SYNTHETIC APPROACHES TO FIVE-MEMBERED

HETEROCYCLES CONTAINING BOTH RING AND

SIDE-CHAIN PHOSPHORUS ATOMS

BY

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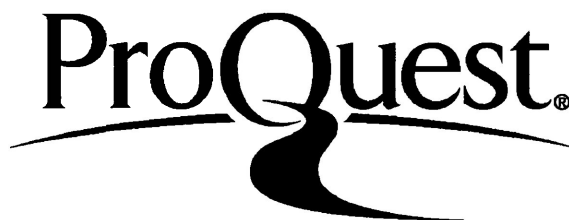Lakehead University

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TO

MY PARENTS

# ABSTRACT

A brief review of the importance and variety of symmetrical and unsymmetrical bisphosphines is given and the possible theoretical and synthetic value of bisphosphines in which one of the phosphorus atoms is included in a phosphole ring is outlined. This is followed by a brief account of the electronic structure of phospholes in the context of the possible aromaticity of such systems and the present conflicting position is discussed. The catalytic activity of phosphole complexes is also briefly reviewed in the context of possible extension to catalytically active systems based upon phosphino-substituted phospholes. Synthetic approaches to bisphosphines in general, and the $^{31}P$ and $^{13}C$ NMR spectral properties of these and some of their metal complexes are discussed in some detail.

In the new work reported in this thesis, a number of synthetically useful and structurally interesting five-membered heterocyclic bisphosphines containing both ring and side-chain P atoms have been synthesized. Their $^{31}P$, $^{1}H$ and $^{13}C$ spectral properties, particularly unusual $^{31}P$ shifts and long-range P - C couplings, have been thoroughly investigated and their structures have been unambiguously established. It has been found that many of the reactions used in these various syntheses are stereospecific or stereoselective.

A new and possibly general route to 4-oxo-2-phospholene oxides

or sulfides from the corresponding 4-methylene compounds is described. This highly unusual reaction involves free-radical catalysed oxidative cleavage of the 4-methylene group by molecular oxygen and the reaction was found to proceed very smoothly when AlBN is used as the radical initiator for the oxidation. A possible mechanism for this oxidation is proposed.

# ACKNOWLEDGMENTS

# ABBREVIATIONS

| | |
|---|---|
| Me | methyl |
| Et | ethyl |
| Pr | propyl |
| n-Bu | n-butyl |
| Ph | phenyl |
| Ar | aryl |
| c | cyclo |
| DBP | 5-phenyl-5$\underline{H}$-dibenzophosphole |
| TPP | 1,2,5-triphenylphosphole |
| PPP | 1,2,3,4,5-pentaphenylphosphole |
| DMP | 1-phenyl-3,4-dimethylphosphole |
| TPPO | 1,2,5-triphenylphosphole 1-oxide |
| AIBN | azobisisobutyronitrile |
| NBS | $\underline{N}$-bromosuccinimide |
| DBU | 1,8-diazabicyclo[5.4.0]undec-7-ene |
| MCPBA | m-chloroperbenzoic acid |
| TMEDA | $N,N,N',N'$-tetramethylethylenediamine |
| THF | tetrahydrofuran |

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# INTRODUCTION

## 1.1    Introductory remarks

Both symmetrical and unsymmetrical bisphosphines
(sometimes called biphosphines or even diphosphines) are very
useful ligands in coordination chemistry and they are also
synthetically useful in phosphorus heterocyclic chemistry.  In co-
ordination chemistry, they act as bidentate ligands when coordina-
ted with metals to give chelate rings of different sizes or bi-
nuclear species depending upon the length of their backbones.  The
ability of the phosphorus atom to accept d-electrons from metals
into its empty, low energy d-orbitals accounts in part for the
formation of the large variety of such complexes known.  Typical
examples of metal complexes of both symmetrical and unsymmetrical
bisphosphines are shown in I(1), II(1), III(2,3), IV(4) and V(5).
Many hundreds, if not thousands, of such structures are now known.



(I)                                     X = I

Et$_2$
P
Au
P
Ph$_2$

Et$_2$
P
P
Ph$_2$

$+$

$X^-$

(II)
$X = I$

Ph$_2$
P
$(CH_2)_n$
$M(CO)_4$
P
$R'$   $R^2$
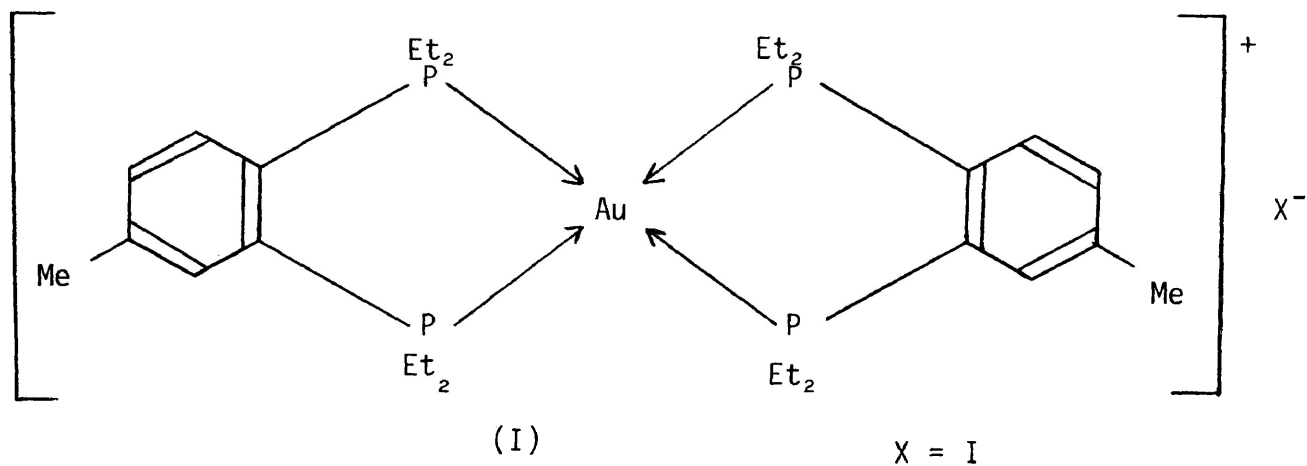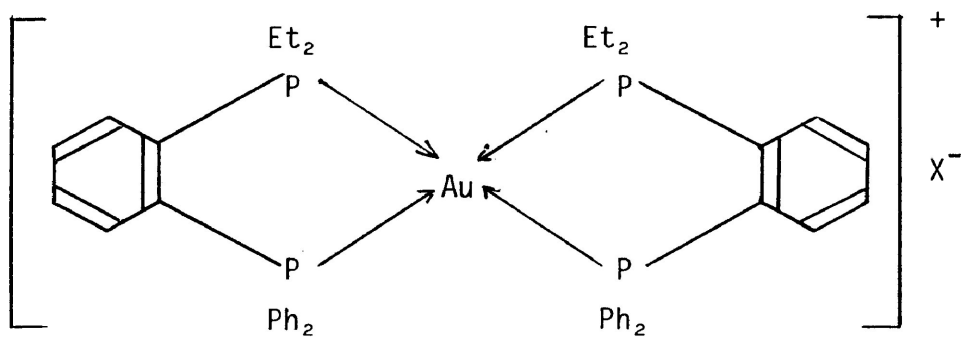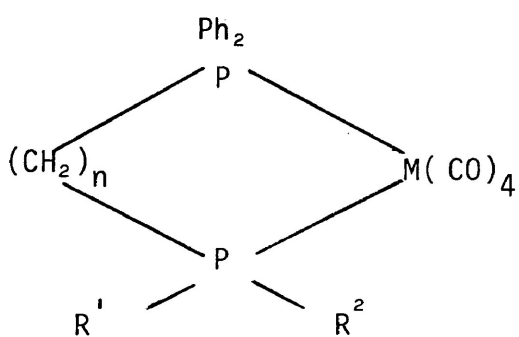
(III)

where,
M = Cr, Mo or W
$R' = R^2 = Ph$
$R' = Ph$, $R^2 = Me$
$R' = Ph$, $R^2 = i\text{-}Pr$
n = 1 or 3

Ph$_2$
P
$(CH_2)_n$
$M(CO)_4$
O
P
Ph$_2$

(IV)

M = Cr, Mo or W
n = 1 or 2

CH$_2$
Ph$_2$   PPh$_2$
X — Pt — Pt — X
Ph$_2$P   PPh$_2$
CH$_2$

X = Cl, Br or I

(V)
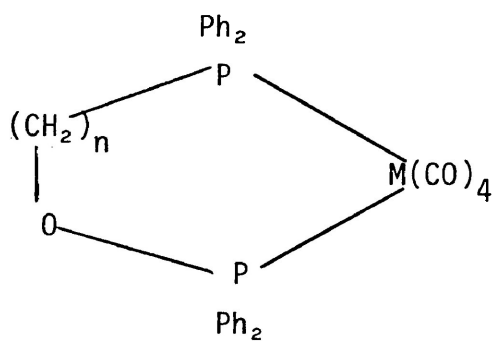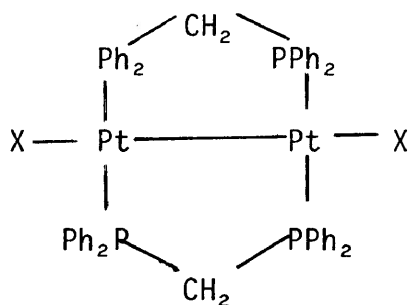
The number and diversity of bisphosphines used to prepare coordina-
tion compounds has increased rapidly during the last twenty-five
years (6). In comparison to tertiary phosphines (such as triphenyl-
phosphine) which act as monodentate ligands, bisphosphines are
more interesting and more useful for several reasons. For example,
a properly designed bisphosphine ligand can simultaneously provide
(a) more control on the coordination number of the metal, the
stereochemistry of the system and the magnetic properties of the
resulting complex; (b) increased electron density at the metal;
and (c) higher optical yields in catalytic asymmetric syntheses (7).

In organophosphorus chemistry, bisphosphines can re-
act with suitable electrophiles such as acetylenic esters to give
(8) a variety of heterocycles containing two phosphorus atoms.
Examples of such reactions are given in the sequences VI→VII and
VIII→IX. Mechanistic details are given elsewhere (8).

$$X \longrightarrow C \equiv C \longrightarrow X$$

$$X = -CO_2Me$$

(VI)                                    (VII)

