 4.47. The mass spectrum shows a strong molecular ion peak at *m/e* = 354.

## Reduction of 3,4,5-Triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (The Cyclopropane LIb) with Trichlorosilane ($HSiCl_3$)

A solution of the cyclopropane LIb (5.0 g, 14.62 mmole) in dry benzene (250 ml) was treated with a large excess of trichlorosilane (20 g, 147.7 m mole) and the mixture was heated under reflux in a slow stream of dry nitrogen for 2 days. Then, with ice-bath cooling and vigorous stirring, the reaction mixture was treated slowly with 125 ml of water. The remainder of the preliminary work-up was essentially as described for the preceding experiment.

The solution of the hydrochloride of the phosphine derived from LIb was neutralized with dilute aqueous sodium hydroxide and saturated with sodium chloride prior to extraction with chloroform (3 X 60 ml). The chloroform extracts were combined, dried over anhydrous sodium sulfate and evaporated to dryness. The crude solid was recrystallized from hot ethanol to give colourless needles (3.5 g, 73% yield) of the phosphine derived from LIb, m.p. 134 - 135° (dec). (Found: C, 84.71; H, 5.94; P, 9.38. $C_{23}H_{19}P$ requires: C, 84.63; H, 5.84; P, 9.53%).

The IR spectrum shows $\nu_{max}$ at 1601, 1580, 1495, 1468, 1445, 1432, 1380, 1304, 1269, 1095, 1088, 1072, 1022, 1000, 935, 911, 902, 871, 851, 828, 760, 751, 698, 688 $cm.^{-1}$ The UV spectrum in absolute ethanol shows $\lambda_{max}$ (log $\varepsilon$) at 214.5 mμ (4.50) and 267 mμ (4.24). The NMR spectrum in deuterated chloroform shows a ratio of 16 aromatic and olefinic protons (complex multiplet at $\tau$ = 2.43 - 3.12) to 1 methine proton (multiplet centered at $\tau$ = 7.32) to 2 methylene protons (multiplet centered at $\tau$ = 8.82). The mass spectrum shows a very strong molecular ion peak at *m/e* = 326.

## Pyrolysis of 3,4,5-Triphenyl-4-phosphabicyclo[3.1.0] hex-2-ene-4-oxide (The Cyclopropane LIb)

A purified sample of the cyclopropane LIb (1 g, 2.92 mmole) was carefully pyrolysed in a Woods metal bath at 238° until gas evolution ceased and the material turned dark brown and resolidified. The crude product, which was rather oily, was washed with diethyl ether followed by ethanol and the reddish-yellow solid left was recrystallized from a hot chloroform/ethanol mixture to give reddish yellow crystals (0.47 g, 47% yield) of 3,3',4,4',5,5'-hexaphenyl-4,4'-diphosphabi-(1,5-cyclohexadienyl)-4,4'-dioxide (LXXXIX), m.p. 386 - 387° (dec). (Found: C, 80.89; H, 5.54; P, 9.55, $C_{46}H_{36}O_2P_2$ requires: C, 80.91; H, 5.28; P, 9.08%).

The IR spectrum shows $\nu_{max}$ at 3062, 2862, 1606, 1500, 1465, 1442 (P-Ph), 1383, 1352, 1180 (P=O), 1117, 1079, 1041, 900, 770, 754, 703, 670 $cm^{-1}$. The UV spectrum in chloroform shows $\lambda_{max}$ (log ε) at 315 mμ (4.83) and 408 mμ (4.87) and the NMR spectrum in trifluoroacetic acid shows a ratio of 17 aromatic and olefinic protons (complex multiplet at $\tau = 2.01 - 3.13$) to 1 tertiary proton (very broad singlet or poorly defined doublet centered at $\tau = 6.11$)

## Pyrolysis of the Cyclopropane LIb Under Vacuum Followed By Mass Spectrometric Studies

A purified sample of the cyclopropane LIb (1 g, 2.92 mmole) was carefully pyrolysed under similar conditions in an evacuated ($< 4 \times 10^{-7}$ torr) small cylindrical tube fitted with a high vacuum tap to which was attached a Ꞩ 10/30 ground glass cone such that the reaction tube could be connected directly to the liquid inlet of the mass spectrometer. Both the water (*m/e* = 18) and hydrogen (*m/e* = 2) peaks were detected by mass spectrometric investigation. The intensity of the water peak was only about double that of the background whereas the hydrogen peak was at least ten times the intensity of the corresponding background peak. The work-up procedure described in the preceding experiment was followed and a slightly better yield (0.51 g, 51%) of the same pyrolysed product (LXXXIX), m.p. 386 - 387° (dec), was obtained.

When the reduced cyclopropane obtained by the action of trichlorosilane on LIb was pyrolysed under similar conditions, only unidentified dark brown resinous material was obtained.

## Pyrolysis of the Pyrazoline LIII under Vacuum

A purified sample of the pyrazoline LIII (1 g, 2.70 mmole) was carefully pyrolysed under vacuum (*ca*. 1 torr) in a Woods metal bath at 238° until gas evolution ceased and the material turned dark brown and resolidified. The crude product was washed successively with diethyl ether and ethanol. The reddish yellow solid left was recrystallized from hot chloroform/ethanol mixture to give reddish yellow crystals (0.55 g, 55% yield) of LXXXIX, m.p. 386 - 387° (dec).

When the reduced pyrazoline LXXXII was pyrolysed under identical conditions, the material turned to a dark brown tar and no crystalline products could be isolated even using chromatographic techniques.

## Pyrolysis of the Pyrazoline Ester XLVIII (Me replaced by Et) Under Vacuum

The pyrazoline ester XLVIII (2.0 g. 4.53 mmole) in an evacuated (*ca*. 1 torr) small cylindical tube was carefully pyrolysed in a Woods metal bath at 220 - 225° for 20 minutes. The resulting material was washed with diethyl ether and the off-white solid left was recrystallized from a benzene/light petroleum mixture to give colourless needles (1.4 g, 75% yield) of ethyl 1,2,6-

triphenyl-1-phosphacyclohexa-2,5-diene-3-carboxylate-1-oxide L (Me replaced by Et), m.p. 217 - 218°, identical in all respects with a sample prepared by Campbell's method.[16]

## Photolysis of 3,4,5-Triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (The Cyclopropane LIb)

A solution of the cyclopropane LIb (3g, 8.76 mmole) in dry, peroxide-free tetrahydrofuran (1000 ml) was irradiated under dry, oxygen-free nitrogen with a medium pressure mercury lamp (100 watt) through pyrex for 8 days. After evaporation to dryness, the resulting solid was digested with ethanol to remove starting material. The crude product was recrystallized from a hot chloroform/ethanol mixture to give reddish yellow crystals (1.3 g, 44% yield) of 3,3',4,4',5,5'-hexaphenyl-4,4'-diphosphabi-(2,5-cyclohexadienylidene)-4,4'-dioxide (LXXXIV), m.p. 436 - 438° (lit.[66], m.p. 425 - 428°). (Found: C, 80.64; H, 4.90; P, 9.45. $C_{46}H_{34}O_2P_2$ requires: C, 80.90; H, 4.98; P, 9.06%)

The IR spectrum shows $\upsilon_{max}$ at 2834, 1604, 1490, 1463, 1443 (P-Ph), 1375, 1336, 1245, 1169 (P=O), 1106, 1075, 1066, 1031, 937, 887, 771, 750, 698 $cm.^{-1}$ The UV spectrum in chloroform shows $\lambda_{max}$ (log $\varepsilon$) at 325 mμ (4.53) and

438 mμ (4.91) and the NMR spectrum in trifluoroacetic acid shows only aromatic and olefinic protons as a complex multiplet at $\tau$ = 2.22 - 2.86.

When the reduced cyclopropane obtained by the action of trichlorosilane on LIb was irradiated under identical conditions, no crystalline products could be isolated.

## Photolysis of the Pyrazoline LIII

A solution of the pyrazoline LIII (8 g,21.65 mmole) in dry, peroxide-free tetrahydrofuran (1000 ml) was irradiated under dry, oxygen-free nitrogen with a medium pressure mercury lamp (100 watt) through pyrex for 8 days. After evaporation to dryness, the resulting solid was digested with ethanol to remove starting material. The crude product was recrystallized from a hot chloroform/ethanol mixture to give reddish yellow crystals (1.0 g, 14% yield) of 3,3',4,4',5,5' -hexaphenyl-4,4'-diphosphabi-(2,5-cyclohexadienylidene)-4,4'-dioxide (LXXXIV), m.p. 436 - 438°, identical in all respects with the sample obtained previously.

When the reduced pyrazoline LXXXII was irradiated under identical conditions, no crystalline products could isolated.

### Attempted Reductions of the Photolysis and Pyrolysis Products (LXXXIV and LXXXIX) with Trichlorosilane ($HSiCl_3$)

A sample of the photolysis product LXXXIV (0.1 g, 0.15 mmole) was treated with a large excess of trichlorosilane under a wide variety of reaction conditions such as heating under reflux in dry benzene (10 ml) for 15 days, heating under reflux in dry ethanol-free chloroform (10 ml) for 15 days, heating under reflux in trichlorosilane (10 ml) without solvent for 15 days and heating a suspension of LXXXIV (0.1 g, 0.15 mmole) with trichlorosilane (10 ml) in a sealed tube under pressure at 100° for 15 days. The attempts at reduction were ineffective and the photolysis product LXXXIV remained unchanged.

The pyrolysis product LXXXIX was also found to be stable under these conditions.

### Reduction of the Photolysis and Pyrolysis Products (LXXXIV and LXXXIX) with Phosphorus Pentachloride and Lithium Aluminium Hydride

A sample of the photolysis product LXXXIV (0.1 g, 0.15 mmole) was fused together with a large excess of phosphorus pentachloride (3g, 14.51 mmole) at 120-130° until the mixture turned deep red (1 hour). The excess of phosphorus pentachloride was removed by sublimation under vacuum at 100°. With cooling (dry ice/actone bath) and vigorous stirring, the resulting deep red powder was treated dropwise with a saturated ethereal solution of lithium aluminium hydride under dry nitrogen until gas evolution ceased. The temperature of the reaction mixture was increased slowly until it reached room temperature and the mixture was maintained at this temperature for a further 15 minutes. Destruction of the excess of lithium aluminium hydride was carried out with water-saturated diethyl ether. Water (10 ml) was then added and the mixture was evaporated under reduced pressure until it was ether free. The resulting aqueous suspension was extracted with chloroform (3 X 10 ml). The chloroform extracts were combined, dried over anhydrous sodium sulfate and evaporated to dryness under reduced pressure. The crude solid was washed with ethanol and recrystallized from a hot chloroform/ethanol mixture to give red crystals (0.07 g, 74% yield) of 3,3',4,4',5,5'-hexaphenyl-4-4'-diphosphabi-(2,5-cyclohexadienylidene)(XCIIa), m.p. 338 - 340° (lit.[66], m.p. 335 - 337°) Found: C, 80.75, H, 5.06; P, 9.66. $C_{46}H_{34}P_2$ requires: C, 85.25; H, 5.24; P, 9.51%).

The IR spectrum shows $\upsilon_{max}$ at 3075, 2869, 1618, 1500, 1446 (P-Ph), 1438, 1369, 1350, 1250, 1100, 1041, 941, 922, 889, 861, 776, 767, 749, 718, 700, 694 $cm^{-1}$.

The UV spectrum in chloroform shows $\lambda_{max}$ (log $\varepsilon$) at 339 mμ (3.88) and 468 mμ (4.64) [lit.[66], $\lambda_{max}$ 337 mμ and 467 mμ ]. The NMR spectrum in trifluoroacetic acid shows only aromatic and olefinic protons as a complex multiplet at $\tau$ = 2.18 - 2.89.

Reduction of the pyrolysis product LXXXIX (0.5 g, 0.73 mmole) with phosphorus pentachloride (15 g, 72.55 mmole) and lithium aluminium hydride under identical reaction conditions gave the same phosphine XCIIa (0.4 g, 84% yield), m.p. 338 - 340° (lit.[66], m.p. 335 - 337°), identical with the sample obtained from the reduction of the photolysis product LXXXIV in all respects.

## Treatment of the Pyrolysis Product LXXXIX with Lithium Aluminium Hydride

With cooling (dry ice/acetone bath) and vigorous stirring, a suspension of the pyrolysis product LXXXIX (0.6 g, 0.88 mmole) in dry diethyl ether (60 ml) was treated dropwise with a solution of lithium aluminium hydride (0.335 g, 8.82 mmole) in dry diethyl ether (50 ml) under dry nitrogen. The temperature of the reaction mixture was increased slowly until it reached room temperature and the mixture was maintained at this temperature for a further 15 minutes. Destruction of the excess of lithium aluminium hydride was carried out as before with water-saturated diethyl ether. Water (60 ml) was added and the mixture was evaporated under reduced pressure until ether free. The resulting aqueous suspension was extracted with chloroform (3 X 60 ml). The chloroform extracts were combined, dried over anhydrous sodium sulfate and evaporated to dryness. The crude solid was washed with ethanol and recrystallized from a hot chloroform/ethanol mixture to give reddish yellow crystals (550 mg, 92% yield) of 3,3',4,4'5,5'-hexaphenyl-4,4'-diphosphabi-(2,5-cyclohexadienylidene)-4,4'-dioxide (LXXXIV), m.p. 436 - 438°, identical in all respects with the photolysis product LXXXIV obtained previously.

## Treatment of the Pyrolysis Product LXXXIX with Sodium Hydride

A suspension of the pyrolysis product LXXXIX (10 mg, 0.015 mmole) in dry benzene (5 ml) was treated slowly with sodium hydride (3.6 mg, 0.15 mmole) and the mixture was heated under reflux in a slow stream of dry nitrogen for 30 minutes. The excess of sodium hydride was destroyed by water-saturated diethyl ether. Water (5 ml) was added and the mixture was evaporated to remove organic solvents. The aqueous suspension was then extracted with chloroform (5 ml) and the chloroform extract was dried over anhydrous sodium sulfate. The UV spectrum of the crude extract showed $\lambda_{max}$ at 325 mμ and 438 mμ; identical with that of the photolysis product LXXXIV obtained previously.

## Treatment of the Pyrolysis Product LXXXIX with Sodium Hydroxide, with Potassium *tert*-Butoxide and with *n*-Butyllithium

A suspension of the pyrolysis product LXXXIX (10 mg, 0.0.15 mmole) in ethanol (5 ml) was treated with a few drops of aqueous 10% sodium hydroxide and the mixture was heated under reflux for 1 hour. Water ( 5 ml) was added and the mixture was evaporated to a volume of 5 ml to remove ethanol. The resulting suspension was extracted with chloroform (5 ml) and the chloroform extract was dried over anhydrous sodium sulfate. The UV spectrum showed $\lambda_{max}$ at 315 mμ and 408 mμ, identical with that of the starting material. Similar results were obtained with potassium *tert*-butoxide in benzene and with *n*-butyllithium in hexane.

## Attempted Reaction of 1,2,5-Triphenylphosphole (XVa) and Its Oxide with Dichlorocarbene and Dibromocarbene

In general, halogenated carbenes were generated *in situ* by either thermal decomposition of the sodium salt of trichloroacetic acid[71] or alkaline decomposition of haloforms.[72] Both 1,2,5-triphenylphosphole (XVa) and its oxide were tried as substrates. The initial work-up procedure was based on the literature[71,72] and the crude reaction gum was chromatographed on a neutral alumina column using a series of solvents such as cyclohexane, benzene, chloroform and acetone as eluents.

The cyclohexane fractions contained only traces of unidentifiable oil.

The benzene fractions contained a small amount of either 1,2,5-triphenylphosphole (XVa) or its oxide contaminated with traces of unidentifiable oil.

The chloroform fractions contained small quantities of greyish, insoluble, high-melting compounds which were not further investigated.

The acetone fractions contained a considerable amount of unidentifiable dark brown tar.

## Reaction of 1,2,5-Triphenylphosphole (XVa) With Methylene Iodide

A well-mixed paste of the phosphole XVa (10 g, 32.05 mmole) and methylene iodide (26 g, 96.95 mmole) in a pressure bottle under dry nitrogen was kept with constant stirring at 80 - 85° for 4 1/2 days. When cooled, the reaction mixture turned to a dark brown solid which was broken up and washed with acetone. The yellow residue (17 g, 91% yield) was found to be almost pure 1-iodomethyl-1,2,5-triphenylphospholium iodide (XCIX), m.p. 174 - 175° (dec). (Found: C, 47.74; H, 3.45; I, 43.82; P, 5.37. $C_{23}H_{19}I_2P$ requires: C, 47.59; H, 3.28; I, 43.79; P, 5.34%). Attempts to recrystallize the yellow powder from a number of solvents such as benzene, chloroform, acetone, ethanol, methanol, water, glacial acetic acid, dimethyl formamide and mixed solvents were unsuccessful. It was therefore used directly for further investigation.

The IR spectrum of XCIX shows $\upsilon_{max}$ at 1579, 1538, 1491, 1472, 1447 (P-Ph), 1441, 1384, 1371, 1318, 1302, 1259, 1233, 1168, 1161, 1110, 1080, 1031, 1000, 946, 923, 860, 800, 766, 750, 740, 730, 700, 690, 679, 660 $cm^{-1}$. The UV spectrum in absolute ethanol shows $\lambda_{max}$ (log $\varepsilon$) at 225 mμ (4.58), 275 mμ (3.71) and 411 mμ (4.19) The NMR spectrum in trifluoroacetic acid shows a ratio of

17 aromatic and olefinic protons (complex multiplet at $\tau$ = 1.75 - 2.76) to 2 methylene protons (doublet centered at $\tau$ = 5.68 with $J_{HP}$ = 8 Hz).

## Complete Alkaline Hydrolysis of 1-Iodomethyl-1,2,5-triphenylphospholium Iodide (XCIX)

To a suspension of the quaternary salt XCIX (8 g, 13.79 mmole) in methanol (800 ml), was added slowly a 10% aqueous solution of sodium hydroxide (55 ml, 137.6 mmole) at room temperature with vigorous stirring. After the addition of sodium hydroxide was complete, the reaction mixture was heated under reflux for 24 hours. The cooled solution was treated dropwise with dilute aqueous hydrochloric acid until it was just acidic to litmus paper. Water (200 ml) was added and the mixture was evaporated on a rotary evaporator to remove methanol. The aqueous suspension was then extracted with chloroform (3 X 100 ml). The chloroform extracts were combined and dried over anhydrous sodium sulfate prior to evaporation on a rotary evaporator to a volume of 50 ml. The concentrated chloroform solution was chromatographed on a silica gel column using chloroform as eluent. The chloroform fraction, upon evaporation to dryness, yielded a pale yellow solid which was recrystallized from hot ethanol to give very pale yellow crystals (3.5 g, 74% yield) of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (the cyclopropane LIb), m.p. 234 - 235° (dec), (lit.[16] m.p. 234 - 235°), identical with an authentic sample in all respects.

## Partial Alkaline Hydrolysis of 1-Iodomethyl-1,2,5-triphenylphospholium Iodide (XCXI)

To a suspension of the quaternary salt XCIX (12 g, 20.68 mmole) in methanol (1200 ml) was added slowly a 10% aqueous solution of sodium hydroxide (83 ml, 207.1 mmole) at room temperature followed by vigorous stirring for 2 hours. The solution was then treated dropwise with dilute aqueous hydrochloric acid until it was just acidic to litmus paper. Water (300 ml) was added and the mixture was evaporated on a rotary evaporator to remove methanol. The aqueous suspension was extracted with chloroform (3 X 150 ml). The chloroform extracts were combined and dried over anhydrous sodium sulfate and then evaporated to dryness on a rotary evaporator. The dark brown residue was chromatographed on a silica gel column using successively benzene and chloroform as eluents. The benzene fraction, upon evaporation to dryness, yielded a colourless solid which was recrystallized from a hot benzene/cyclohexane mixture to give colourless long needles (5.6 g, 58% yield) of 4-iodomethyl-1,2,5-triphenyl-2-phospholene-1-oxide (CVII), m.p. 199 - 200° (dec). (Found: C, 59.01; H, 4.25; I, 27.09; P, 6.60. $C_{23}H_{20}OIP$ requires: C, 58.71; H, 4.26; I, 27.08; P, 6.60%).

The IR spectrum shows $\upsilon_{max}$ at 3058, 2961, 2860, 1601, 1587, 1499, 1453 (P-Ph), 1438, 1422, 1379, 1304, 1268, 1180 (P=O), 1159, 1148, 1104, 1068, 1025, 1000, 918, 881, 824, 792, 760, 748, 719, 699, 691, 666, 649 $cm.^{-1}$ The UV spectrum in absolute ethanol shows $\lambda_{max}$ (log $\varepsilon$) at 220 mμ (4.33) and 261 mμ (4.07). The NMR spectrum in deuterated chloroform shows a ratio of 16 aromatic and olefinic protons (complex multiplet at $\tau$ = 2.19 - 3.16) to 2 methine protons (multiplet at $\tau$ = 5.52 - 6.08) to 2 methylene protons (multiplet of at least five peaks at $\tau$ = 6.65 - 7.02). The mass spectrum shows a fairly strong molecular ion peak at *m/e* = 470.

The chloroform fraction, upon evaporation to dryness, yielded a pale yellow solid which was recrystallized from hot ethanol to give very pale yellow crystals (0.7 g, 10% yield) of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide(the cyclopropane LIb), m.p. 234 - 235° (dec) (lit.[16], m.p. 234 - 235°), identical with an authentic sample in all respects.

## Treatment of 4-Iodomethyl-1,2,5-Triphenyl-2-phospholene Oxide (CVII) with Aqueous Sodium Hydroxide

To a solution of the 2-phospholene oxide CVII (1 g, 2.13 mmole) in methanol (100 ml), was added slowly a 10% aqueous solution of sodium hydroxide (8.5 ml. 21.28 mmole) at room temperature with vigorous stirring. After the addition of sodium hydroxide was complete, the reaction mixture was heated under reflux for 24 hours. The cooled solution was treated dropwise with dilute aqueous hydrochloric acid until it was just acidic to litmus paper. Water (25 ml) was added and the mixture was evaporated to remove methanol. The resulting aqueous suspension was extracted with chloroform (3 X 15 ml). The chloroform extracts were combined and dried over anhydrous sodium sulfate and then concentrated on a rotary evaporator to a volume of 10 ml. The concentrated chloroform solution was chromatographed on a silica gel column using chloroform as eluent. The chloroform fraction on evaporation yielded a pale yellow solid which was recrystallized from hot ethanol to give very pale yellow crystals (0.65 g, 90% yield) of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (the cyclopropane LIb), m.p. 234 - 235° (dec), (lit.[16], m.p. 234 - 235°), identical with an authentic sample in all respects.

## Attempted Reduction of 4-Iodomethyl-1,2,5-triphenyl-2-phospholene Oxide (CVII) with Lithium Aluminium Hydride

With cooling (dry ice/acetone bath) and vigorous stirring, a solution of the 2-phospholene oxide CVII (1 g, 2.13 mmole) in dry benzene (50 ml) was treated dropwise with a solution of lithium aluminium hydride (0.8 g, 21.03 mmole) in dry diethyl ether (10 ml) under dry nitrogen. The temperature of the reaction mixture was maintained at *ca.* - 40° for a further 15 minutes and then the excess of lithium aluminium hydride was destroyed with water-saturated diethyl ether. Water (25 ml) was added and the mixture was evaporated to remove organic solvents. The resulting aqueous suspension was extracted with chloroform (3 X 25 ml). The chloroform extracts were combined, dried over anhydrous sodium sulfate and evaporated to dryness on a rotary evaporator to give resinous materials. Attempts to isolate crystalline products from this material were unsuccessful.