$$
\text{(VIII)} \quad
\begin{array}{c} \text{PPh}_2 \\[2pt] \text{PPh}_2 \end{array}
\quad + \quad X-C\equiv C-X \quad \longrightarrow \quad
\text{(IX)} \quad X = -CO_2Me
$$
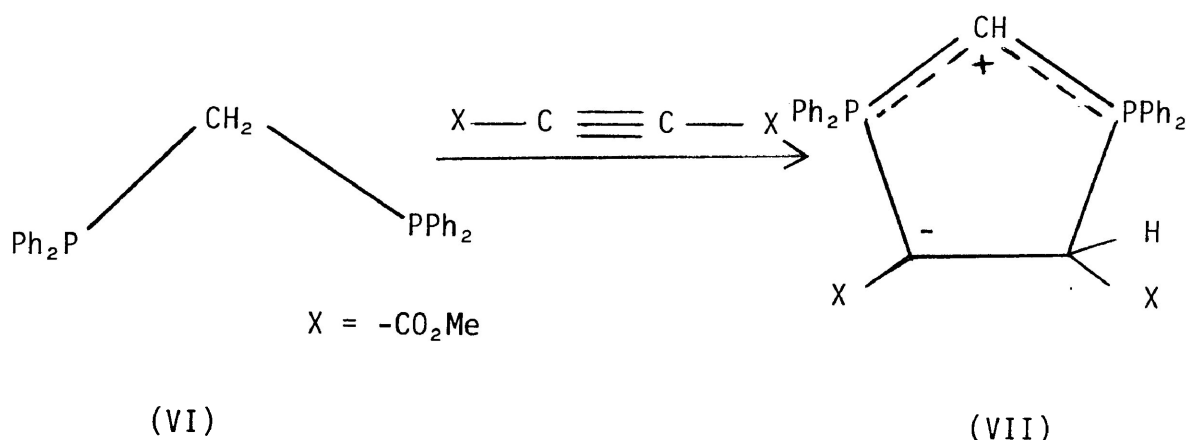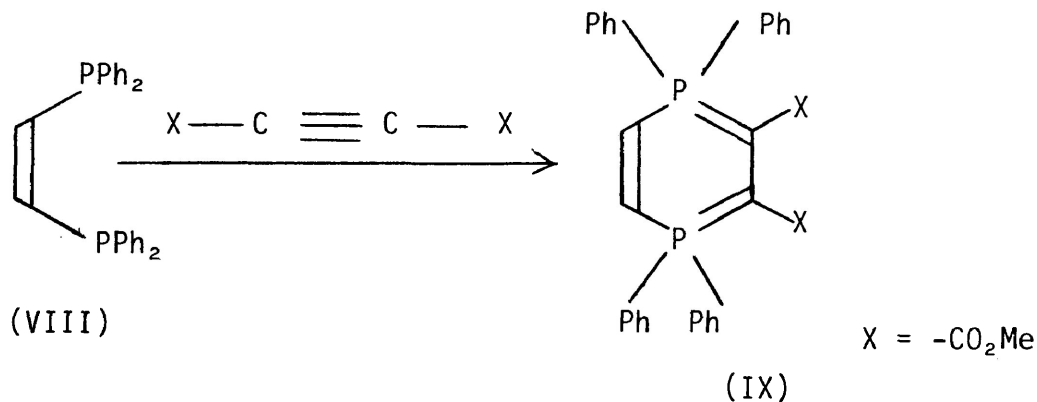
Most of the bisphosphines which were synthesized and studied earlier are symmetrical. However, extensive developments in the fields of syntheses and spectroscopic studies of unsymmetrical bisphosphines have occurred since 1970. Most of the bisphosphines (symmetrical or unsymmetrical) studied so far are open chain compounds although a considerable number of symmetrical cyclic bisphosphine derivatives are now known as are a few unsymmetrical cyclic bisphosphine derivatives (9,10). Some of the unsymmetrical cyclic bisphosphine derivatives which have been synthesized are listed in Table I. Others are listed in references 9 and 10. In these compounds, the two phosphorus atoms are both included in the ring system and, as can be seen, they mostly do not have the potential to be chelating phosphines. More recently, Mathey et al. reported (12) the syntheses of a number of cyclic bisphosphine complexes where the biphosphines have the exo, and therefore chelating, form (XVI) but are otherwise similar to the endo-structures (XV). Although these bisphosphines (XVI) themselves have not been isolated in the free state, their corresponding phosphine sulfide derivatives have been synthesized (12). Bisphos-

TABLE I

Some known unsymmetrical cyclic bisphosphine derivatives
(References are in parentheses)
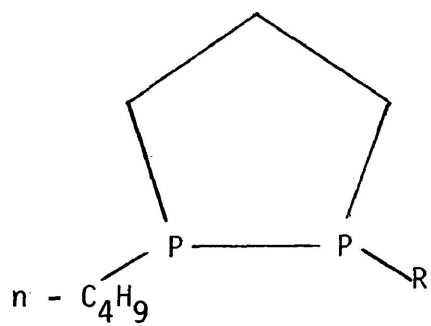
R = H or Li

(X) (9)
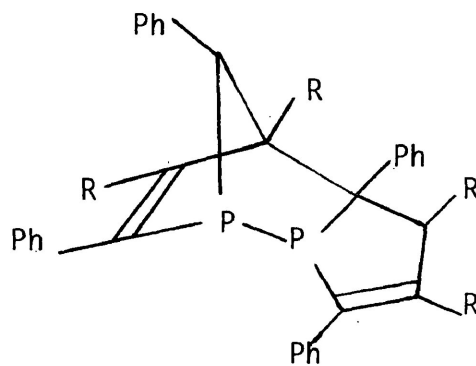
R = H or Ph

(XI) (11)
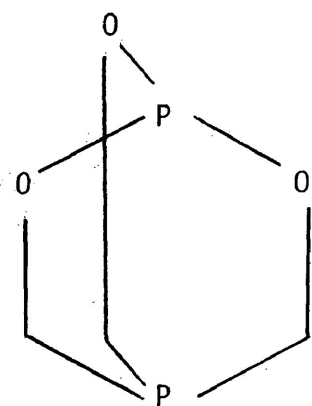
(XII) (9)

(XIII) (9)

(XIV) (9)

(XV) (9)
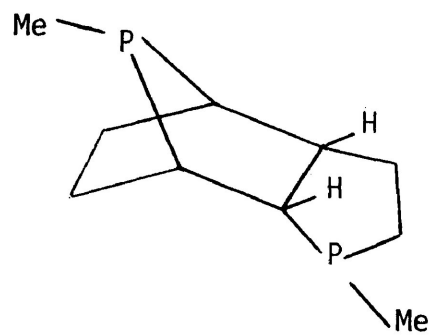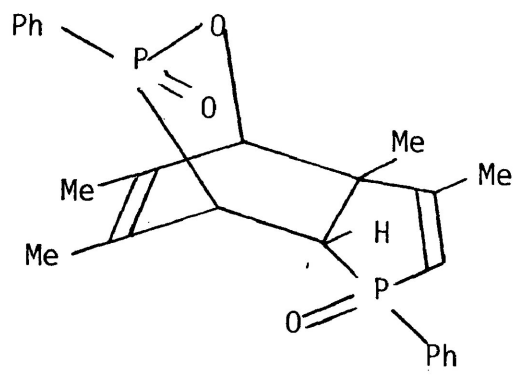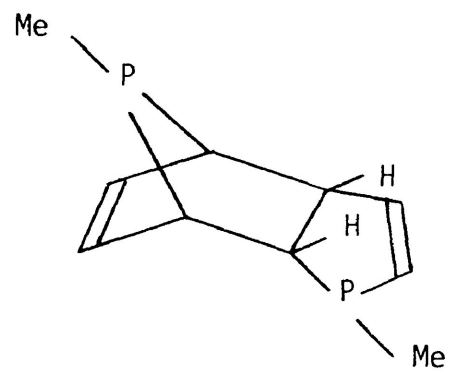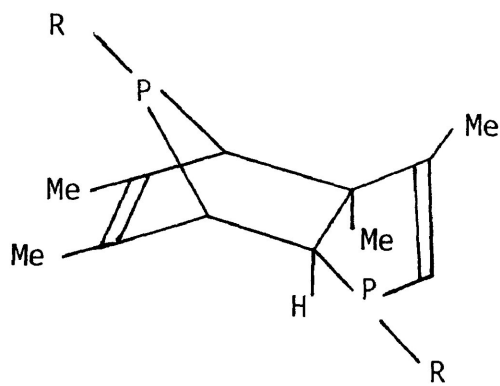
(XVI) (12)

R = Ph, Me or CMe$_3$

phines having one phosphorus atom in the ring, particularly an
unsaturated ring, and the other in a side chain (which would have
chelating potential) have apparently not yet been investigated.

In the work described in this thesis, the author has
prepared some unsymmetrical bisphosphines containing one phosphorus
atom in a ring and the other in a side chain. The ultimate aim
was the preparation of phospholes containing an additional phosphorus
atom in a side chain (e.g. XVII) which would give rise to both a



R
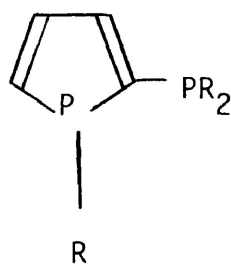
(XVII)

new class of phospholes and a new class of unsymmetrical bisphos-
phines. There were several reasons for undertaking this work.

First, the chemistry of phospholes is very interesting
because of their possible aromaticity. Although many reviews (13-18)
have been published which are concerned directly or indirectly with
the possible pyrrole-type aromatic character in the phosphole ring,
the controversy on this point is not settled yet. Therefore, it
is not surprising that one of the major areas of interest in phosphole
chemistry is still the question of the extent to which the P lone-

pair is available for chemical reactions. The possible lone pair-$\pi$ interaction of phospholes with different substituents has been investigated and it has been observed that apparently the extent of this is greatly influenced by the nature of the substitution pattern. The possible aromaticity of phospholes containing side chain phosphorus would therefore be of some theoretical as well as practical interest.

Second, since the coordination chemistry of simple phospholes (17-20) has been investigated, it would be interesting to compare this with the coordination chemistry of phospholes having an additional side chain phosphorus atom. In such systems, the two phosphorus atoms should have entirely different reactivities.

Third, some transition metal complexes of phosphole derivatives have been found to show interesting homogeneous catalytic properties (21-24) and, again, extension of this work to side chain phosphorus-containing phospholes would be of considerable interest.

Finally, such phosphine substituted phospholes could be useful precursors for complex heterocyclic systems containing two phosphorus atoms and reactions of the type shown in XVIII→XIX, analogous to the open chain bisphosphine reactions already mentioned, can be envisaged. In this context, certain phospholes have already

been shown to be reactive towards dimethyl acetylenedicarboxylate (8).



$$X \text{---} C \equiv C \text{---} X$$

$$X = -CO_2Me$$

(XVIII)                    (XIX)
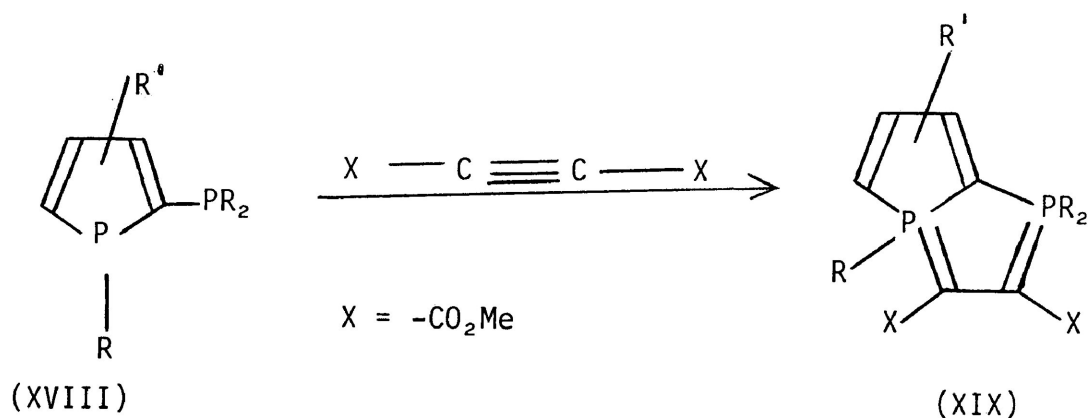
Although the original aim of the present work has not been fully achieved, a number of synthetically useful and structurally interesting bisphosphine derivatives closely related to phosphine-substituted phospholes have been synthesized. Some new mono-phosphine derivatives which are related in some respects to the above bisphosphines have also been synthesized.

A discussion of synthetic approaches to phospholes and phosphole derivatives is not appropriate here since this topic has been thoroughly reviewed elsewhere (9,14,16-18). The possible aromaticity of phospholes and phosphole derivatives has also been discussed in detail elsewhere (13-18). However, in order to give an adequate background to the reasons why the work to be described in the later chapters of this thesis was undertaken, a brief

account of current ideas regarding the electronic structure of phospholes is presented here. The catalytic activity of phosphole complexes will also be reviewed briefly since one of the long term aims of this author's work is a study of phosphine substituted phospholes as ligands in potentially catalytic systems. It is also appropriate to review, though not exhaustively, in this introductory chapter, both the syntheses of symmetrical and unsymmetrical bisphosphines, and the $^{31}$P and $^{13}$C NMR spectral properties of these and some of their metal complexes. As has already been observed, and as will be seen in the new work to be described later, bisphosphines (25), phosphorus heterocycles in general (26), and phosphine substituted phosphorus heterocycles in particular, show very interesting $^{31}$P and $^{13}$C NMR spectral properties.

Brief reviews of these topics now follow.

1.2        The electronic structure of phospholes

Although this topic is still the subject of much debate, a considerable amount of information (some of which leads to conflicting conclusions) regarding the electronic structure of phospholes has been obtained from various chemical, physico-chemical, spectroscopic, and theoretical studies (13-18). Each of these approaches to the problem is briefly reviewed in the following subsections of this chapter.