## Pyrolysis of 1,2,5-Triphenyl-1-carbethoxymethylenephosph(V)ole (The Ylid XXVIII) Under Vacuum

A freshly prepared sample of the ylid XXVIII (1.1 g, 2.77 mmole) was carefully pyrolysed under vacuum in a

Woods metal bath at 170 - 175° for 15 minutes. The resulting dark brown solid was washed with diethyl ether and the greenish yellow solid left was recrystallized from hot ethanol to give 1,2,5-triphenylphosphole (XVa) (440 mg, 56% yield), m.p. 186 - 187° (lit.,[16] m.p. 187 - 189°), identical with an authentic sample in all respects.

### Photolysis of 1,2,5-Triphenyl-1-carbethoxymethylenephosph(V)ole (The Ylid XXVIII)

A solution of the ylid XXVIII (1.1g, 2.77 mmole) in dry tetrahydrofuran (1000 ml) was irradiated under dry nitrogen with a medium pressure mercury lamp (100 watt) through quartz for 2 weeks. After evaporation to dryness on a rotary evaporator, the resulting brownish yellow solid was recrystallized from hot ethanol to give 1,2,5-triphenylphosphole oxide (530 mg, 58% yield), m.p. 238 - 239° (lit.[16], m.p. 237 - 239°), identical with an authentic sample in all respects.

### Reaction of 1,2,5-Triphenyl-1-carbethoxymethylene Phosph(V)ole (The Ylid XXVIII) With Dimethyl Acetylenedicarboxylate

The ylid XXVIII (1 g, 2.50 mmole) and freshly distilled dimethyl acetylenedicarboxylate (1.8 g, 12.75 mmole) in dry benzene (100 ml) were heated under reflux in a dry nitrogen atmosphere for 20 hours. The resulting mixture was evaporated to dryness on a rotary evaporator and the dark brown residue was chromatographed on a neutral alumina column using successively cyclohexane/benzene (1:1), benzene and chloroform as eluents.

The cyclohexane/benzene fraction, upon evaporation to dryness, yielded an oily solid which was recrystallized from hot diethyl ether to give dimethyl-3,6-diphenylphthalate (150 mg, 17% yield), m.p. 190 - 191° (lit.[82] m.p. 191°),identical with an authentic sample in all respects.

The benzene fraction was evaporated to dryness and was then allowed to stand in a small volume of acetone for a long period (2 weeks). This yielded pale yellow crystals (50 mg, 3.7% yield) of the rearranged ylid CXI, m.p. 182 - 185°. The IR spectrum shows $\upsilon_{max}$ at 3059, 2850, 2241, 1745, 1700 -1624, 1450, 1378, 1314, 942, 908, 851, 826, 774, 684, 665 $cm.^{-1}$ The UV spectrum in absolute ethanol shows $\lambda_{max}$ at 219 mμ and 356 mμ. The NMR spectrum in deuterated chloroform shows four main regions of absorption at $\tau$ = 2.33 - 3.15 (complex multiplet), 6.01 (quartet), 7.16 (singlet) and 9.04 (triplet). The mass spectrum shows a fairly strong molecular ion peak at *m/e* = 540.

The chloroform fraction contained only unidentifiable resinous material.

## Reaction of 1,2,5-Triphenylphosphole (XVa) with Allyl Bromide

The phosphole XVa (15 g, 48.09 mmole) and allyl bromide (29g,240 mmole) in dry benzene (500 ml) were heated under reflux in a dry nitrogen atmosphere for 5 days. The yellow solid which separated upon cooling was collected and recrystallized from either hot water or hot methanol/benzene mixture to give yellow crystals (19 g, 91% yield) of 1-allyl-1,2,5-triphenylphospholium bromide (CXV), m.p. 202-203° (dec). (Found: C, 68.97; H, 5.01; Br, 19.05, P, 7.10. $C_{25}H_{22}BrP$ requires: C, 69.26, H, 5.07, Br, 18.52; P, 7.15%).

The IR spectrum shows $\upsilon_{max}$ at 3038, 2853, 1635, 1610, 1579, 1490, 1465, 1443, 1377, 1344, 1313, 1259, 1190, 1154, 1108, 1078, 1030, 998, 981, 939, 906, 878, 813, 761, 748, 726, 685, 666, 652, 620 $cm.^{-1}$ The UV spectrum in absolute ethanol shows $\lambda_{max}$ (log $\varepsilon$) at 212 mμ (4.52), 227 mμ (4.58) and 410 mμ (4.12). The NMR spectrum in deuterated chloroform shows a ratio of 20 aromatic and olefinic protons (complex multiplet at $\tau$ = 1.26 - 2.96) to 2 methylene protons (poorly defined quartet centered at $\tau$ = 5.27).

## Treatment of 1-Allyl-1,2,5-triphenylphospholium Bromide (CXV) with *n*-Butyllithium and with Aqueous Sodium Hydroxide

A suspension of the quaternary salt CXV (2 g, 4.62 mmole) in dry benzene (100 ml) was treated dropwise with a 15.21% solution of *n*-butyllithium in hexane (19 ml, 46.39 mmole) at room temperature under dry nitrogen with constant stirring for 10 minutes. The excess of *n*-butyllithium was destroyed by water-saturated diethyl ether. Water (50 ml) was added and the mixture was evaporated to remove organic solvents. The resulting aqueous suspension was extracted with chloroform (3 X 50 ml) and the chloroform extracts were dried over anhydrous sodium sulfate and evaporated to dryness. The residue was chromatographed on a neutral alumina column using successively benzene and chloroform as eluents.

The benzene fraction contained unidentifiable oils and traces of 1,2,5-triphenylphosphole (XVa).

The chloroform fraction, upon concentration to a volume of 10 ml, yielded *p*-terphenyl (CXIX) (80 mg, 7% yield), m.p. 206 - 208° (lit.[83], m.p. 209°).

Under similar reaction conditions, the quaternary salt CXV (2 g, 4.62 mmole) reacted with 10% aqueous sodium hydroxide (10 ml, 25 mmole) to give *p*-terphenyl (CXIX) (48 mg, 4% yield), m.p. 206 - 208°, together with some unidentifiable oils and traces of 1,2,5-triphenylphosphole (XVa).

## Hydrolysis of 1-Allyl-1,2,5-triphenylphospholium Bromide (CXV) with Aqueous Sodium Hydroxide Containing Methanol

A solution of the quaternary salt CXV (1.4 g, 3.24 mmole) in methanol (70 ml) was treated dropwise with a 10% aqueous solution of sodium hydroxide (6.5 ml, 16.25 mmole) at room temperature with constant stirring for 10 minutes. Water (50 ml) was added and the mixture was evaporated to remove methanol. The aqueous suspension was extracted with chloroform (3 X 50 ml) and the chloroform extracts were dried over anhydrous sodium sulfate and evaporated to dryness. The residue was chromatographed on a neutral alumina column using successively benzene and chloroform as eluents.

The benzene fraction, upon evaporation to dryness, yielded an oily solid which was recrystallized from hot ethanol to give 1,2,5-triphenylphosphole (XVa) (120 mg, 12% yield), m.p. 186 - 187° (lit.[16] m.p. 187 - 189°), identical with an authentic sample in all respects.

Evaporation of the chloroform fraction also yielded an oily solid which was sublimed under vacuum (*ca.* 1 torr) at 165° to give a colourless compound (160 mg, 12% yield), m.p. 171 - 172°. (Found: C, 77.74; H, 6.73; P, 7.60; O-$CH_3$, 6.83. $C_{26}H_{27}O_2P$ requires: C, 77.71; H, 6.72; P, 7.71; O-$CH_3$, 7.71 %).

The IR spectrum shows $\upsilon_{max}$ at 3051, 2813, 1610, 1600, 1578, 1494, 1460, 1442, 1431, 1368, 1299, 1262, 1220, 1170 (P=O), 1105, 996, 955, 920, 878, 826, 791, 774, 752, 743, 718, 688, 662, 649 $cm.^{-1}$ The UV spectrum in absolute ethanol shows $\lambda_{max}$ at 219.5 mμ and 257.5 mμ. The NMR spectrum shows 16 aromatic and olefinic protons as a complex multiplet at $\tau$ = 2.15 - 3.14, 3 methoxy protons as a sharp singlet at $\tau$ = 6.97, 5 methylene and methine protons as a complex multiplet at $\tau$= 5.81 - 7.99 and 3 methyl protons as a distorted triplet (J = 6Hz) at $\tau$ = 8.95. The mass spectrum shows a strong molecular ion peak at *m/e* = 402.

## Pyrolysis of 1-Allyl-1,2,5-triphenylphospholium Bromide (CXV) Under Vacuum

A purified sample of the quaternary salt CXV (1 g, 2.31 mmole) was carefully pyrolysed under vacuum (*ca.* 1 torr) in a Woods metal bath at 205 - 210° for 10 minutes. The resulting mixture was chromatographed on a neutral alumina column using successively benzene and chloroform eluents.

The Benzene fraction contained only unidentifiable oils.

The chloroform fraction, upon concentration to a volume of 10 ml, yielded *p*-terphenyl (CXIX) (67 mg, 13% yield), m.p. 206 - 298° (lit.[83], m.p. 209°).

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# APPENDICES

Manuscripts of papers
based upon this thesis
which have been accepted
for publication in the
Canadian Journal of Chemistry

# Thermal and Photochemical Ring Expansion of Some Phosphole Derivatives

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Keywords:

Phosphacyclohexa-2,4-diene, derivatives of
Phosphacyclohexa-2,5-diene, derivatives of
Phosphole, 1,2,5-triphenyl-
Phospholes, ring expansion

Pyrolysis and photolysis of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide and the 1:1 adduct of diazomethane with 1,2,5-triphenylphosphole oxide lead to the formation of compounds of formula $C_{46}H_{36}O_2P_2$ and $C_{46}H_{34}O_2P_2$, respectively. These compounds are shown to be derivatives of the 4,4'-diphosphabi(cyclohexa-1,5-dienyl) and 4,4'-diphosphabi(cyclohexa-2,5-dienylidene) systems, respectively, and possible mechanisms for the formation of these systems are briefly discussed.

Unsaturated six-membered ring phosphorus heterocycles - particularly the phosphorins - have received considerable attention recently, and several synthetic routes to these systems have been developed (1). It is well known that pyrrole derivatives will undergo ring expansion reactions to give pyridine derivatives, sometimes in good yield. For example, pyrrole on treatment with methylene chloride and methyl lithium gives pyridine in 32% yield (2). In principle then, phosphole (**1**) derivatives should also undergo ring expansion reactions although not necessarily by the same mechanistic path as for pyrrole derivatives. Indeed, certain 9-phosphafluorene (dibenzophosphole) derivatives have already been shown to undergo ring expansion on treatment with methyl propiolate in the presence of water (3) or with methylene iodide followed by alkaline hydrolysis (4). There is, however, only one report of the ring expansion of a simple phosphole derivative (5). In this reaction, treatment of 1,2,5-triphenylphosphole oxide (2) with methyl diazoacetate in boiling dioxan leads to the formation of the phosphacyclohexa-2,5-diene derivative 3(R=Me). The same workers showed that reactions of the phosphole oxide 2 with diazomethane followed by treatment of the intermediate pyrazolino derivative 4 with copper in boiling diglyme leads to the formation of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0] hex-2-ene-4-oxide (5) which could possibly be a convenient starting material for ring expansion reactions of the phosphole system. Moreover, it was observed (5) that this compound resolidifies above its melting point to give a dark red compound which was not further investigated. The following is therefore an account of the thermal and photochemical ring expansion reactions of 4 and 5.

The cyclopropano derivative 5 was carefully pyrolysed in a Woods metal bath at 238° until gas evolution ceased and the material turned dark brown and resolidified. The crude product was recrystallized from a chloroform/ethanol mixture and a good yield of a deep orange compound, m.p. 386-387°, was obtained. Pyrolysis of 5 under vacuum gives a slightly higher yield of the same compound. The high melting point and very low solubility of the pyrolysis product indicate a higher molecular weight than the starting material Elemental analyses are consistent with a formula of $C_{46}H_{38}O_2P_2$, $C_{46}H_{36}O_2P_2$, or $C_{46}H_{34}O_2P_2$, *i.e.* a dimer of the starting material, a dimer minus $H_2$ or a dimer minus $2H_2$, although trimeric structures cannot be entirely ruled out. Because of the highly involatile nature of the product, its molecular weight could not be determined by mass spectrometry. However, pyrolysis of 5 under high vacuum ($<4 \times 10^{-7}$ torr) followed by mass spectrometric analysis of the gas evolved showed that hydrogen is given off in substantial amounts during the reaction and that water is not a significant product. This suggests that thermal dimerization of 5 occurs with elimination of hydrogen and, therefore, the molecular formula $C_{46}H_{38}O_2P_2$ can be tentatively ruled out.

A compound of molecular formula $C_{46}H_{34}O_2P_2$ having two unsaturated phosphorus-containing six-membered rings has previously been prepared (6) by treatment of 1,2,6-triphenyl-1-phosphacyclohexa-2,5-diene-4-one-1-oxide (6) with triethylphosphite to give 3,3',4,4',5,5'-hexaphenyl-4,4'-diphosphabi(cyclohexa-2,5-dienylidene)-4,4'-dioxide (7). This compound melts at 425-428° and shows $\lambda_{max}$ at 324.5 mμ and 437 mμ. It is therefore not identical with the pyrolysis product of 5 which shows in ethanol $\lambda_{max}$(log ε) at 315 mμ (483) and 408 mμ (4.87). Furthermore, the i.r. spectrum (Nujol) of the pyrolysis product shows a typical P=O stretching band at 1180 $cm^{-1}$ and the n.m.r. spectrum (in trifluoroacetic acid) shows a ratio of 17 aromatic and olefinic protons (complex multiplet at $\tau$=2.01-3.13) to one tertiary proton (very broad unresolved hump at $\tau$=6.11). The n.m.r. evidence then is consistent with the formula $C_{46}H_{36}O_2P_2$.

A number of modes of reaction are open to the cyclopropane **5** on pyrolysis. For example, the vinylcyclopropane → cyclopentene type of rearrangement (7) could possibly occur although this seems unlikely in this case since the products would contain little conjugation. A more likely mode of reaction is one in which one of the three bonds of the cyclopropane ring (probably the bond forming the ring junction) is cleaved to give a diradical such as **8** which dimerizes and eliminates molecular hydrogen to give **9** or **10**. However, since mechanistic studies were not undertaken, a dipolar mechanism cannot be ruled out. Clearly structure **9** may be discarded because there would be insufficient conjugation to account for the ultraviolet spectrum although this structure is consistent with the n.m.r. spectrum. Moreover, the related structure **3** is colourless (5). Cleavage of the other bonds of the cyclopropane ring followed by dimerization and elimination of hydrogen would again give products containing too little conjugation to account for the ultraviolet spectrum. Thus, it seems that structure **10** is the most likely structure for the pyrolysis product since it fits all the evidence available at this point.

The same compound is obtained in good yield (60%) by pyrolysis of 4 under vacuum at 238° although pyrolysis of the related compound 11 yields only the phosphacyclohexadiene 3(R=Et) in excellent yield (75%). Reduction of 4 and 5 with trichlorosilane in dry benzene (8) gives the corresponding tertiary phosphines 12 and 13 respectively in good yield (60% and 73% respectively) but pyrolysis of these phosphines only gives general decomposition and no ring expanded products could be isolated. It should also be noted that in the reduction of 4 to 12 a prototropic shift occurs to give the 2-pyrazoline structure rather than the 1-pyrazoline structure which is present in 4. Evidence for this comes from the fact that in the i.r. spectrum of 12 there is a strong N-H stretching absorption at 3280 $cm^{-1}$ which is not present in the i.r. spectrum of 4. The prototropic shift is not unexpected since the reduction of 4 is carried out under acidic conditions and it is known (9) that 1-pyrazolines isomerize under these conditions to give the corresponding 2-pyrazolines.

Irradiation of the cyclopropane 5 in dry, peroxide-free tetrahydrofuran under dry, oxygen-free nitrogen with a medium pressure mercury lamp (100 watt) through pyrex for 8 days gives a 44% yield of a deep orange compound (m.p. 439-440°) similar, but not identical, to the pyrolysis product. Irradiation of the pyrazoline 4 under similar conditions gives a 14% yield of the same compound.

Elemental analyses of the photolysis product are in excellent agreement with the formula $C_{46}H_{34}O_2P_2$. The ultraviolet spectrum shows $\lambda_{max}$(log $\varepsilon$) at 325 $m\mu$(4.53) and 438 $m\mu$(4.91) which confirms extensive conjugation in the molecule. The i.r. spectrum shows a typical P=O stretching vibration at 1169 $cm^{-1}$ and the n.m.r. spectrum (in trifluoroacetic acid) shows only aromatic and olefinic protons as a complex multiplet at $\tau$=2.22 - 2.96. The melting point of the photolysis product is very similar to that of Märkl's compound 7 (6) and the n.m.r. spectrum is in good agreement with this structure. The ultraviolet spectrum is virtually identical with that of compound 7 (although Märkl does not quote values for the extinction coefficients) and it therefore appears that the photolysis product has structure 7.

Confirmation of this structure is provided by the fact that it may be reduced to the corresponding phosphine 14 by treatment first with phosphorus pentachloride to give an unisolated deep red P,P,P',P'-tetrachloro compound which is reduced smoothly to **14** with lithium aluminum hydride as briefly outlined by Märkl (6). The sample of **14** isolated is identical (m.p. and ultraviolet spectrum) with that described by Märkl (6) and the molecular weight was confirmed as 648 by mass spectrometry.

The mechanism of formation of the photolysis product **7** is again uncertain although it is probable that an intermediate such as **8** is involved. However, both further pyrolysis at 380° under vacuum of the initial pyrolysis product **10** and irradiation of the same compound in dry, peroxide-free tetrahydrofuran under nitrogen for several days leave the material unchanged and it therefore seems likely that **10** is not an intermediate in the formation of **7**. Since the irradiation of **5** occurs over a very long period of time, ring enlargement to a phosphacyclohexadiene of type **3** (without the $CO_2R$ group) followed by photo-oxidation by trace amounts of oxygen to give **6** which condenses with unoxidized material to give **7** cannot be excluded. However, both pyrolysis and irradiation of the phosphacyclohexadiene **3** (R=Et) under conditions very similar to those used for **5** for extended periods result in virtually complete recovery of the starting material and the intermediacy of **6** and its phosphacyclohexadiene precursor in the photolysis of **5** therefore seems unlikely.

Irradiation of **12** and **13** under similar conditions gives only some general decomposition and recovery of some starting material.

Turning again to the pyrolysis product tentatively assumed to be 10, treatment of this compound with a large excess of phosphorus pentachloride followed by reduction of the intermediate deep-red P,P,P',P'-tetrachloro compound with lithium aluminum hydride gives the 4,4'-diphosphabi(cyclohexa-2,5-dienylidene) system 14 identical in all respects with an authentic sample. This, then, confirms the basic skeleton of the pyrolysis product. Final confirmation of the ring structure of the compound assigned structure 10 comes from the fact that on treatment with ethereal lithium aluminum hydride alone, it is transformed into the photolysis product 7 in good yield. A similar reaction occurs between the pyrolysis product and sodium hydride in benzene. The mechanisms of these last two reactions are obscure but, in view of all the foregoing evidence, the structures of the pyrolysis and photolysis products of 4 and 5 are established as 10 and 7 respectively.

Compounds of type 14 (with the P-Ph grouping replaced by the P-$CH_2$Ph grouping) have recently been found (10) to be converted into the previously unknown biphosphorinyl system 15 on heating and it is possible that pyrolysis or irradiation of compounds such as **12** or **13**, in which the P-Ph grouping is similarly replaced by the P-$CH_2$Ph grouping, could lead directly to the biphosphorinyl system.

Attempts to prepare other compounds of type **5** by addition of dichlorocarbene or dibromocarbene to **2** were unsuccessful.

## Experimental

Infrared spectra were recorded in Nujol mulls using a Beckman 1R12 spectrophotometer while ultraviolet spectra were obtained on dilute ethanol or chloroform solutions using a Unicam SP800 spectrophotometer. N.m.r. measurements were made with a Varian Associates model A60-A spectrometer using deuteriochloroform or trifluoroacetic acid solutions with tetramethylsilane as internal reference. Mass spectra were determined using an Hitachi-Perkin Elmer model RMU-7 double focussing mass spectrometer fitted with a direct heated inlet system. Melting points are uncorrected and were recorded using a Mel-Temp high-temperature melting point apparatus.

Ether was dried by distillation from sodium or lithium aluminum hydride while tetrahydrofuran and benzene were dried by distillation from calcium hydride.

1,2,5-Triphenylphosphole, 1,2,5-triphenylphosphole oxide (2), the phosphacyclohexadiene 3 (R=Et), 3,4,5-triphenyl-4-phosphabicyclo [3.1.0]hex-2-ene-4-oxide (5) and the pyrazolines 4 and 11 were prepared by the method of Campbell (5).

Reduction of 4 and 5 with Trichlorosilane

A solution of the pyrazoline 4 (4.0 g, 10.82 mmole) in dry benzene (200 ml) was treated with a large excess of trichlorosilane (15 g, 110.5 mmole) and the mixture was heated under reflux in a slow stream of dry nitrogen for 48 h. With ice-bath cooling and vigorous stirring the reaction mixture was then treated slowly with water (100 ml) until evolution of hydrogen chloride ceased. The mixture was filtered and the benzene layer was separated and washed with water ( 3 x 50 ml ) as was the residue in the funnel. All of the washings were added to the acidic aqueous layer. The aqueous solution was neutralized with dilute aqueous sodium hydroxide, saturated with sodium chloride and extracted with chloroform ( 3 x 50 ml ). The chloroform extracts were combined, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The crude solid was recrystallized from hot ethanol to give long colourless needles (2.3g, 60%) of the pyrazoline 12, m.p. 211-212°(decomp.)

Anal. Calcd. for $C_{23}H_{19}N_2P$: C, 77.95; H, 5.36; N, 7.91; P, 8.77. Found: C, 77.67; H, 5.46; N, 8.04; P, 8.54.

The i.r. spectrum shows $\upsilon_{max}$ at 3280, 1596, 1490, 1443, 1431, 1329, 1300, 1201, 1119, 1084, 1065, 1040, 1024, 1019, 998, 946, 910, 899, 880, 850, 814, 758, 740, and 690 $cm^{-1}$. The ultraviolet spectrum in absolute ethanol shows $\lambda_{max}$ at 224 mμ and 250 mμ and the n.m.r. spectrum ($CDCl_3$) shows 16 aromatic and olefinic protons at $\tau$=2.32-3.06, one amino proton at $\tau$=3.39, and two methine protons at $\tau$=4.47. The mass spectrum shows a strong molecular ion peak at *m/e*=354.

3,4,5-Triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (5)(5.0g, 14.62 mmole) was reduced in a similar manner with trichlorosilane (20g, 147.7 mmole) to give the bicyclic phosphine 13 (3.5g, 73%) as colourless needles, m.p. 134-135° (decomp.).