1.2.1  <u>Information derived from chemical reactions of phosphole</u>
<u>derivatives</u>

Chemical reactions so far studied which could provide

information regarding the electronic structure of phospholes are:

oxidation, quaternization, basicity studies, Diels-Alder type

reactions, metal complex formation, and base catalysed retrocyano-

ethylation reactions.  It should be noted at the outset that the

results obtained from such studies should be treated with caution

since, at the moment of reaction, the phosphole molecule is no

longer an isolated structure, but is rather a structure electroni-

cally perturbed by an attacking species.  However, with this

reservation in mind some evidence regarding possible non-bonding

pair delocalization in phospholes may be obtained from the above

mentioned reaction types.

Phospholes undergo oxidation readily (14,27,28) to

give phosphole oxides.  This is ordinary tertiary phosphine type

behaviour which, superficially, indicates little or no lone pair

delocalization in phospholes.  However, Mortimer <u>et al</u>. (29,30)

found that in certain phosphole oxides, the P=O link is <u>ca.</u>

20 kcal/mole weaker than is normal for ordinary phosphine oxides.

This implies significant lone pair delocalization in simple

phospholes.

In related reactions, numerous examples of the quater-

nization of phospholes are known (16,27) which again apparently

indicate little or no lone pair-diene interaction in phospholes.

On the other hand, it has been found (31) that the rate of

quaternization depends markedly upon the substitution pattern and

is generally slower than the rates for ordinary phosphines. For

example, Allen et al. (32) showed that the fused ring phosphole

5-phenyl-5H-dibenzophosphole (XX,DBP) undergoes quaternization

with phenacyl bromide ($C_6H_5COCH_2Br$) five times more slowly than

does triphenylphosphine. Similarly, the simple phosphole 1-benzyl
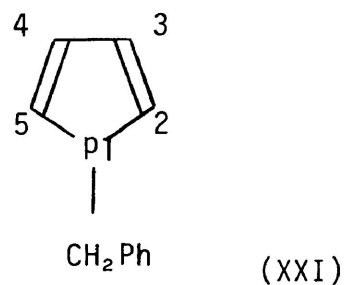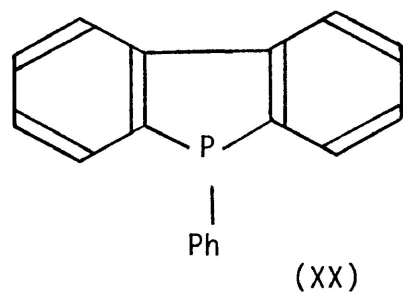


phosphole (XXI) quaternizes (31) very slowly with benzyl bromide

(28% conversion after 11 days). These results clearly indicate

much reduced tertiary phosphine character in the phospholes mentioned.

In the context of the above observations, if the non-

bonding electron pair of the P atom in phospholes undergoes delocali-

zation significantly, then phospholes would have lower basicity than

the corresponding tertiary phosphines. Few basicity studies have

been carried out but Quin et al. (28,33) found that 1-methylphosphole

has the unusually low $pK_a$ value of 0.50 compared with those of

trialkylphosphines ($pK_a \sim 7$), divinylphosphines (calculated $pK_a \sim 5.2$)
(33) and triphenylphosphine ($pK_a = 2.73$) (34). Moreover, when dry
hydrogen chloride is passed through a dry benzene solution of 1,2,5-
triphenylphosphole (TPP), no phosphonium salt of the type $TPPH^+Cl^-$
is formed whereas triphenylphosphine readily forms P-protonated
salts under similar conditions. These results strongly indicate
much reduced lone pair availability in phospholes as compared with
tertiary phosphines.

Considering now reactions at the ring carbon atoms,
1,2,5-triphenylphosphole (TPP) and 1,2,3,4,5-pentaphenylphosphole
(PPP) react only under severe conditions with dimethyl acety-
lenedicarboxylate and with maleic anhydride to give Diels-Alder
type adducts (35,36). The reluctance of these phospholes to
react as dienes might be attributed to possible lone pair-diene
interaction. However, it has been found (37) that less heavily
substituted phospholes like 1-phenylphosphole, 3-methyl-1-phenyl-
phosphole and 3,4-dimethyl-1-phenyl phosphole react fairly readily
with dimethyl acetylenedicarboxylate to give 1:2 adducts. These
adducts, however, are not Diels-Alder type products and arise from
initial reaction of the acetylenic linkage with the phosphorus atom
rather than the ring carbon atoms (8,37). This again suggests
that the lone pair-diene interaction in these phospholes is not
great although it should be remarked that reaction rates are much
slower than for conventional phosphines.

There have been numerous investigations on the co-ordination chemistry of phospholes and these have been reviewed in considerable detail elsewhere (16,18,19). Many phospholes, e.g. 1,2,5-triphenylphosphole (TPP), 5-phenyl-5H-dibenzophosphole (DBP,XX), 1,2,3,4,5-pentaphenylphosphole (PPP) and 1-phenyl-3,4-dimethylphosphole (DMP) form a large variety of complexes (16,18,19) with transition metal halides and carbonyls. Formation of such a large variety of complexes implies that the non-bonding electron pair is readily available for donation to transition metals and hence the degree of delocalization in phospholes may not be significant. However, evidence suggestive of possible delocalization in phosphole systems is also available from studies of phosphole coordination chemistry. For example, TPP does not form (38) complexes with the chlorides of Ag(I), Mn(II), Fe(II), Co(II), Th(IV) and U(IV), although phosphine complexes of these metals are well known. Similarly, 1-methylphosphole (28) and 1-benzylphosphole (39) do not react at all under normal conditions with Ni(II) chloride whereas their 3-phospholene counterparts do so extremely readily (28,40). Furthermore, although TPP, as mentioned above, forms complexes with certain metals, it is very weakly bound to the metal. For example, TPP is displaced from (TPP)TaCl$_5$ by acetonitrile or ether and the complex is easily hydrolysed whereas the corresponding Ph$_3$P complex is stable to moisture and does not react with ether (38).

The foregoing reactions involve interaction of the

phosphole system, usually <u>via</u> the lone pair, with some attacking

species but relevant information may also be obtained from re-

actions in which a free phosphole is regenerated from one of its

reaction products. For example, Farnham and Mislow (41) showed

that cyanoethylphospholium ions (<u>e.g.</u> XXII) undergo base

catalysed retrocyanoethylation to give the corresponding phospholes

very rapidly compared with similar ions derived from other cyclic

(but non-aromatic) or acyclic phosphines. These results are in

agreement with a significant degree of lone pair-diene interaction



(XXII)                                        (XXIII)
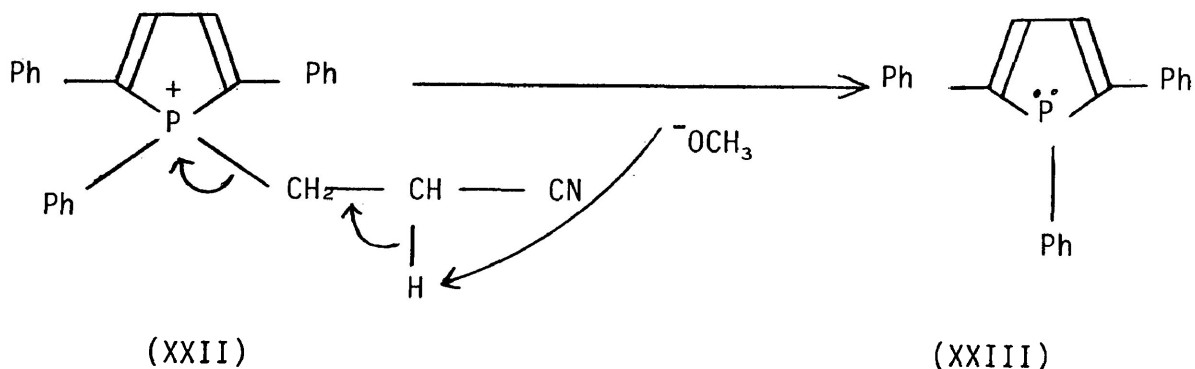
in the resulting phospholes because the cleavage of the exocyclic

P-C bond in the phospholium ion would be accelerated considerably

if the lone pair of electrons in the product is not localized upon

the phosphorus atom.

In concluding this subsection on reactivity studies,

one further point should be made. Thus, while the results briefly

reported here suggest that the phosphole lone pair is less readily available for reaction than is the lone pair of more conventional phosphines, this is not necessarily because of lone-pair delocalization. In particular, it is possible that in some phospholes at least, the lone-pair is not in the highest occupied molecular orbital (HOMO). This would certainly reduce reactivity and would also be consistent with the results of the retrocyanoethylation experiments. Some studies in this area have been made (see next subsection) but relatively little is known about the orbital sequences in phospholes. However, it is worth noting that in the phosphorus analogues of pyridine (e.g. XXIV), the lone pair is normally in the second highest
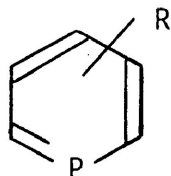


(XXIV)

orbital. This confers much lower lone-pair reactivity and basicity upon the system (42).

1.2.2        Physical and spectroscopic properties of phospholes

Numerous studies on the physical properties of phospholes in the context of electron delocalization have been carried out. Such studies include spectroscopic measurements ($^1$H, $^{31}$P, $^{13}$C, UV, photoelectron and mass spectra), X-ray crystallographic studies,

and dipole moment measurements. Like chemical investigations, some
of these studies give considerable support for possible aromaticity,
some offer inconclusive results and some indicate little if any
aromatic character in phospholes. However, the conclusions drawn from
these results may be more reliable because electronic perturbation
is much less in such studies.

Considering first the NMR studies, it has been
observed in $^1$H NMR spectra of phospholes (16,18) that the ring
protons of phospholes resonate in the aromatic region, the range
being more or less the same as that observed for the corresponding
pyrrole, furan and thiophene nuclei. Moreover, Quin et al. (31)
showed that $^1$H-$^1$H coupling constants for the ring protons of a
variety of phospholes are similar to those of structurally related
thiophenes. These results are consistent with some lone pair de-
localization in the phosphole ring. However, Mathey et al. (43,44)
showed that the nature of the $^1$H spectra and hence, possibly, the
degree of delocalization in phospholes markedly depends upon the
substitution pattern. Thus, it has been found that with substituents
at the 3- and 3,4-positions of the phosphole system, both the ring
proton signals and the methyl proton signals shift to higher field
which suggests that these substituents in the ring decrease aromatic
character and, therefore, inductive and steric effects due to
substituents might be important in determining the degree of delocali-
zation.

A comparison of $^{31}$P NMR data for various phospholes

and classical phosphines (16,18), including phospholenes, reveals that

the phosphorus atom in phospholes resonates at much lower fields

than that in similar acyclic phosphines and phospholenes. This

indicates considerable deshielding of $^{31}$P in phospholes which might

be attributed to decreased electron density at the P atom due to

lone-pair electron delocalization in the phosphole ring. However, by

considering the Letcher-Van Wazer approach (45), Mathey (18) suggested

that such a deshielding may not be due to delocalization, but may be

due to other factors such as a decrease in the intracyclic CPC bond

angles towards 90°, an increase of the exocyclic CPC bond angles,

an increase of the electronegativity of the α-carbon atoms and an

increase in (2p-3d)π conjugation. Some evidence for the effect

of a decrease of the intracyclic CPC bond angle upon deshielding is

that the $^{31}$P shift of 1-phenyl-2,2,3,3-tetramethylphosphetane

(XXV) is δ=8.5 (46).



(XXV)
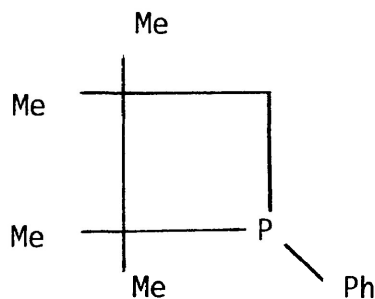
In this case, since no double bond is available for

delocalization, the most obvious explanation for deshielding is the

decrease in the ring CPC bond angle which is ∿82° (47).