Anal. Calcd. for $C_{23}H_{19}P$: C, 84.63; H, 5.84; P, 9.53. Found: C, 84.71; H, 5.94; P, 9.38.

The i.r. spectrum shows $\upsilon_{max}$ at 1601, 1580, 1495, 1445, 1432, 1304, 1269, 1095, 1088, 1072, 1022, 1000, 935, 911, 902, 871, 851, 828, 760, 751, 698, and 688 $cm^{-1}$. The ultraviolet spectrum in absolute ethanol shows $\lambda_{max}(\log \varepsilon)$ at 214.5 mμ (4.50) and 267 mμ (4.24). The n.m.r. spectrum ($CDCl_3$) shows a ratio of 16 aromatic and olefinic protons (complex multiplet at $\tau$=2.43-3.12) to one methine proton (multiplet centered at $\tau$=7.32) to 2 methylene protons (multiplet centered at $\tau$=8.82). The mass spectrum shows a very strong molecular ion peak at m/e=326.

### Pyrolysis of 3,4,5-Triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (5)

A pure sample of the cyclopropane 5 (1g, 2.92 mmole) was carefully pyrolysed in a Woods metal bath at 238° until gas evolution ceased and the material turned dark brown and resolidified. The crude product was washed with ether followed by ethanol and the reddish-yellow solid left was recrystallized from a hot chloroform/ethanol mixture to give orange crystals (0.47g, 47%) of 3,3'4,4',5,5'-hexaphenyl-4-4'-diphosphabi(cyclohexa-1,5-dienyl)-4,4'-dioxide (10), m.p. 386-387°(decomp.).

Anal. Calcd. for $C_{46}H_{36}O_2P_2$: C, 80.91; H, 5.28; P, 9.08. Found: C, 80.46; H, 5.33; P, 9.34.

The i.r. spectrum shows $\upsilon_{max}$ at 3062, 2862, 1606, 1500, 1465, 1442, 1352, 1180, 1117, 1079, 1041, 900, 770, 754, 703, 670 $cm^{-1}$. The ultraviolet spectrum in chloroform shows $\lambda_{max}$(log $\varepsilon$) at 315 mμ (4.83) and 408 mμ (4.87) and the n.m.r. spectrum in trifluoroacetic acid shows a ratio of 17 aromatic and olefinic protons (complex multiplet at $\tau$=2.01-3.13) to 1 tertiary proton (very broad unresolved hump centered at $\tau$=6.11).

The experiment was repeated on the same quantity of material at the same temperature in an evacuated (<4 x $10^{-7}$torr) small cylindrical tube fitted with a high vacuum tap to which was attached a 10/30 Ŧ glass cone such that the reaction tube could be connected directly to the liquid inlet of the mass spectrometer. A yield of 51% of **10** was obtained and mass spectral analysis of the gas evolved showed a tenfold increase in the intensity of the $H_2$ peak over the background but no significant increase in the water peak.

## Pyrolysis of the Pyrazoline **4**

The pyrazoline (1g, 2.7 mmole) was carefully pyrolysed under vacuum (ca. 1 torr) in a Woods metal bath at 238° until gas evolution ceased and the dark brown material resolidified. The crude product was worked up as before to give orange crystals of the pyrolysis product **10** (0.55g, 60%).

## Pyrolysis of the Pyrazoline Ester **11**

The pyrazoline ester (2.0g, 4.53 mmole) in an evacuated (ca. 1 torr) tube was pyrolysed at 220-225° in a Woods metal bath for 20 min. The crude product was washed with a little ether and the off-white solid left was recrystallized from a benzene/light petroleum (60°-80°) mixture to give colourless needles (1.4g, 75%) of ethyl 1,2,6-triphenyl-1-phosphacyclohexa-2,5-diene-3-carboxylate-1-oxide (3, R= Et), m.p. 217-218°, identical in all respects (m.p. i.r., n.m.r., mass spectrum) with a sample prepared by Campbell's method (5).

### Photolysis of 3,4,5-Triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (5)

A solution of the cyclopropane 5 (3g, 8.76 mmole) in dry, peroxide-free tetrahydrofuran (1000 ml) was irradiated under dry, oxygen-free nitrogen with a medium pressure mercury lamp (100 watt) through pyrex for 8 days. After evaporation of the mixture to dryness, the crude solid was digested with ethanol to remove starting material and the residue was recrystallized from a hot chloroform/ethanol mixture to give orange crystals (1.3 g, 44%) of 3,3',4,4',5,5'-hexaphenyl-4,4'-diphosphabi(cyclohexa-2,5-dienylidene)-4,4'-dioxide (7), m.p. 436-438°[lit. (6) m.p. 425-428°].

Anal. Calcd. for $C_{46}H_{34}O_2P_2$: C, 80.90; H, 4.98; P, 9.06. Found: C, 80.64; H, 4.90; P, 9.45.

The i.r. spectrum shows $\upsilon_{max}$ at 1604, 1490, 1463, 1443, 1336, 1245, 1169, 1106, 1075, 1066, 1031, 937, 887, 771, 750, 698cm.$^{-1}$ The ultraviolet spectrum in chloroform shows $\lambda_{max}$(log ε) at 325 mμ

(4.53) and 438 mμ (4.91) and the n.m.r. spectrum in trifluoroacetic acid shows only aromatic and olefinic protons as a complex multiplet at τ=2.22-2.86.

Irradiation of the pyrazoline 4 (8 g, 21.65 mmole) under very similar conditions gave the same product (1.0g, 14%)

### Reduction of the Photolysis (7) and Pyrolysis (10) Products with Phosphorus Pentachloride and Lithium Aluminum Hydride

The photolysis product 7 (0.1g, 0.15 mmole) was fused with a large excess of phosphorus pentachloride (3g, 14.51 mmole) at 120-130° until the mixture turned deep red (1 h). The excess of phosphorus pentachloride was removed by sublimation at 100° under vacuum. With dry ice/acetone cooling, the resulting deep red powder was treated dropwise with saturated ethereal lithium aluminum hydride under dry nitrogen until gas evolution ceased and the mixture was allowed to warm slowly to room temperature. The excess of hydride was decomposed with water-saturated ether and water (100 ml) was then added and the ether removed under vacuum. The resulting aqueous suspension was extracted with chloroform (3 x 10 ml) and the chloroform extracts were combined and dried over anhydrous sodium sulfate. The chloroform solution was then evaporated to dryness and the crude solid was washed with ethanol and recrystallized from a hot chloroform/ethanol mixture to give red crystals (0.07g, 74%) of 3,3',4,4',5,5'-hexaphenyl-4,4'-diphosphabi(cyclohexa-2,5-dienylidene)(14), m.p. 338-340° [lit.(6)m.p. 335-337°].

Anal. Calcd. for $C_{46}H_{34}P_2$: C, 85.18; H, 5.24; P, 9.57. Found: C, 84.37; H, 5.32; P, 9.50.

Good analyses are difficult to obtain since the compound crystallizes with up to 4% occluded chloroform which is very difficult to remove. Pumping the compound at 180-200° under high vacuum leads to slow loss of the chloroform but, even under vacuum, oxygen scavenging also takes place and slow oxidation of 14 occurs.

The i.r. spectrum shows $\upsilon_{max}$ at 3075, 1618, 1500, 1446, 1438, 1369, 1350, 1250, 1100, 1041, 941, 922, 889, 861, 776, 767, 749, 718, 700 and 694 $cm^{-1}$, i.e. the P=O bond present in the spectrum of 7 at 1168 $cm^{-1}$ has vanished. The ultraviolet spectrum in chloroform shows $\lambda_{max}$(log ε) at 339 mμ (3.88) and 468 mμ (4.64) [lit.(6) $\lambda_{max}$ 337 mμ and 467 mμ]. The n.m.r. spectrum in trifluoroacetic acid shows only aromatic and olefinic protons as a complex multiplet at τ=2.18-2.87. The mass spectrum shows a molecular weight of 648.

Reduction of the pyrolysis product 10(0.5g, 0.73 mmole) with phosphorus pentachloride (15g, 72.55 mmole) and lithium aluminum hydride under very similar conditions also gave 14 (0.4g, 84%).

As stated by Märkl (6) the phosphine 14 is air stable but with traces of acid it oxidizes back to 7 very rapidly.

### Treatment of the Pyrolysis Product 10 with Lithium Aluminum Hydride

With cooling (dry ice/acetone)and vigorous stirring, a suspension of the pyrolysis product 10 (0.6g, 0.88 mmole) in dry ether (60 ml) was treated dropwise with a solution of lithium aluminum hydride (0.34g, 8.82 mmole) in dry ether under dry nitrogen. The temperature of the reaction mixture was allowed to rise to room temperature and the mixture was maintained at this temperature for a further 15 min. Destruction of the excess of the hydride was carried out with water saturated ether. Water (60 ml) was added and the mixture was evaporated until ether-free. The resulting aqueous suspension was extracted with chloroform (3 x 60 ml). The chloroform extracts were combined, dried over anhydrous sodium sulfate, and evaporated to dryness. The crude solid was washed with ethanol and recrystallized from a hot chloroform/ethanol mixture to give orange crystals (0.55g, 92%) of 3,3',4,4',5,5'-hexaphenyl-4,4'-diphosphabi(cyclohexa-2,5-dienylidene)-4,4'-dioxide (the photolysis product 7) identical in all respects with an authentic sample.

The same reaction occurs with sodium hydride.

We thank the National Research Council of Canada and the Ontario Department of University Affairs for generous financial support.

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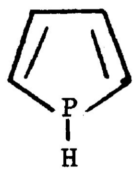

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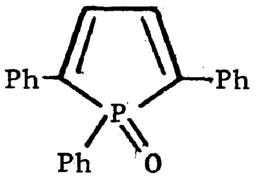

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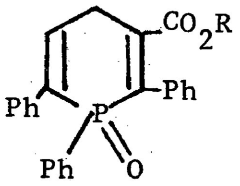

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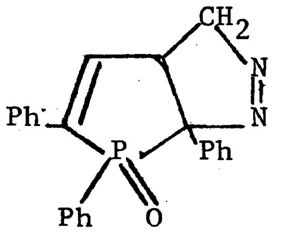

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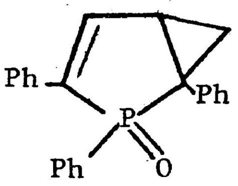

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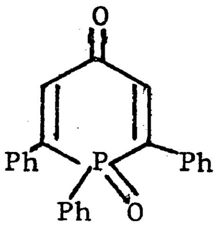

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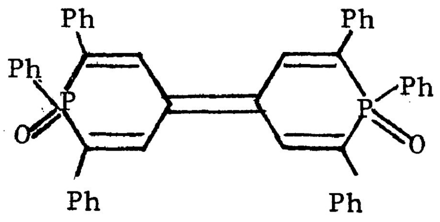

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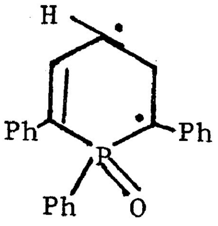

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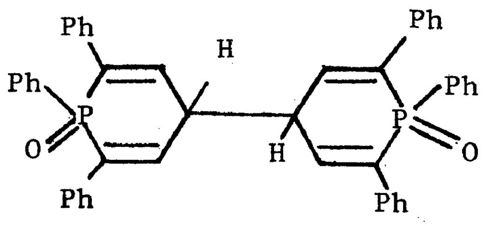

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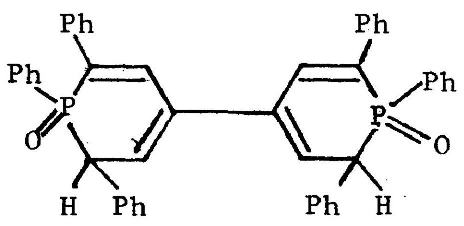

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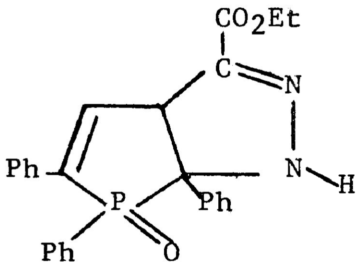

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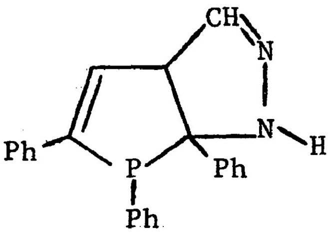

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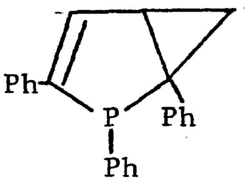

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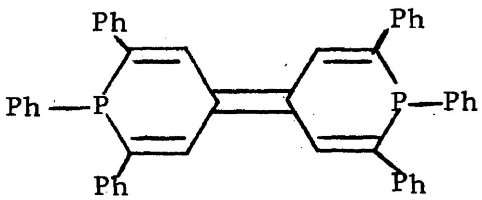

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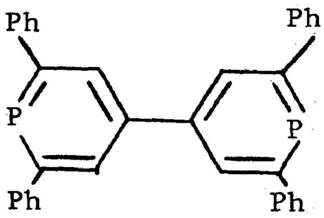

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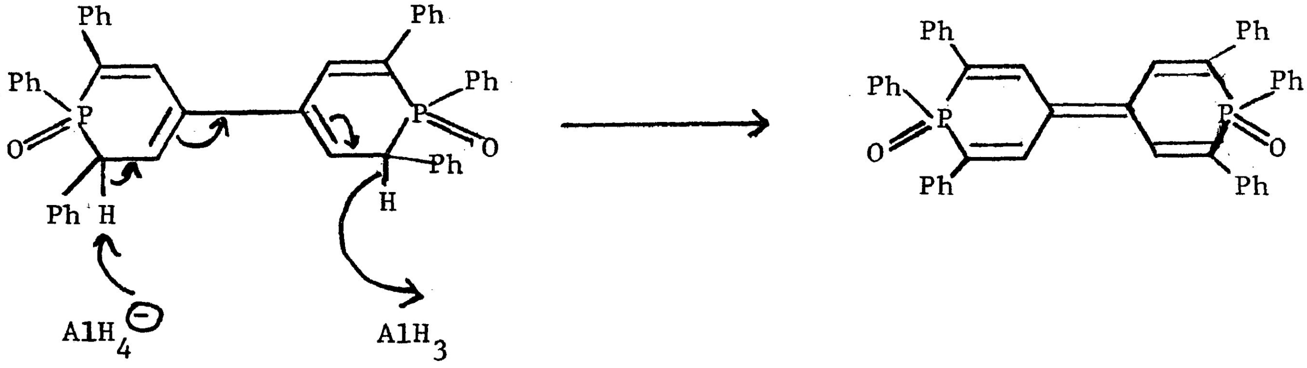

SCHEME A

# Alkaline Hydrolysis of 1-Iodomethyl-1,2,5-triphenylphospholium Iodide - A New Route to the 4-Phosphabicyclo[3.1.0] hex-2-ene System

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Keywords:

4-Phosphabicyclo[3.1.0]hex-2-ene, 3,4,5-triphenyl-, 4-oxide
Phospholium salts, hydrolysis
Phospholium salts, rearrangement in

Alkaline hydrolysis of 1-iodomethyl-1,2,5-triphenylphospholium iodide gives 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide in very high yield. Three possible mechanisms are discussed and isolation of a key intermediate allows one of these mechanisms to be discarded. Alkaline hydrolysis of 1-allyl-1,2,5-triphenylphospholium bromide in methanol gives 1,2,5-triphenylphosphole and small quantities of a compound $C_{26}H_{27}O_2P$ which is an adduct of the original phospholium ion, hydroxide ion and methanol.

Ring expansion reactions of the phosphole system have been comparatively little explored as possible routes to six-membered unsaturated phosphorus heterocycles (1-4). One approach, due to Millar (3), involves the reaction of 9-phenyl-9-phosphafluorene (the dibenzophosphole 1) with methylene iodide to give the salt 2 which on treatment with hydroxide ion gives 3 (in very good yield) by cleavage of the phosphole ring in the manner observed by Bergesen (5) followed by attack of the resulting carbanion [which migrates from the apical position of a trigonal bipyramidal intermediate (3)] upon the methylene group and displacement of iodide ion. This type of 1,2-migration has been shown to be fairly general in the hydrolysis of suitably substituted phosphonium compounds and similar ring expansions occur in the phosphetan system (6).

Simple phospholes are now relatively easily available (7) and the above reaction applied to simple phospholes could prove to be a convenient route to phosphorins--particularly those with unsymmetrical substitution patterns. In order to explore this possibility, 1,2,5-triphenylphosphole (4) was treated with methylene iodide in a pressure bottle for 4½ days to give an excellent yield of the corresponding phospholium iodide 5. Alkaline hydrolysis of 5 was expected to give the phosphacyclohexa-2,4-diene 6 since the five membered ring should occupy an apical-equatorial arrangement in the expected trigonal bipyramidal intermediate (6) but, rather surprisingly, a 74% yield of 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene-4-oxide (7) [identical with an authentic sample (1)] was obtained when 5 was treated with aqueous methanolic sodium hydroxide for 24 hours under reflux followed by acidification of the reaction mixture. This bicyclic compound has recently been shown (4) to be of value in the synthesis of six-membered ring phosphorus heterocycles.

There are several possible mechanisms for the formation of 7 from 5. At first sight perhaps the most likely of these is a 1,2-migration of the iodomethyl group followed by proton abstraction by hydroxide ion and ring closure involving expulsion of iodide ion as shown in Scheme A.

However, hydroxide ion abstraction of the allylic protons would seem unlikely. This reaction would parallel the 1,2-migrations observed (6) in other phosphonium salt hydrolyses but it would imply that in this case the five membered ring does not occupy an apical-equatorial arrangement in the intermediate or that in the case of 2 a $-CH_2I$ migration of the type outlined in Scheme A is inhibited by the fused nature of the ring system.

A second possible mechanism is illustrated in Scheme B. In this case a 1,3-migration of the iodomethyl group occurs and the intermediate carbanion 11 could be to some extent stabilized by overlap with the d-orbitals of the neighboring phosphorus atom. However, this would be a most unusual type of rearrangement which would be difficult to account for except that it involves attack at the β-position of a vinylphosphonium type of system.

A third possibility[1] (Scheme C) is that the intermediate 10 is formed by two consecutive 1,2-shifts of the iodomethyl group rather than a single 1,3-shift. The driving force for the second of these migrations would presumably come from the conversion of an allylic carbanion type of intermediate into the protonated α-phosphoryl benzylic carbanion 10.

If any of these Schemes operates and if the predicted intermediate 8 or 10 has a significant lifetime it could possibly be isolated. Therefore, in an attempt to isolate the predicted intermediate, the reaction was carried out under much milder conditions at room temperature

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[1] We are indebted to one of the referees for this suggestion.

for two hours. The product (obtained in good yield) was not **7** but analyzed well for $C_{23}H_{20}OPI$ and the mass spectrum confirmed the molecular weight as 470. The i.r. spectrum shows a typical P=O stretching vibration at 1180 $cm^{-1}$ and the ultraviolet spectrum (ethanol) shows $\lambda_{max}$($\log \varepsilon$) at 220 mμ (4.33) and 261 mμ (4.07) indicating considerable loss of conjugation relative to **5**. The n.m.r. spectrum shows a ratio of 16 aromatic and olefinic protons (complex multiplet at τ=2.19-3.16) to 2 methylene or methine protons (multiplet at τ=5.52-6.08) to 2 methylene protons (multiplet at τ=6.65-7.02). That the compound is not a mixture of **8** and **10** was shown by a detailed t.l.c. examination on both alumina and silica of various activities using several solvent systems.

In our opinion, this evidence fits structure **10** considerably better than it fits structure **8**. Thus, structure **8** contains two allylic methylene protons which could possibly account for the multiplet in the n.m.r. spectrum at τ=6.65-7.02 although a signal at somewhat higher field would be expected. However, this would mean that the methylene protons of the iodomethyl group would be responsible for the signal at τ=5.52-6.08 which is clearly at too low field for such protons even bearing in mind the probable deshielding effect of the P=O grouping. Indeed, even in **5**, where the deshielding effect of the neighboring phosphonium grouping (8) is at a maximum, the methylene protons appear only as low as τ=5.68.

Equally, if the n.m.r. signal assignments for **8** are reversed, the signal at $\tau$=6.65-7.02 would agree well with that expected for the methylene protons of the iodomethyl group [*cf* ethyl iodide (9)] but the signal at $\tau$=5.52-6.08 is again at too low field for the allylic methylene group which is relatively remote from the P=O grouping and attached to only a mildly electron-withdrawing group. Such a signal would be unlikely to occur below $\tau$=7 unless some additional strong deshielding effect were present. For example, even in allyl bromide, where deshielding is very strong, the allylic methylene protons still resonate at $\tau$=6.07 (10). The additional deshielding effect could conceivably be provided by the neighboring phenyl group but, if this were the case, it seems unlikely that both of the non-equivalent protons would be deshielded to the same extent bearing in mind the probable stereochemistry of the system.

On the other hand, in structure **10**, the signal at $\tau$=6.65-7.02 agrees well with that expected for the iodomethyl group as in ethyl iodide (9) and the signal at $\tau$=5.52-6.08 could be generated by the two tertiary protons both of which are allylic (or benzylic) and adjacent to electron-withdrawing groups. Furthermore, the benzylic protons in **12** have been shown to resonate in the same region at $\tau$=6.11 (4).

It is worth noting that the side-chain methylene group of **10** appears as multiplet of at least five peaks rather than a doublet in the n.m.r. spectrum. This is almost certainly because the two methylene protons are non-equivalent due to the adjacent asymmetric centre since long range coupling with the phosphorus atom would be very small. Such a case is similar to that of the diastereomeric methylene protons of 1,2-dichloropropane (11). The methine protons appear as a multiplet because of coupling with each other, the non-equivalent methylene protons and the phosphorus atom. In structure 8, the protons in both methylene groups would be non-equivalent due to the neighboring asymmetric centre so that the mutiplicities of the signals are of little value in distinguishing between 8 and 10. Also, the fact that both 8 and 10 could be mixtures of the various possible stereoisomers cannot be ignored.

Further treatment of 10 with sodium hydroxide in aqueous methanol under reflux for 24 hours gives an almost quantitative yield of the cyclopropane 7. This supports our tentative conclusion that 10 (and not 8) is the intermediate isolated since it is unlikely that the protons of the allylic methylene group in 8 would be sufficiently acidic to be abstracted by hydroxide ion whereas benzylic protons of the type present in 10 and 12 are known to be abstractable by strong base (4). The compound assumed to be 10 is also converted very rapidly into 7 on treatment with sodium hydride in rigorously dried (molecular sieves) dimethylformamide. This, then, strongly suggests that 10 is formed as an intermediate in the alkaline hydrolysis of 5 and that the reaction proceeds *via* Scheme B or Scheme C. Attempts to reduce the side-chain iodomethyl group of 10 with lithium aluminum hydride gave only resinous materials.