Quin et al. (31,48) studied ^{13}C chemical shifts of a number of phospholes and found that all of the ring carbon atoms in all of the phospholes studied have almost identical ^{13}C chemical shifts and this is not normally the case for 2-phospholenes and vinyl-phosphines. This might be an indication of electron delocalization in phospholes. Furthermore, 1-phenylphosphole has been found (49) to have higher $^2J(C_3-P)$ values than the corresponding 1-phenyl-2-phospholene which was taken to reflect a decrease in the average C-C-P-lone pair dihedral angle resulting from a reduced pyramidal inversion barrier (see later discussion) in phospholes. This again is consistent with some delocalization of the lone pair.

Regarding ultraviolet spectroscopic studies of phospholes, Quin et al. (33) noted that the UV spectrum of 1-methylphosphole resembles that of N-methylpyrrole. It has also been observed that 1-methylphosphole and a number of other phospholes give transitions at ∿286 nm. These results were considered to be indicative of lone pair delocalization. However, Raciszewski et al. (50) showed that the UV spectra of a number of heavily substituted phospholes are similar to one another but are totally different from that of 1,2,3,4,5-pentaphenylpyrrole which suggests reduced aromatic character in the phospholes. Moreover, from the UV spectra of phospholes like 1-n-butylphosphole and its 3-methyl and 3,4-dimethyl derivatives, other

workers (51) suggested that the UV spectra are more consistent with a

butadienoid system. It is clear that little can be deduced from

UV measurements but more information regarding bonding might be obtain-

able from photoelectron spectroscopy.


A comparative study of the photoelectron spectra of

phospholes (52) and those of their saturated analogues reveals that

there is no appreciable change in the ionization potential of the lone

pair electrons (n) when passing from a phosphole structure to a

pholsphoholane structure. From this, Schäfer et al. (52) concluded

that there is no noticeable interaction between the lone pair and the

diene system. However, in considering these results in the light of

a theoretical investigation of the problem, the same group (53) reversed

their views and stated that the n orbital and the highest $\pi$ orbital

in some phospholes are degenerate, that the n orbital energy is not a

suitable means to examine possible aromatic character and that phospholes

are aromatic but pyramidal species with $n/\pi^*$ conjugation and $P-C/\pi^*$ hyper-

conjugation. Clearly, photoelectron spectra must be interpreted with great

care.

Perhaps the best physical evidence for significant de-

localization in phospholes comes from pyramidal inversion barrier

studies. If the lone pair in phospholes interacts significantly

with the $\pi$-system, the inversion barrier about the phosphorus atom

should be lower than that observed for the corresponding phospholanes.

Mislow et al. (54) have, in fact, measured the inversion barriers of

a number of dissymmetric phospholes using NMR coalescence techniques
and they found that phospholes have much lower inversion barriers than
the corresponding phospholanes. For example, the inversion barrier
$(\Delta G_{25}^{\ddagger})$ for 1-isopropyl-2-methyl-5-phenylphosphole is about 16 kcal/mole
compared with the expected value of over 36 kcal/mole for a non-
aromatic model. This indicates a significant lone pair-diene inter-
action in a pyramidal ground state and considerable aromatic character
in the planar transition state of phospholes. There are few other
possible explanations for these NMR observations.

X-ray crystallographic studies have given conflicting
evidence regarding the possible aromatic character of phospholes.
For example, in 1-benzylphosphole (55), the ring P-C bonds have been
found to be shorter than the exocyclic P-C bond and in fact shorter
than the sum of the normal P-C single bond radii. This was considered
to be an indication of some type of lone pair-diene interaction. On
the other hand, in 1,2,5-triphenylphosphole (56), the ring P-C bonds
and the exocyclic P-C bond are of identical length and these are in
turn the same length as P-C bonds in simple tertiary phosphines.
This again suggests that the electronic structure of phospholes is
very sensitive to the substitution pattern although it must be
remembered that a molecule in a crystal lattice is subject to strong
lattice forces and cannot be regarded as a free molecule.

Several other studies relating to the aromaticity

problem including dipole moment measurements, Faraday Effect investigations, ESR studies of phosphole radical anions, and mass spectra have been made and these have been adequately reviewed elsewhere (16,18). The only statement necessary here is that these studies have yielded little in the way of positive information.

### 1.2.3 Theoretical studies

Nine theoretical studies on the electronic structure of phospholes have been reported so far and most of these have been reviewed in considerable detail elsewhere (16,18). Although most of these theoretical studies are reasonably informative and generally favour some degree of aromatic character in the system, some disagreement is still apparent. A brief digest of these theoretical treatments, roughly in chronological order, follows.

The first of these studies was HMO calculations by Brown (57) who estimated that the conjugation energy in the phosphole system is similar to that of the pyrrole system. However, Brown's calculations have only historical interest now since he used an oversimplified formulation and no reliable parameterization for phosphorus was available at that time.

In a much later study, Mislow et al. (27,58) calculated the pyramidal inversion barriers of a number of phospholes using the Pople CNDO/2 approach and found that the results are in excellent

agreement with the inversion barriers measured by the NMR coalescence technique (54). This supports the earlier suggestion (54) that there is a significant lone pair-diene interaction in the pyramidal ground state and this interaction increases in the planar transition state.

In a related study Schweig et al. (59) obtained considerable information regarding conformational effects, orbital energies and orbital sequences of phospholes (and arsoles) using the extended CNDO/2 method. From these results, this group concluded that phospholes (and arsoles) are pyramidal molecules in the ground state with little n-π interaction but, as will be seen shortly, this group reinterpreted much of this information in a later study.

At about the same time as the above study, Mathey et al. (60) calculated the effect of conformational changes upon delocalization in the phosphole ring using the LCAO-MO-CNDO/2 method and concluded that the inversion barriers are lowered by delocalization in the planar transition state, that this delocalization is of the (3p-2p)π type, that (2p-3d)π conjugation plays an important role in the pyramidal state and that the substituents on the phosphorus atom have some effect.

Using a somewhat different approach, Palmer et al. (61) reported a little later a very detailed treatment of the phosphole system using the LCGO procedure. On the basis of such studies, they

concluded that the phosphole system is non-aromatic and non-planar,
that the phosphole system has no resonance energy, that the previously
published ^{1}H NMR data are more closely related to those of cyclo-
pentadiene than those of pyrrole, furan and thiophene, and that the
low inversion barriers in phospholes are due to a rather vaguely
discussed valence force field effect which does not require delocali-
zation in the planar transition state. These results are indeed in
serious contrast to those of Mathey et al. (60) and Mislow et al.
(27,58), although there is some apparent agreement with Schweig's
earlier results (59).

On the other hand, in a later paper, Schweig's group
(53) reinvestigated the electronic structure of phospholes using
the extended CNDO/S and MINDO/2 procedures. In contrast to their
earlier report (59), they stated that despite their pyramidal ground
state structures, phospholes are aromatic and the aromaticity is
stabilized by the interaction between the ring and the phosphorus
atom through $n/\pi^*$ conjugation and $P-C/\pi^*$ hyperconjugation.

In yet another study, Epiotis et al. (62) carried out
a one-electron MO analysis of phospholes (and arsoles) using the
explicit SCF-MO-CNDO/2 approach. The results of this study are again
in good agreement with some degree of aromaticity in phospholes
(and arsoles).

Finally, two "ab initio" calculations have been reported; one by Palmer (63) and another by von Niessen (64). Since these calculations were made on the basis of the most reliable possible geometry of the system in the ground state, they might be the most reliable ones. The results of these calculations also indicate significant aromatic character in the phosphole system.

Careful evaluation of the foregoing discussion on various chemical, physico-chemical, spectroscopic and theoretical investigations regarding the electronic structure of phospholes, reveals that the picture is still rather confused. Only the studies concerning inversion barriers and certain of the theoretical approaches offer reasonable "proof" of something like aromatic character in phospholes. However, from the discussion, one thing that is clear is that the lone pair of phospholes is less readily available for chemical reactions than those in simple phosphines. In conclusion, it might be very cautiously stated that the phosphole system appears to possess some aromatic character resulting from $(3p-2p)\pi$ delocalization in its pyramidal ground state, that this aromatic character is probably greater in the planar transition state, and that the electronic structure is highly sensitive to the substitution pattern.

## 1.3      <u>Metal-phosphole complexes as homogeneous hydrogenation catalysts</u>

As mentioned earlier, one of the ultimate objectives of
the work described in this thesis is a study of the potential homo-
geneous catalytic activity of metal complexes of phosphine-substituted
phospholes since complexes of some simpler phospholes have been found
to exhibit such activity. A brief review of this facet of phosphole
chemistry is therefore included here.

Catalytic hydrogenations in heterogeneous systems using
metals, metal oxides and some salts have been known for a long time
but the wide application of catalytic hydrogenation in homogeneous
systems using metal ions and complexes has become significant only
during the last twenty years even though the first such reaction
was reported as long ago as 1938 by Calvin (65,66). Various types
of metal complex, particularly transition metal complexes, have been
used as catalysts in homogeneous hydrogenations and organophosphorus-
metal complexes are particularly useful in this area. This aspect
of the chemistry of phosphine-metal complexes has been discussed in
considerable detail elsewhere (67).

On the other hand, the behaviour of phosphole-metal
complexes as catalysts in homogeneous catalytic reactions has received
relatively little attention even though the unusual nature of the
phosphorus atom in such systems is of considerable interest. However,

a few reports in this area have appeared (21-24) and some very active phosphole-containing homogeneous hydrogenation catalysts have been prepared.

In an early account, Hughes et al. (21) reported the catalytic activities of several Rh-complexes of TPP and DBP (XX). Thus, it was found that the TPP complex $RhHCl_2(TPP)_2$ catalyzes the hydrogenation of 1-hexene at a rate which is comparable with that at which $RhH(CO)(PPh_3)_3$ catalyzes the same reaction. Furthermore, the Rh(I) complexes, $RhCl(DBP)_3$ and $Rh_2Cl_2(DBP)_4$ also catalyze 1-hexene hydrogenation with the former complex being about twice as active as the latter. Similarly, mixtures such as $Rh_2Cl_2(C_2H_4)/DBP$ and $Rh_2Cl_2(C_2H_4)_4/TPP$ catalyze 1-hexene hydrogenation where the DBP system is again twice as reactive as the TPP system. Other related phosphole complexes of Rh(I) and phosphole-derivative complexes such as $RhCl(CO)(TPP)_2$, $RhHCl(TPPO)(TPP)$, and $Rh_2Cl_2(TPPO)_2$ [TPPO= 1,2,5-triphenylphosphole 1-oxide] show no catalytic activity at 20°, although the last complex shows a slight activity at higher temperatures (60°C).

The complexes $RhCl(TPP)_3$ and $RhCl(DBP)_3$, which are heterocyclic analogues of the well known Wilkinson's catalyst $[RhCl(PPh_3)_3]$, have much lower catalytic activity than $RhCl(PPh_3)_3$ and the reason for this was thought to be due to the interaction of the phosphorus lone pair with the π-system in the free phosphole

which would reduce the electron density on the Rh atom.  Steric effects might also have some influence upon such a decrease in activity.

Two years later, the same group (22) reported RhH(DBP)$_4$ as an extremely active catalyst for the hydrogenation of quite a large number of unsaturated compounds.  Thus, it has been found that RhH(DBP)$_4$ catalyzes 1-hexene hydrogenation at a rate which is 7-9 times higher than that of Wilkinson's catalyst, RhCl(PPh$_3$)$_3$, or the structurally more closely related catalyst RhH(PPh$_3$)$_4$.  Another advantage of this catalyst is that it is not susceptible to poisoning in solution due to traces of oxygen (or peroxide) as is, for example, the excellent catalyst, RuHCl(PPh$_3$)$_3$ (68).  Later in the same year the same group reported (23) another excellent and closely related DBP-metal complex catalyst, RhH(DBP)$_3$.  The rate of 1-hexene hydrogenation in the presence of this catalyst was found to be ∿10% faster than that observed with RhH(DBP)$_4$ under similar conditions.  Therefore, RhH(DBP)$_3$ may be considered as the best catalyst among the phosphole-metal complex catalysts so far obtained.