In a final attempt to confirm the identity of 10, deuterium exchange studies were undertaken. Thus, it was observed that a solution of the compound assigned structure 10 in perdeuteroacetone containing NaOD and $D_2O$ showed no exchange (n.m.r. studies) at room temperature over a period of two days. Treatment of the same compound in rigorously dried (molecular sieves) dimethylsulfoxide with NaOD and $D_2O$ resulted in the formation of 7. The reaction was complete in little over a minute and n.m.r. measurements showed no incorporation of deuterium into the product. A solution of the compound assigned structure 10 in perdeuteroacetone containing NaOD and $D_2O$ was heated under reflux until about 75% conversion into 7 had occurred (approximately 30 minutes). N.m.r. studies of the mixture of the product and starting material showed that no deuterium exchange had occurred in the starting material (the peaks at $\tau$=6.65-7.02 and at $\tau$=5.52-6.08 remained of equal area) and that no deuterium had been incorporated into 7. These studies are inconclusive in that they do not favour either structure 10 or structure 8. They show only that the proton abstraction step 8 → 9 (Scheme A) or 10 → 11 (Scheme B and Scheme C) is not reversible under the conditions used and that intramolecular cyclization occurs before reprotonation can occur. However, in our opinion, all the evidence available strongly favours structure 10 in preference to structure 8 for the hydrolysis intermediate $C_{23}H_{20}OPI$.

Similar experiments were carried out with 1-allyl-1,2,5-triphenylphospholium bromide (13) in order to see if any corresponding migration of the allyl group occurs.

The quaternary salt 13 is readily prepared in very high yield by heating the phosphole 4 with allyl bromide in dry benzene under reflux for several days. Treatment of the quaternary salt with aqueous methanolic sodium hydroxide at room temperature gives at least two products together with large amounts of oily material. The first of these is the phosphole 4 - *not* its oxide as would be expected from normal attack (5) of hydroxide ion at the phosphorus atom - and it therefore appears that attack occurs at the terminal carbon atom of the allyl group with displacement of the neutral phosphole 4 as shown in Scheme D.

The second product, obtained in very small quantities, is a colourless material analyzing for $C_{26}H_{27}O_2P$ and which is therefore an adduct of the phospholium ion 13, hydroxide ion and methanol. The mass spectrum confirms the molecular weight as 402 and elemental analyses show the presence of one methoxy group. The ultraviolet spectrum shows $\lambda_{max}$ (log$\varepsilon$) at 219.5m$\mu$ (4.27) and 258 m$\mu$ (4.01) indicating that the diphenylbutadiene portion of the molecule is no longer intact and that the molecule contains little unsaturation. The i.r. spectrum shows P=O and ether-type C-O stretching vibrations at 1170 cm$^{-1}$ and 1105 cm$^{-1}$ respectively. The n.m.r. spectrum shows 16 aromatic and olefinic protons as a complex multiplet at $\tau$=2.15-3.14, 3 methoxy protons as a sharp singlet at $\tau$=6.97, 5 methylene and/or methine protons as a complex multiplet at $\tau$=5.81-7.99 and 3 methyl protons as a doublet (J=6Hz) at $\tau$=9.0. Since the methoxy protons appear as a sharp singlet in the n.m.r. spectrum, the methoxy group is not attached to the phosphorus atom because this would give a doublet due to $^{31}$P coupling (12).

It therefore seems likely that migration of the allyl group has occurred and that some kind of addition of methanol to the unsaturated portion of the allyl group has also occurred to give a methyl group adjacent to a tertiary proton. Since only very small quantities of the product were available, the structure determination was not completed. However, structures **14** and **15** are consistent with all the evidence (with **14** preferred by analogy with **10**) but, apart from migration of the allyl group to the 2-or 3-position of the phosphole ring, it is difficult to visualize the reaction sequence which could lead to these structures. Some further evidence for the proposed structures **14** and **15** is given by the ultraviolet spectrum which is almost identical with that of **10** and by the mass spectrum which shows a very intense peak at *m/e* 329 corresponding to loss of the allylic or tertiary $-CH_2CH(OMe)CH_3$ group and another strong peak at *m/e* 328 which suggests that the oxide of the phosphole **4** is regenerated on electron impact. The peak at *m/e* 329 is also present in the spectrum of the product tentatively assigned structure **10** but is much weaker. This is presumably due to the easy loss of the iodine atom which would lead to a different major fragmentation pattern. The structure of this adduct must, however, remain in doubt pending a complete structure determination.

## Experimental

Infrared spectra were recorded in Nujol mulls using a Beckman IRI2 spectrophotometer while ultraviolet spectra were obtained on dilute ethanol solutions using a Unicam SP800 spectrophotometer. N.m.r. measurements were made with a Varian Associates model A60-A spectrometer using trifluoroacetic acid or deuteriochloroform solutions with tetramethylsilane as internal reference. Mass spectra were determined using an Hitachi-Perkin Elmer model RMU-7 double focussing mass spectrometer.

1,2,5-Triphenylphosphole was prepared by the method of Campbell (1).

## 1-Iodomethyl-1,2,5-triphenylphospholium Iodide (5)

A well-mixed paste of 1,2,5-triphenylphosphole (10 g, 32.05 mmole) and methylene iodide (26 g, 96.95 mmole) in a pressure bottle under dry nitrogen was kept with constant stirring at 80-85° for 4½days. When cooled, the reaction mixture turned to a dark brown solid which was broken up and washed thoroughly with acetone. The yellow residue (17 g, 91%) was found to be almost pure 1-iodomethyl-1,2,5-triphenylphospholium iodide, m.p. 174-175° (decomp.)

Anal. Calcd. for $C_{23}H_{19}I_2P$: C, 47.59; H, 3.28; I, 43.79; P, 5.34. Found: C, 47.74; H, 3.45; I, 43.82; P, 5.37.

Attempts to recrystallize the yellow powder from a number of solvents such as benzene, chloroform, acetone, ethanol, methanol, water, acetic acid, dimethylformamide and mixed solvents were unsuccessful and the material was therefore used directly for further investigation.

The i.r. spectrum of 5 shows $\nu_{max}$ at 1579, 1538, 1491, 1472, 1447, 1441, 1384, 1371, 1318, 1302, 1259, 1233, 1168, 1161, 1110, 1080, 1031, 1000, 946, 923, 860, 800, 766, 750, 740, 730, 700, 690 $cm.^{-1}$

The ultraviolet spectrum in absolute ethanol shows $\lambda_{max}$(log $\varepsilon$) at 225 m$\mu$ (4.58), 275 m$\mu$ (3.71) and 411 m$\mu$ (4.19). The n.m.r. spectrum in trifluoroacetic acid shows a ratio of 17 aromatic and olefinic protons (complex multiplet at $\tau$=1.75-2.76) to 2 methylene protons (doublet centered at $\tau$=5.68 with $J_{HP}$=8 Hz).

### Complete Alkaline Hydrolysis of 1-Iodomethyl-1,2,5-triphenylphospholium Iodide (5)

To a suspension of the quaternary salt 5 (8g, 13.79 mmole) in methanol (800 ml) was added slowly a 10% aqueous solution of sodium hydroxide (55 ml, 137.6 mmole) at room temperature with vigorous stirring. After the addition was complete, the reaction mixture was heated under reflux for 24h. The cooled solution was then treated dropwise with dilute aqueous hydrochloric acid until it was just acidic to litmus paper. Water (200 ml) was added and the mixture was evaporated under reduced pressure to remove most of the methanol. The aqueous suspension was then extracted with chloroform (3 x 100 ml). The extracts were combined, dried over anhydrous sodium sulfate, reduced to a volume of 50 ml and chromatographed on a silica gel column using chloroform as the eluent. Evaporation of the eluate to dryness yielded a pale yellow solid which was recrystallized from hot ethanol to give very pale yellow crystals (3.5 g, 74%) of 3,4,5-triphenyl-4-phosphabicyclo [3.1.0]hex-2-ene-4-oxide (7), m.p. 234-235° (decomp.), identical in all respects with an authentic sample (1).

## Incomplete Alkaline Hydrolysis of 1-Iodomethyl-1,2,5-triphenylphospholium Iodide(5)

To a suspension of the quaternary salt 5 (12 g, 20.68 mmole) in methanol (1200 ml) was added slowly a 10% aqueous solution of sodium hydroxide (83 ml, 207.1 mmole) at room temperature followed by vigorous stirring for 2 h. The solution was then treated dropwise with dilute aqueous hydrochloric acid until it was just acidic to litmus paper. Water (300 ml) was added and the mixture was evaporated under reduced pressure to remove most of the methanol. The aqueous suspension was extracted with chloroform (3 x 50 ml) and the extracts were combined, dried over anhydrous sodium sulfate and evaporated to dryness. The dark brown residue was dissolved in the minimum amount of benzene and chromatographed on a column of silica gel using successively benzene and chloroform as eluents. The benzene fraction, upon evaporation, yielded a colourless solid which was recrystallized from a hot benzene/cyclohexane mixture to give long colourless needles (5.6 g, 58%) of 4-iodomethyl-1,2,5-triphenyl-2-phospholene-1-oxide (10), m.p. 199-200° (decomp.).

Anal. Calcd. for $C_{23}H_{20}OPI$: C,58.71; H, 4.26; I, 27.08; P, 6.60. Found: C, 59.01; H, 4.25; I, 27.09; P, 6.60.

The i.r. spectrum shows $\nu_{max}$ at 3058, 1601, 1587, 1499, 1438, 1422, 1304, 1268, 1180, 1159, 1148, 1104, 1068, 1025, 1000, 918, 881, 824, 792, 760, 748, 719, 699, 691 $cm^{-1}$. The ultraviolet spectrum in absolute ethanol shows $\lambda_{max}(\log \varepsilon)$ at 220 mμ (4.33) and 261 mμ (4.07). The n.m.r. spectrum in deuterated chloroform shows a ratio of 16 aromatic and olefinic protons (complex multiplet at $\tau$=2.19-3.16) to 2 tertiary protons (multiplet at $\tau$=5.52-6.08) to 2-methylene protons (multiplet of at least 5 peaks at $\tau$=6.65-7.02). The mass spectrum shows a good molecular ion peak at m/e=470.

The chloroform fraction, upon evaporation to dryness yielded pale yellow crystals of 7 (0.7 g, 10%) identical in all respects with an authentic sample.

## Alkaline Hydrolysis of 4-Iodomethyl-1,2,5-triphenyl-2-phospholene-1-oxide (10)

To a solution of the 2-phospholene oxide 10 (1 g, 2.13 mmole) in methanol (100 ml), was added slowly a 10% aqueous solution of sodium hydroxide (8.5 ml, 21.28 mmole) at room temperature with vigorous stirring. After the addition was complete, the mixture was heated under reflux for 24 h. The cooled solution was treated dropwise with dilute hydrochloric acid until it was acidic to litmus paper and the mixture was worked up and chromatographed in chloroform solution as before. The eluate from the silica column yielded a pale yellow solid which was crystallized from hot ethanol to give very pale yellow crystals (0.65 g, 90%) of the cyclopropane 7 identical in all respects with an authentic sample.

### 1-Allyl-1,2,5-triphenylphospholium Bromide (13)

The phosphole 4 (15 g, 48.09 mmole) and allyl bromide (29 g, 240 mmole) in dry benzene (500 ml) were heated under reflux in a dry nitrogen atmosphere for 5 days. The yellow solid which separated was collected and recrystallized from hot water or a hot methanol/benzene mixture to give yellow crystals (19 g, 91%) of 1-allyl-1,2,5-triphenylphospholium bromide (13), m.p. 202-203° (decomp).

Anal. Calcd. for $C_{25}H_{22}BrP$: C, 69.26; H, 5.07; Br, 18.52; P, 7.15. Found: C, 68.97; H, 5.01; Br, 19.05; P, 7.10.