The skeleton of the ligand DBP (XX) appears to be very useful in such catalytic systems since, in the hydrogenation of α-acetamidocinnamic acid in the presence of the chiral rhodium complex catalysts XXVI  (containing the Ph$_2$P-unit) and XXVII  (containing this DBP skeleton) reported by Kegan et al. (24), XXVI  gave N-acetylphenyl-alanine with the R absolute configuration whereas, with XXVII, the S

(XXVI),  $PR_2$ ═══  $P(Ar)_2$

(XXVII),  $PR_2$ ═══
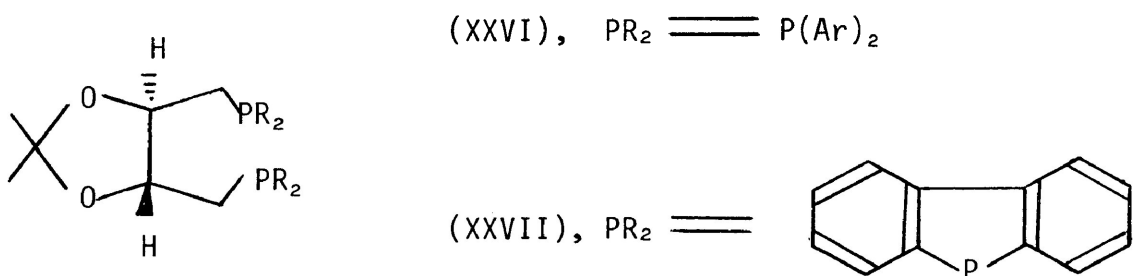
configuration was obtained.  No explanations for the configurational differences in the products formed by these two catalysts were advanced in this paper (24).


Clearly, homogeneous catalytic systems containing phosphole derivatives have much potential.


1.4        Synthesis of bisphosphines


Since one of the more immediate aims of the present work was the synthesis of phospholes (and 2-phospholenes) containing an additional phosphorus atom in the side chain (e.g. XVII) which would give rise to a new class of bisphosphines, other approaches to the synthesis of bisphosphines in general should be briefly discussed.  A complete review of the topic is, however, beyond the scope of this thesis and only a short account of the more recent and more extensively used methods is presented here.

Numerous reports of methods for the synthesis of bis-
phosphines (and also polyphosphines) are scattered throughout the
literature. The various methods reported could be organized for
discussion in several different ways but the approach based upon
reaction type gives, in the opinion of this author, the best over-
view of the subject and this approach is therefore used in the
following subsections. The syntheses of both symmetrical and un-
symmetrical bisphosphines are discussed together, but the nature
of this thesis dictates that emphasis be given to the synthesis of
unsymmetrical bisphosphines. It should be noted that unsymmetrical
bisphosphines may be unsymmetrical by virtue of having different
substituents upon the phosphorus atoms or by virtue of the unsym-
metrical nature of the chain linking the two phosphorus atoms. These
two types will be treated together in the following discussion.

## 1.4.1 From halogenophosphines

Both symmetrical and unsymmetrical bisphosphines and
their derivatives can be prepared by the reaction of halogenophosphines
with other organophosphorus compounds such as simple phosphines,
alkali metal phosphides, alkali metal derivatives of alkyl or
hydroxyalkyl substituted phosphines, and Grignard reagents.

Halogenophosphines react with simple phosphines (69-73)
or alkali metal phosphides (74-76) to give bisphosphines (Sequences 1

and 2) in which the two phosphorus atoms are directly bonded to each other. No further discussion of the synthesis of this type of phosphine will be given here since the work described in later chapters mainly concerns bisphosphines with phosphorus atoms separated by a carbon chain and it is this aspect of bisphosphine synthesis which therefore requires review.

$$R_2PH + R_2'PX \longrightarrow R_2P-PR_2' + HX \tag{1}$$

$$R_2PLi + R_2'PX \longrightarrow R_2P-PR_2' + LiX \tag{2}$$
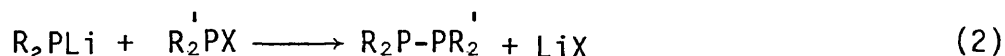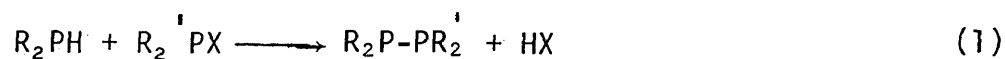
(R=R' for symmetrical bisphosphines).

Bisphosphines with two phosphorus atoms separated by one or more other atoms have been prepared by the reaction of halogenophosphines with alkali metal substituted alkylphosphines. For example, Grim et al. (2) reported the synthesis of a number of unsymmetrical bisphosphines containing the $-PCH_2P-$ unit (Sequence 3).

$$Ph_2PCH_2Li + R'R^2PCl \longrightarrow Ph_2PCH_2PR'R^2 + LiCl \tag{3}$$
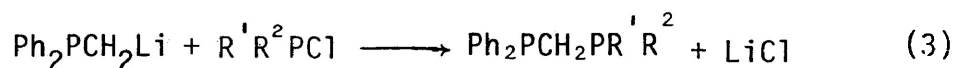
($R'=R^2=$Me or i-Pr and $R'=$Ph, $R^2=$Me, Et or i-Pr).

This method is very suitable for the synthesis of bisphosphines of the type shown in sequence 3 but the drawback of

the method is that the metallation of the starting material $Ph_2PMe$ with n-BuLi (Sequence 4) is incomplete and the removal of unreacted $Ph_2PMe$ is very difficult.

$$Ph_2PCH_3 + n\text{-}BuLi \longrightarrow Ph_2PCH_2Li + nC_4H_{10} \qquad (4)$$
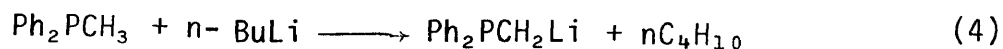
In related reactions, bisphosphines containing aromatic backbones have also been prepared from halogenophosphines and alkali metal substituted phosphines. Thus, Hart (77) synthesized o-phenyl-enebisdiethylphosphine (XXVIII) and o-diethylphosphinophenyldiphenyl-phosphine (XXIX) in the following manner (Sequence 5).



(XXVIII)

(XXIX)

(5)
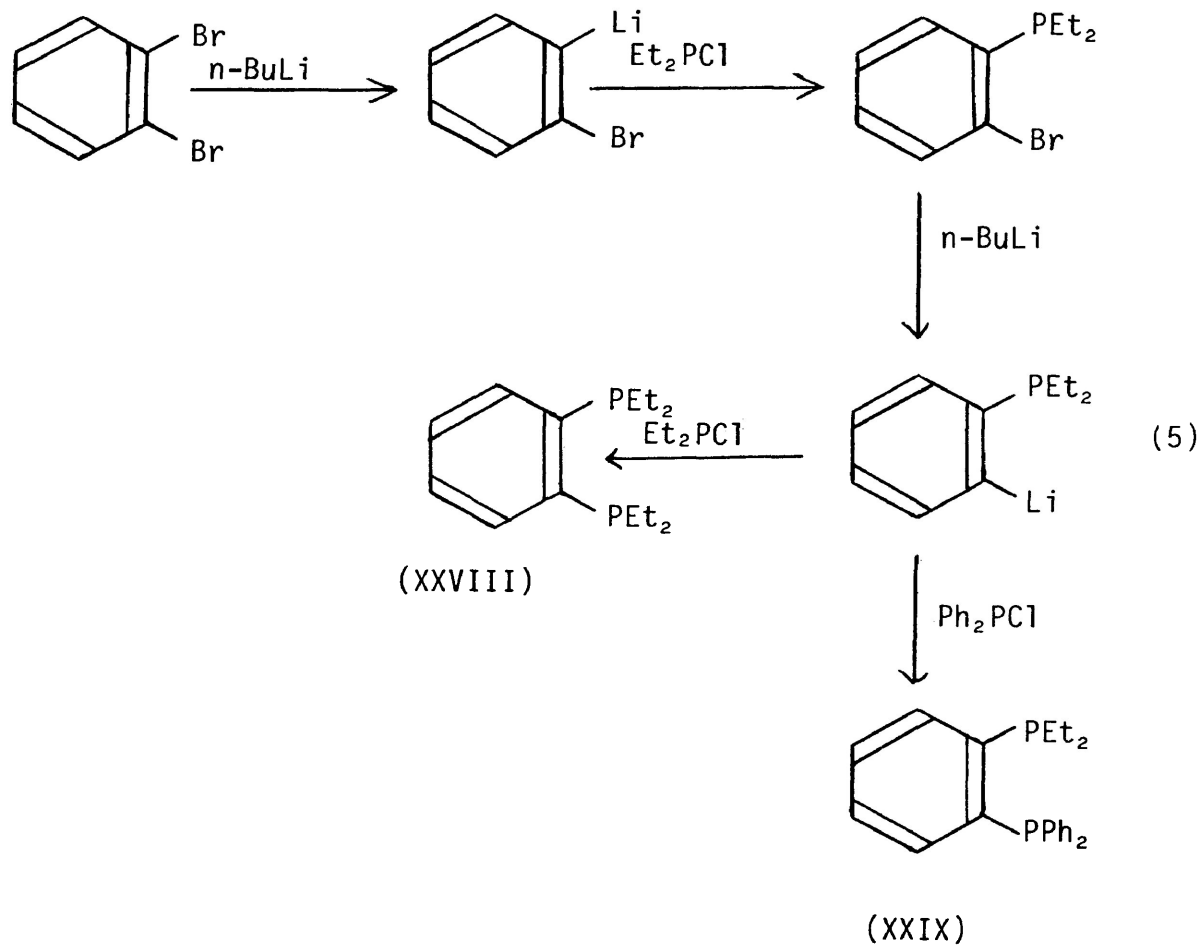
This approach has been extended to unsymmetrical bis-phosphines containing oxygen atoms in their backbones which have been synthesized by Grim et al. (4) by the reaction of halogeno-phosphines with alkali metal phosphino-alkoxide derivatives (Sequence 6).

$$Ph_2PCH_2CH_2OLi + R_2PCl \longrightarrow Ph_2PCH_2CH_2OPR_2 + LiCl \qquad (6)$$
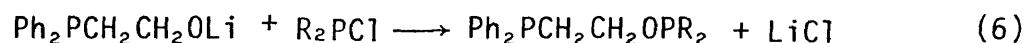
(R=Ph or n-Bu).

The starting material, $Ph_2PCH_2CH_2OLi$, was prepared in the following manner (Sequence 7).

$$Ph_2PCl + 2Li \longrightarrow Ph_2PLi \xrightarrow{\quad CH_2\text{---}CH_2 \ \diagdown O \diagup \quad} Ph_2PCH_2CH_2OLi \qquad (7)$$
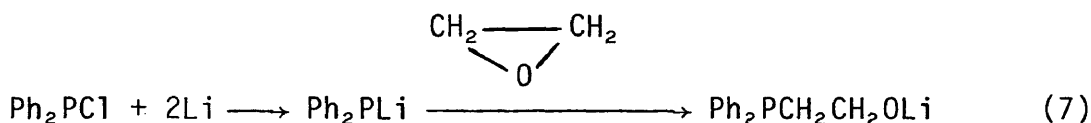
The corresponding bisphosphine containing the $-CH_2O-$ backbone was synthesized in a related but modified manner (Sequence 8).

$$Ph_2PLi \xrightarrow{\ CH_2O\ } Ph_2PCH_2OLi \xrightarrow{\ HCl\ }$$

$$Ph_2PCH_2OH \xrightarrow{\ Ph_2POCH_3\ } Ph_2PCH_2OPPh_2 \qquad (8)$$
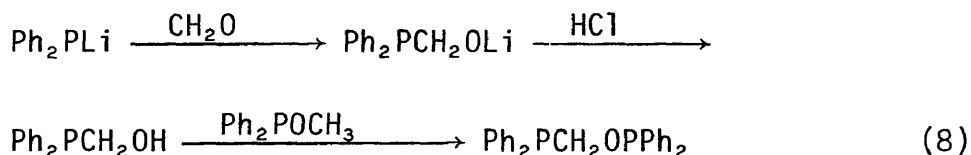
Unsymmetrical bisphosphine derivatives with two phosphorus atoms in different oxidation states have also been prepared in related reactions by Grim and his co-workers. Thus, $Ph_2P(O)CHRPPh_2$ (R=H, Me or n-Pr) have been prepared (78) by the reaction of $Ph_2PCl$

with various alkali metal phosphine derivatives (Sequence 9) with
the metal

$$Ph_2P(O)CHRLi + Ph_2PCl \longrightarrow Ph_2P(O)CHRPPh_2 + LiCl \qquad (9)$$
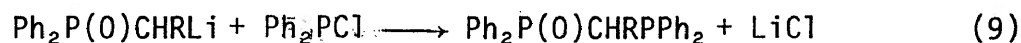
derivatives $Ph_2P(O)CHRLi$ being prepared from a phosphine oxide and
a metal alkyl (Sequence 10).