The i.r. spectrum shows $\nu_{max}$ at 3038, 1635, 1610, 1579, 1490, 1443, 1344, 1313, 1259, 1190, 1154, 1108, 1078, 1030, 998, 981, 939, 906, 878, 813, 761, 748, 726, 685 $cm.^{-1}$ The ultraviolet spectrum in absolute ethanol shows $\lambda_{max}(\log \varepsilon)$ at 212 mμ (4.52) 227 mμ (4.58) and 410 mμ (4.12). The n.m.r. spectrum in deuterated chloroform shows a ratio of 20 aromatic and olefinic protons (complex multiplet at $\tau$=1.26-2.96) to two methylene protons (poorly defined quartet centered at $\tau$=5.27)

## Alkaline Hydrolysis of 1-Allyl-1,2,5-triphenylphospholium Bromide (**13**)

A solution of the quaternary salt **13** (1.4 g, 3.24 mmole) in methanol (70 ml) was treated dropwise with a 10% aqueous solution of sodium hydroxide (6.5 ml, 16.25 mmole) at room temperature with constant stirring for 10 min. Water (50 ml) was added and the mixture was evaporated to remove most of the methanol. The aqueous suspension was extracted with chloroform (3 x 50 ml) and the chloroform extracts were combined, dried and evaporated as before. The residue was chromatographed on a neutral alumina column using successively benzene and chloroform as eluents.

The benzene fraction, upon evaporation to dryness, yielded an oily solid which, on recrystallization from hot ethanol gave the phosphole **4** (0.12 g, 12%) identical with an authentic sample.

Evaporation of the chloroform fraction also yielded an oily solid which was sublimed under vacuum (*ca*. 1 torr) at 165° to give a colorless compound,(0.16 g, 12%) m.p. 171-172°

Anal. Calcd. for $C_{26}H_{27}O_2P$: C, 77.71; H, 6.72; P, 7.71; $OCH_3$, 7.71. Found: C, 77.4; H, 6.73; P, 7.60; $OCH_3$, 6.83.

The i.r. spectrum shows $\nu_{max}$ at 3051, 1610, 1600, 1578, 1494, 1431, 1368, 1299, 1262, 1220, 1170, 1105, 996, 955, 920, 878, 826, 791, 774, 752, 743, 718, 688 cm.$^{-1}$ The ultraviolet spectrum in absolute ethanol shows $\lambda_{max}$(log $\varepsilon$) at 219.5 mμ (4.27) and 258 mμ (4.01). The n.m.r. spectrum shows 16 aromatic and olefinic protons as a complex multiplet at $\tau$=2.15-3.14, 3 methoxy protons as a sharp singlet at $\tau$=6.97, 5 methylene and methine protons as a complex multiplet at $\tau$=5.81-7.99 and 3 methyl protons as a doublet (J=6 Hz) at $\tau$=9.0. The mass spectrum shows a strong molecular ion peak at *m/e*=402.

Alkaline hydrolysis using only water as solvent gave a mixture of uncrystallizable oils together with traces of the phosphole **4** and *p*-terphenyl.

We thank the National Research Council of Canada and the Ontario Department of University Affairs for generous financial support.

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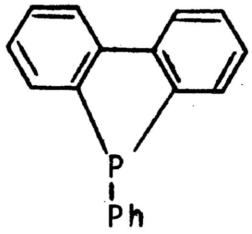

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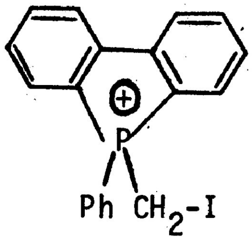

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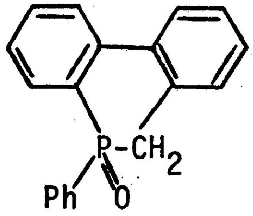

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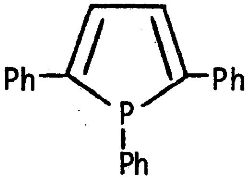

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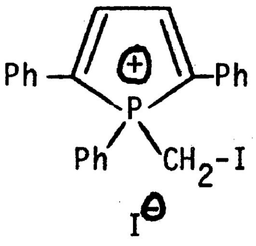

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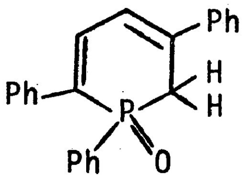

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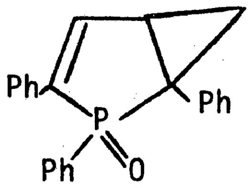

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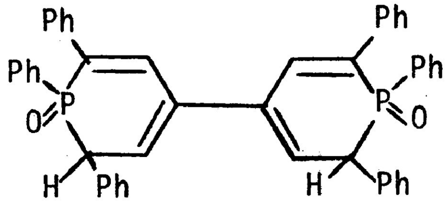

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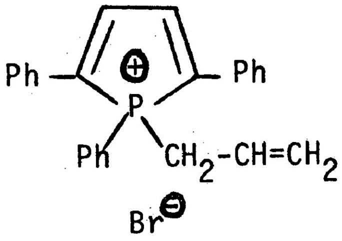

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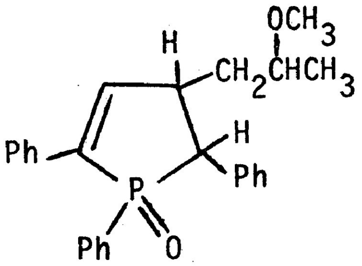

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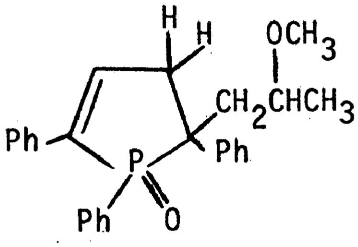

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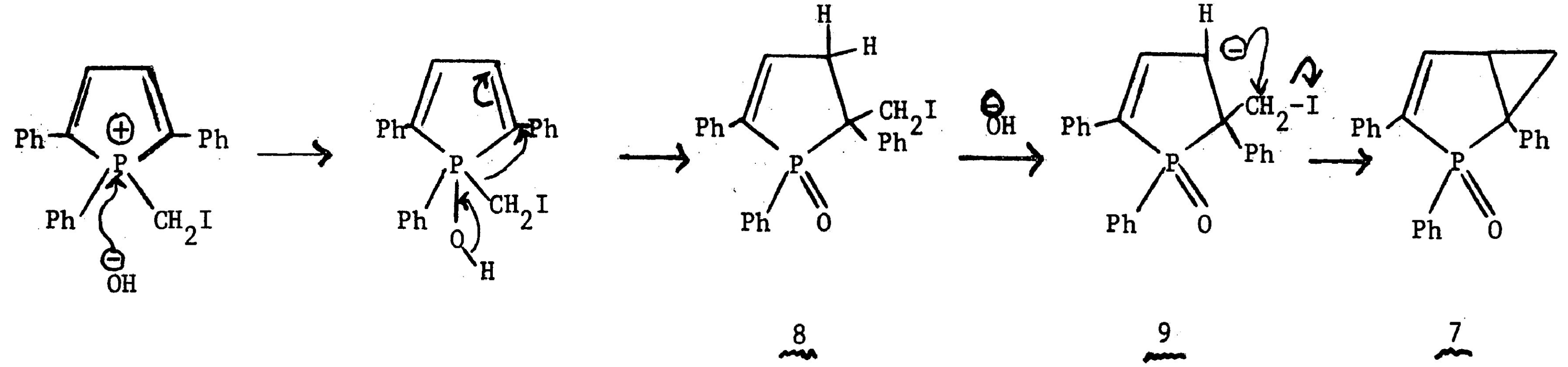

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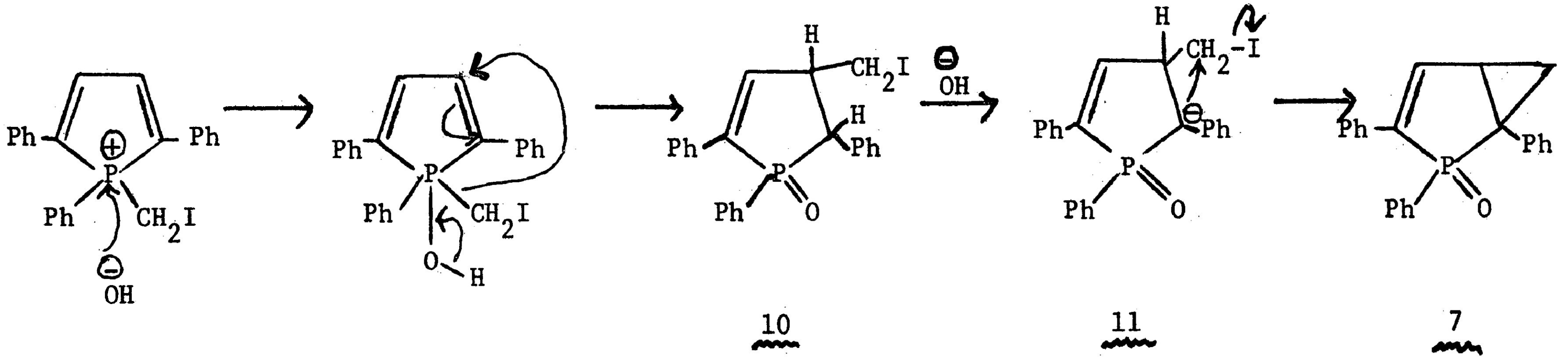

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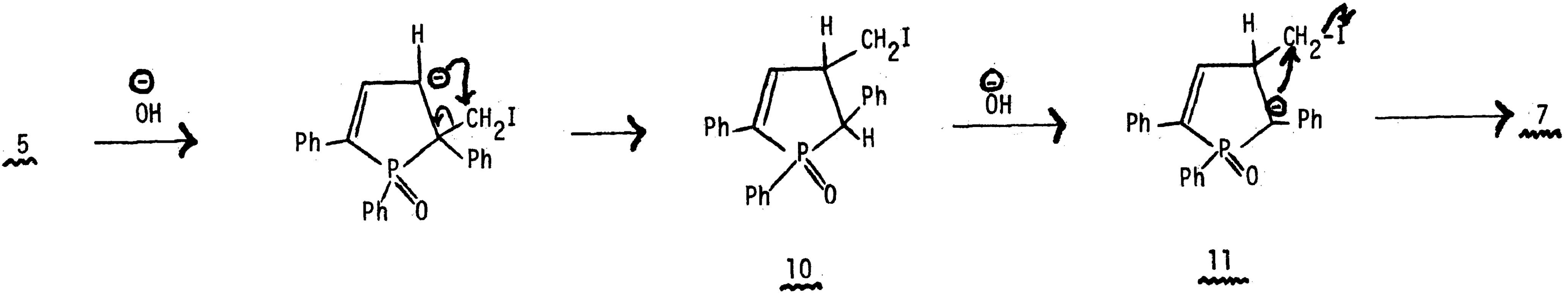

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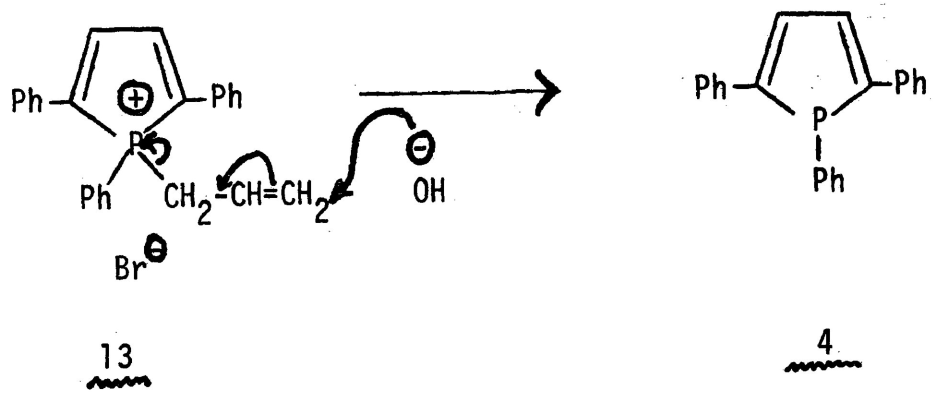

SCHEME D