$$Ph_3P(O) + RCH_2Li \longrightarrow Ph_2P(O)CHRLi + C_6H_6 \qquad (10)$$
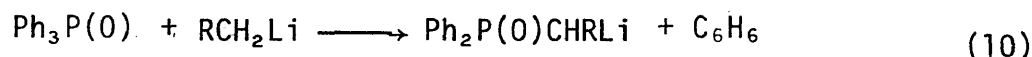
The corresponding sulfides, $Ph_2P(S)CH_2PR'R^2$ ($R'$=Ph,
$R^2$=Et, Me, i-Pr or $NEt_2$ and $R'$=$R^2$=Ph or i-Pr), have been synthesized
(79) in a similar manner (Sequence 11) but it should be noted that,

$$Ph_2P(S)CH_2Li + R'R^2PCl \longrightarrow Ph_2P(S)CH_2PR'R^2 + LiCl \qquad (11)$$
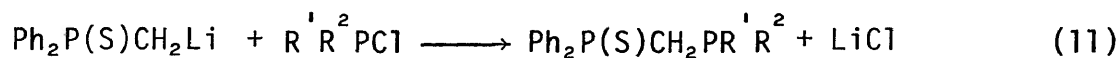
in these sulfide syntheses, sulfur may be transferred from the less
basic diphenylphosphino group to the more basic dialkylphosphino
group on heating (Sequence 12).

$$Ph_2P(S)CH_2PR'R^2 \xrightarrow{\Delta} Ph_2PCH_2P(S)R'R^2 \qquad (12)$$
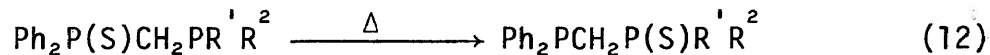
Turning now to the Grignard approach, some bisphosphines
have been prepared by the reaction of halogenophosphines with phos-
phorus-containing Grignard reagents. Thus, Grim et al. (80) synthesized

the unsymmetrical bisphosphines $Ph_2P(CH_2)_nPMe_2$ (n = 2 or 3) in the manner shown in sequence 13.

$$Ph_2P(CH_2)_nMgCl + Me_2PCl \longrightarrow Ph_2P(CH_2)_nPMe_2 \qquad (13)$$
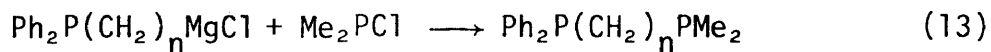
Similarly, the symmetrical bisphosphines $R_2PC_6H_4PR_2$ (R=NEt$_2$ or OH) have been synthesized by other workers (81) using aromatic Grignard reagents (Sequences 14 and 15) while in another study,

$$\underline{p}\text{-}BrMgC_6H_4MgBr + (Et_2N)_2PCl \longrightarrow \underline{p}\text{-}(Et_2N)_2PC_6H_4P(Et_2N)_2 \qquad (14)$$

$$\underline{p}\text{-}(Et_2N)_2PC_6H_4P(Et_2N)_2 \xrightarrow{\text{aq. HCl}} \underline{p}\text{-}(HO)_2PC_6H_4P(OH)_2 \qquad (15)$$
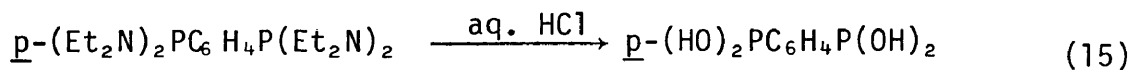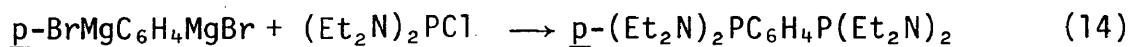
Davis <u>et al</u>. (82) also prepared the unsymmetrical bisphosphines (XXX) and (XXXI) containing an aromatic backbone using appropriate Grignard reagents and halogenophosphines.
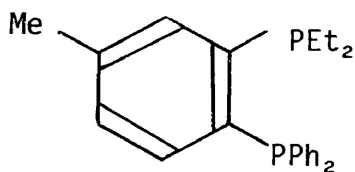


(XXX)
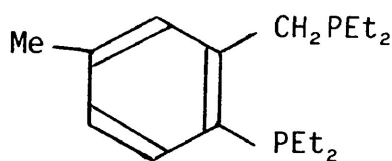


(XXXI)

More recently, Burt <u>et</u> <u>al</u>. (83) reported a convenient method of synthesis of the symmetrical bisphosphines, $R_2PCH_2CH_2PR_2$ (R=Me, Et or $c-C_6H_{11}$) by the reaction of 1,2-bis(dichlorophosphino)-ethane with appropriate Grignard reagents (Scheme 16). The 1,2-bis-(dichlorophosphino) ethane was prepared by heating yellow phosphorus, phosphorus trichloride and ethylene in a stainless steel autoclave and

$$Cl_2PCH_2CH_2PCl_2 \xrightarrow{\quad RMgX \quad} R_2PCH_2CH_2PR_2 \qquad (16)$$

(R=Me, Et or $c-C_6H_{11}$)
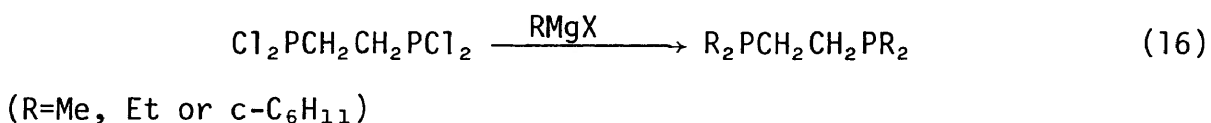
it is worth noting that this valuable reagent is now commercially available (Strem Chemicals, Inc.).

## 1.4.2    From organic dihalides

$\alpha,\omega$-Organic dihalides with a variety of carbon chain lengths undergo exchange reactions with alkali metal phosphides (scheme 18) to give both symmetrical and unsymmetrical bisphosphines. The principal advantage of this method is that a bisphosphine with the desired number of $-CH_2-$ units in between the two phosphorus atoms can be prepared by choosing an appropriate dihalide, many of which are readily available. The metal phosphide required for these reactions can be prepared by the reaction of an alkali metal with either a simple phosphine or a halogenophosphine (Scheme 17).

$$R_2PX + M \longrightarrow R_2PM \longleftarrow M + R_3P \qquad (17)$$
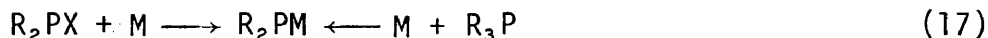
(X=Cl or Br and M=Li or Na)

$$R_2PM + X(CH_2)_nX \longrightarrow R_2P(CH_2)_nPR_2 \qquad (18)$$
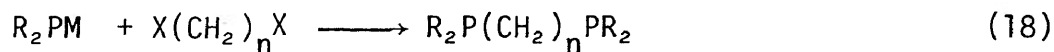
(n=1,2,3 etc.)

A large variety of symmetrical bisphosphines, e.g. $Me_2PCH_2CH_2PMe_2$ (84), $Ph_2P(CH_2)_nPPh_2$ (n=1-6) (74,85,86), and $(\underline{o}\text{-tolyl})_2P(CH_2)_nP(\underline{o}\text{-tolyl})_2$ (n=1-4, 6 or 8) (87) have been synthesized by this method.

Grim et al. (80) synthesized a number of unsymmetrical bisphosphines, $Ph_2P(CH_2)_nPR'R^2$ (n=2 or 3; R'=Ph, $R^2$= Me, Et, i-Pr; $R'=R^2=Me$), using dihalides but in a slightly different manner. They first isolated the intermediate monohalogenated alkylphosphines which were then treated separately with suitable alkali metal phosphides to give unsymmetrical bisphosphines (Sequences 19 and 20).

$$Ph_2PNa + Cl(CH_2)_nCl \longrightarrow Ph_2P(CH_2)_nCl \qquad (19)$$

$$Ph_2P(CH_2)_nCl + R'R^2PLi \longrightarrow Ph_2P(CH_2)_nPR'R^2 \qquad (20)$$
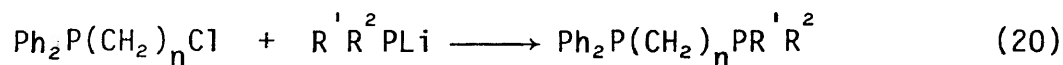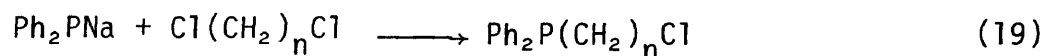
The bisphosphine $PhP(H)(CH_2)_3PPh_2$ has also been synthesized (88) in a similar manner using NaP(H)Ph.

In closely related reactions, some cyclic bisphosphines

(e.g. XXXII, XXXIII) have been synthesized (89,90) by the reaction of $\alpha,\omega$-dihalogenoalkanes with dialkali metal diphosphides (Sequences 21 and 22).

$$PhP(Li)(CH_2)_3P(Li)Ph + BrCH_2CH_2Br \longrightarrow$$



$$+ 2LiBr + CH_2 = CH_2 \qquad (21)$$

XXXII



$$R(K)P-P(K)R + Cl(CH_2)_4Cl \longrightarrow \qquad + KCl \qquad (22)$$
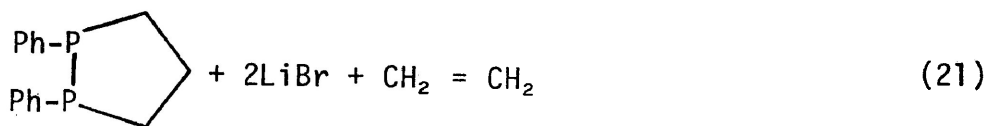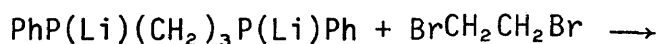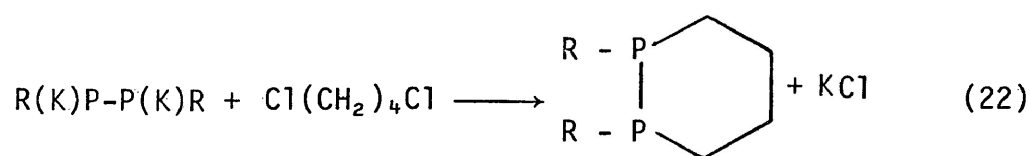
XXXIII

Briggs et al. have very recently reported a new method of using $\alpha,\omega$-dihalogenoalkanes for the synthesis of unsymmetrical bisphosphines. In this method, the dihalogenoalkane is treated directly with the phosphine to give a quaternary salt which is hydrolysed and the resulting bisphosphine dioxide is reduced by trichlorosilane (Sequence 23).

$$Br(CH_2)_nBr \xrightarrow{Ph_3P} [Br(CH_2)_nPPh_3]Br \xrightarrow{RPh_2P}$$

$$[RPh_2P(CH_2)_nPPh_3]Br_2 \xrightarrow{NaOH/H_2O} RPhP(O)(CH_2)_nP(O)Ph_2$$

$$\xrightarrow{HSiCl_3} RPhP(CH_2)_nPPh_2 \qquad (23)$$
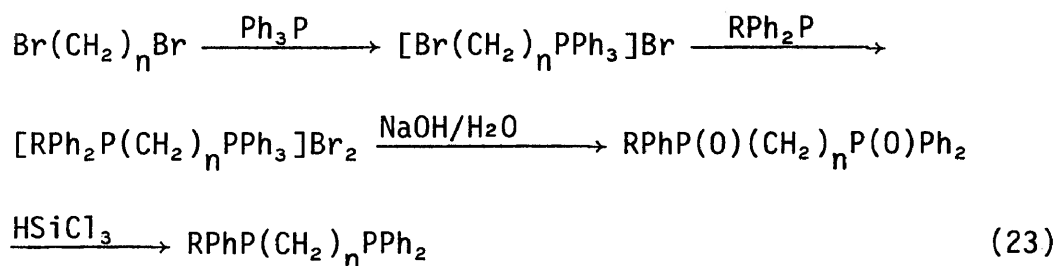
$(n=3-6, R=Me, Et \text{ or } c-C_6H_{11})$

Briggs et al. (91) also suggested the above method could be general for the synthesis of unsymmetrical bisphosphines of the types $RPhP(CH_2)_nPPh_2$, $R_2'P(CH_2)_nPPh_2$, $R'R^2P(CH_2)_nPPh_2$, and other similar combinations (R=alkyl, R'=alkyl or aryl and $n \geqslant 3$) by varying the nature of the monophosphines. It was not clear from this publication why this method is not convenient for the cases where n=1 or 2.

## 1.4.3        From vinylphosphines

Most of the known bisphosphines contain two carbon atoms in their linking backbones and vinylphosphines are the most useful reagents for the preparation of such bisphosphines. Vinylphosphines undergo addition reactions with alkali metal phosphides or certain simple phosphines under various reaction conditions to give a large variety of both symmetrical and unsymmetrical bisphosphines.

For example, Keiter (92) reported the synthesis of the well known bisphosphine $Ph_2PCH_2CH_2PPh_2$ (also known as Diphos) by the addition of $Ph_2PLi$ to diphenylvinylphosphine followed by hydrolysis (Sequence 24).

$$Ph_2PLi + Ph_2PCH=CH_2 \longrightarrow Ph_2PCHLiCH_2PPh_2$$

$$\xrightarrow{\text{H}_2\text{O}} Ph_2PCH_2CH_2PPh_2 + LiOH \qquad (24)$$
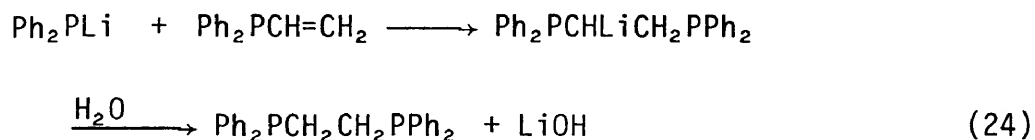
Later, Grim et al. (93) used basically the same method for the preparation of a number of unsymmetrical bisphosphines of the general form $Ph_2PCH_2CH_2PRPh$ (R=Me, Et, n-Pr, i-Pr, s-Bu, i-Bu or n-amyl).

In a similar approach, King et al. also reported the synthesis of a large number of bisphosphines containing $-PCH_2CH_2P-$ units by the addition of phosphorus-hydrogen bonds to the carbon-carbon double bonds of vinylphosphines (94,95), vinylphosphonates (96-99), vinylphosphine sulfides (99,100) and various other vinylphosphine derivatives in the presence of a base such as phenyllithium or potassium tert-butoxide ($KOBu^t$). As an example of this method, $Ph_2PCH_2CH_2PPh_2$ was readily synthesized (94) by the reaction of diphenylphosphine with diphenylvinylphosphine in the presence of phenyllithium. The reaction is thought (93) to proceed in the following manner (Sequence 25).

$$PhLi \ + \ Ph_2PH \longrightarrow Ph_2PLi \xrightarrow{\quad Ph_2PCH=CH_2 \quad}$$

$$Ph_2PCHLiCH_2PPh_2 \xrightarrow{\quad Ph_2PH \quad} Ph_2PCH_2CH_2PPh_2 \ + \ Ph_2PLi \qquad (25)$$
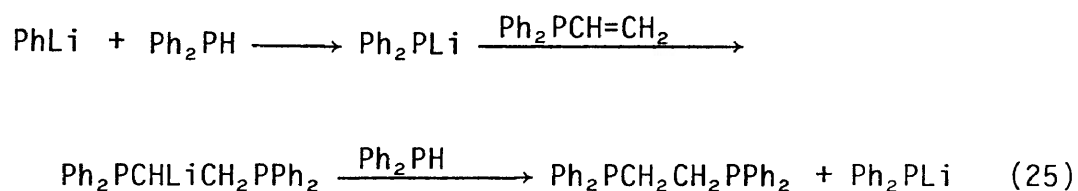
The versatility of this approach is demonstrated by the synthesis of $Ph_2PCH_2CH_2P(H)Ph$ (95) by the addition of $PhPH_2$ to $CH_2=CHPPh_2$ in the presence of $KOBu^t$. However, in this particular case, the yield is very low because the bisphosphine further reacts

with an excess of the vinylphosphine to give the tritertiary phosphine (XXXIV).

$$PhP \begin{cases} CH_2CH_2PPh_2 \\ CH_2CH_2PPh_2 \end{cases}$$
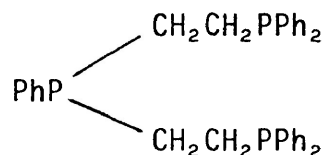
(XXXIV)

The bulky ditertiary bisphosphine $(Me_3C \cdot CH_2)_2PCH_2CH_2P-(CH_2 \cdot CMe_3)_2$ has also been synthesized (101) by the addition of $(Me_3C \cdot CH_2)_2PH$ to $(Me_3C \cdot CH_2)_2PCH=CH_2$ in the presence of $KOBu^t$ while similar addition of $PhPH_2$ to $(Me_3C \cdot CH_2)_2PCH=CH_2$ gave (101) the tertiary-secondary bisphosphine $(Me_3C \cdot CH_2)_2PCH_2CH_2P(H)Ph$ .

When vinylphosphonates are used, the base catalysed addition is followed by reduction of the intermediate with $LiAlH_4$. For example, King et al. (99) prepared the secondary-primary phosphines $RP(H)CH_2CH_2PH_2$ (R=Ph, $n-C_6H_{13}$ or $Me_3C \cdot CH_2$) by the addition of $RPH_2$ to $CH_2 = CHP(O)(OR')_2$ (R' = $-CHMe_2$) in the presence of $KOBu^t$ followed by $LiAlH_4$ reduction. In a similar manner, the tertiary-primary bisphosphine $Ph_2PCH_2CH_2PH_2$ has been prepared (98) by the reaction of $Ph_2PH$ with $CH_2 = CHP(O)(OEt)_2$. In related syntheses, various bisphosphine monosulfides have been prepared (99,101) by the addition of secondary phosphines to vinylphosphine sulfides in the presence of $KOBu^t$. The resulting monosulfides were

easily reduced to the corresponding bisphosphines by LiAlH₄.

In these reactions, the various steps involved in the base catalysed addition of the phosphorus-hydrogen bonds to vinylphosphorus compounds may be represented as follows (Sequence 26).

$$R'R^2PH \: + \: base \: \longrightarrow \: base-H^+ + R'R^2P^- \: \xrightarrow{\quad CH_2=CHPR^3R^4 \quad}$$

$$R'R^2PCH_2\bar{C}HPR^3R^4 \: \xrightarrow{\quad base-H^+ \quad} \: R'R^2PCH_2CH_2PR^3R^4$$

$$+ \: base \tag{26}$$
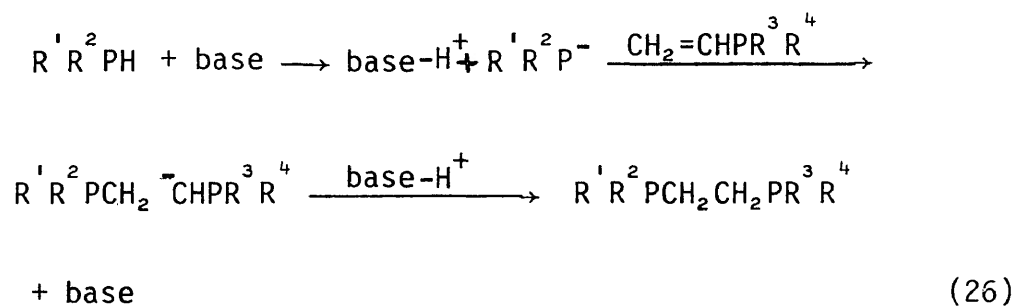
It should also be made clear here that the base catalysed addition of a primary phosphine to a diphenylvinylphosphine containing a tricoordinated phosphorus atom gives a 1:2 adduct (e.g. XXXIV) as the major product whereas the similar addition of a primary phosphine to vinylphosphine derivatives containing tetra coordinated phosphorus (such as in vinylphosphonates or vinylphosphine sulfides) gives the desired 1:1 adduct as the major product. Considerable control over product distribution can therefore be exercised. Thus, the yield of $Ph_2PCH_2CH_2P(H)Ph$ obtained from the reaction of $PhPH_2$ and $CH_2=CHPPh_2$ is only 20% (95) whereas the same compound has been obtained in 57% yield (98,102) from the reaction of $PhPH_2$ and $CH_2=CHP(O)Ph(OCHMe_2)$. The mechanisms of such additions have been discussed adequately elsewhere (99).

In addition to phenyllithium and potassium tert-butoxide,
another base which may be used as a catalyst in the addition of the
P-H bond of primary and secondary phosphines to vinylphosphines is
potassium hydride. This base is found to be particularly useful in
the synthesis of bisphosphines containing terminal dialkylamino
groups where such terminal groups may undergo further exchange
reactions readily with groups derived from the basic catalysts men-
tioned before. The replacement of the terminal amino groups by
hydrogen atoms was never, in fact, observed in any of the reactions
carried out in the presence of potassium hydride. For example,
King et al. (103) carried out the addition of both primary and
secondary phosphines to vinylaminophosphines in the presence of
potassium hydride (Sequences 27, 28 and 29) and very clean additions
were observed.

$$R_2PH + CH_2=CHP[NMe_2]_2 \xrightarrow{KH} R_2PCH_2CH_2P[NMe_2]_2 \qquad (27)$$

$$RPH_2 + CH_2=CHP[NMe_2]_2 \xrightarrow{KH} RP(H)CH_2CH_2P[NMe_2]_2 \qquad (28)$$

$$R_2PH + (CH_2=CH)_2PNEt_2 \xrightarrow{KH} R_2PCH_2CH_2P(CH=CH_2)NEt_2 \qquad (29)$$
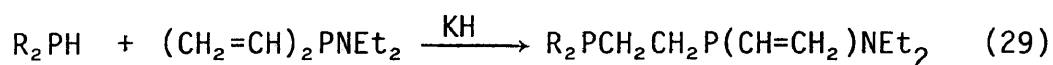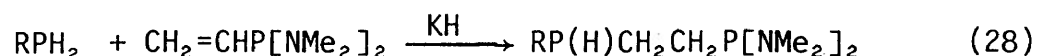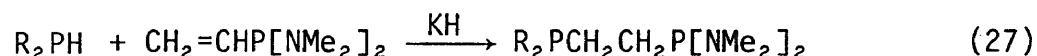
R=(Me or Ph)

The addition of phosphorus-hydrogen bonds to carbon-
carbon double bonds of vinylphosphines has also been carried out under

free radical conditions. However, the chief disadvantage of such additions is that the formation of 1:1 adducts $RPHCH_2CH_2PR_2'$ can not be controlled so as to avoid the formation of appreciable quantities of the 1:2 adducts $RP(CH_2CH_2PR_2')_2$. Using this approach, Issleib et al. (104) synthesized some unsymmetrical bisphosphines (Sequence 30) using azobisisobutyronitrile (AIBN) as the catalyst.

$$R_2'PC=CH_2 + R^2PH_2 \xrightarrow{\text{AIBN}} R_2'PCH_2CH_2PHR^2 \qquad (30)$$
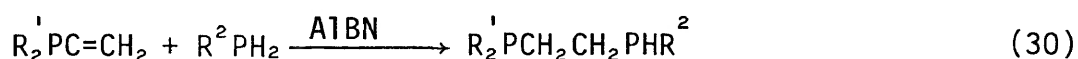
$(R'$=n-Pr, n-Bu, or Ph; $R^2$=n-hexyl or Ph)

In related studies, Manojlovic-Muir et al. (105,106) synthesized some unsymmetrical bisphosphines containing electron withdrawing groups on one phosphorus atom. For example, $Ph_2PCH_2CH_2P-(CF_3)_2$ was obtained (105) by the addition of $(CF_3)_2PH$ to $Ph_2PCH=CH_2$ where the reaction was initiated photochemically while the bis-phosphine $Ph_2PCH_2CH_2P(C_6F_5)_2$ was obtained (106) by the addition of $(C_6F_5)_2PH$ to $Ph_2PCH=CH_2$ in the presence of a radical initiator.

DuBois et al. (107) also reported the synthesis of a number of bisphosphines in good yields by free radical catalysed addition of phosphorus-hydrogen bonds to vinylphosphines. In this study, the bisphosphines $Ph_2PCH_2CH_2PPh_2$ and $Ph_2PCH_2CH_2P(O)[OCH(CH_3)_2]Ph$ were prepared in the presence of AIBN.

## 1.4.4     From phosphole derivatives

The methods so far discussed give mostly open chain bisphosphines. However, cyclic bisphosphines and their derivatives (oxides or sulfides), in which two phosphorus atoms are in different rings (e.g. XXXV), have recently become well known. This type of bisphosphine derivative is the subject of much current attention because of the interesting structural and spectrosopic properties of such systems and it should be noted here that although this subsection concerns mainly the synthesis of oxides and sulfides related to XXXV, these systems are readily reduced by silane derivatives to the corresponding phosphines.



(X = lone pair, O or S)
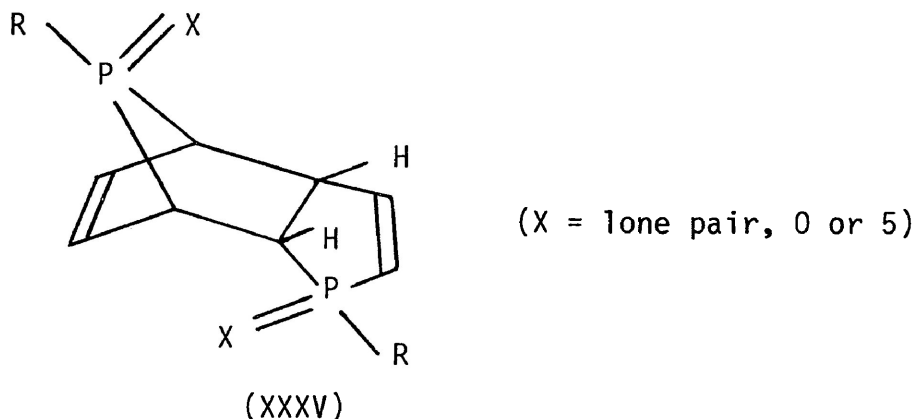
(XXXV)

Such bisphosphine oxides or sulfides may be obtained (9) by spontaneous dimerization of simple phosphole oxides or sulfides (e.g. Sequences XXXVI→XXXVIII, and XXXIX→XLI).

(XXXVI)          (XXXVII)          (XXXVIII)



(XXXIX)          (XL)          (XLI)
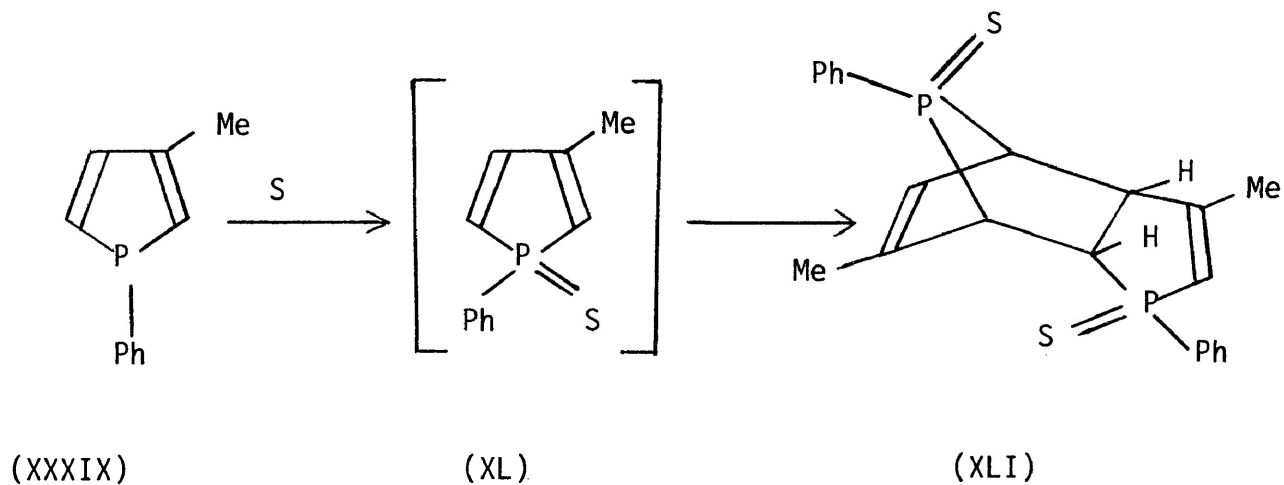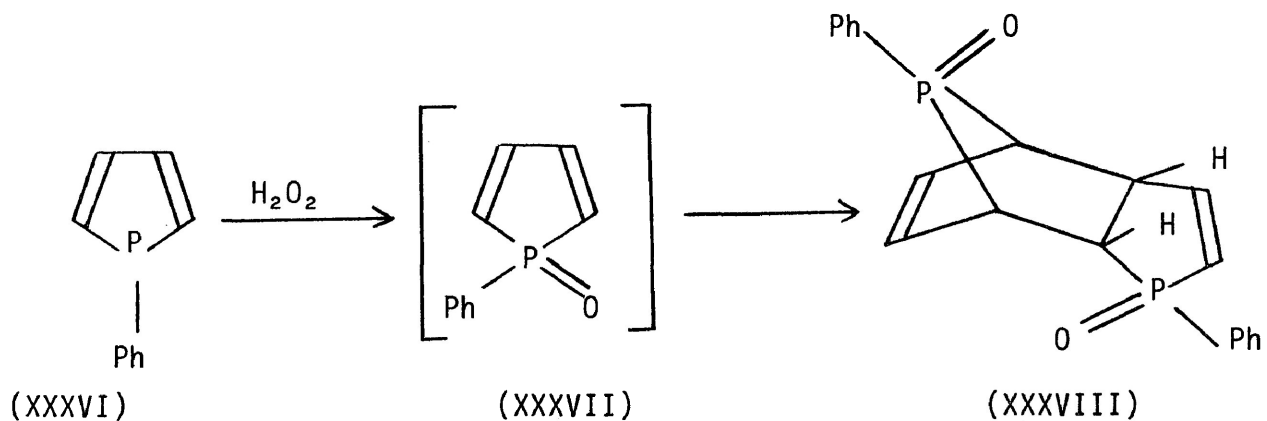
Very recently, Quin et al. (108) reported the synthesis of a number of phosphole oxide and sulfide dimers of this general type (Table II). The phosphole oxide dimers were obtained by dehydrobromination of 3,4-dibromophospholane oxides (109) where phosphole oxides were formed as transient intermediates and undergo dimerization readily. Phosphole sulfide dimers may also be obtained from the corresponding dimeric oxides by treatment

## TABLE II

### Some dimeric phosphole oxides and sulfides
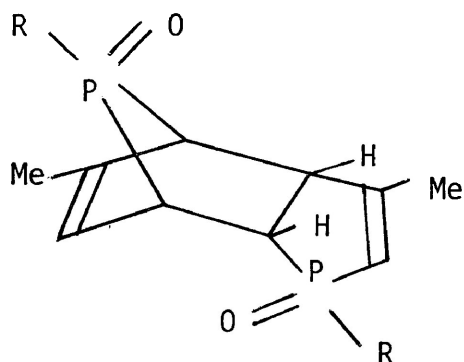


(XLII)   (R = Me   or Ph)
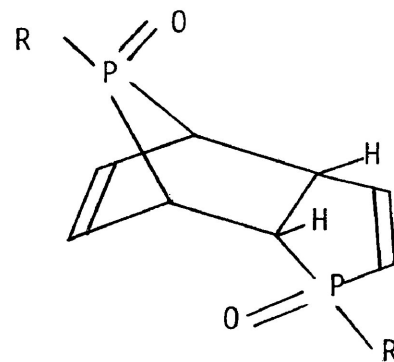


(XLIII)   (R = Me or Ph)
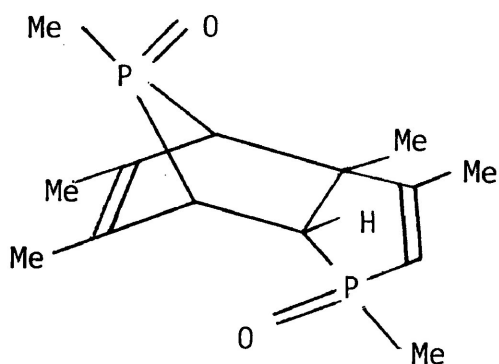


(XLIV)
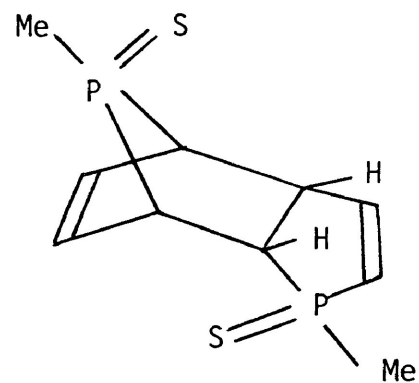


(XLV)
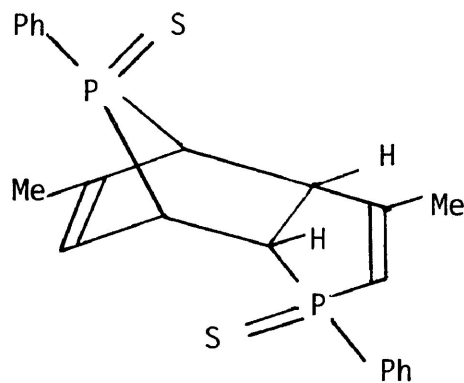


(XLVI)

with $P_2S_5$ (110).

Dimeric phosphole oxides or sulfides containing completely saturated ring skeletons have been prepared (108) by the hydrogenation of the unsaturated analogues over $PtO_2$ (Sequence XLVII→XLVIII).



(XLVII)  (X = O or S)                    (XLVIII) (X = O or S)
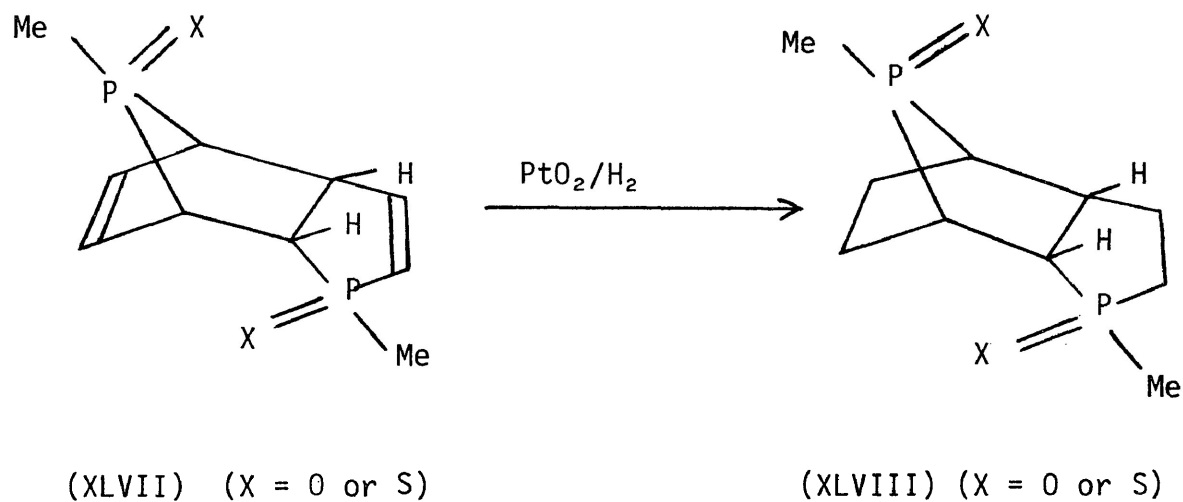
Saturated dimeric phosphole oxides having a cage type of structure have been obtained (108,111) by intramolecular [2+2] photocyclo addition reactions (Sequence XLIX→L). These too are of spectroscopic interest because the symmetry properties in certain instances dictate that the $^{13}C$ spectra are non first order.

(XLIX)



(L)

where, R    R'

Ph    H
Me    H
Me    Me
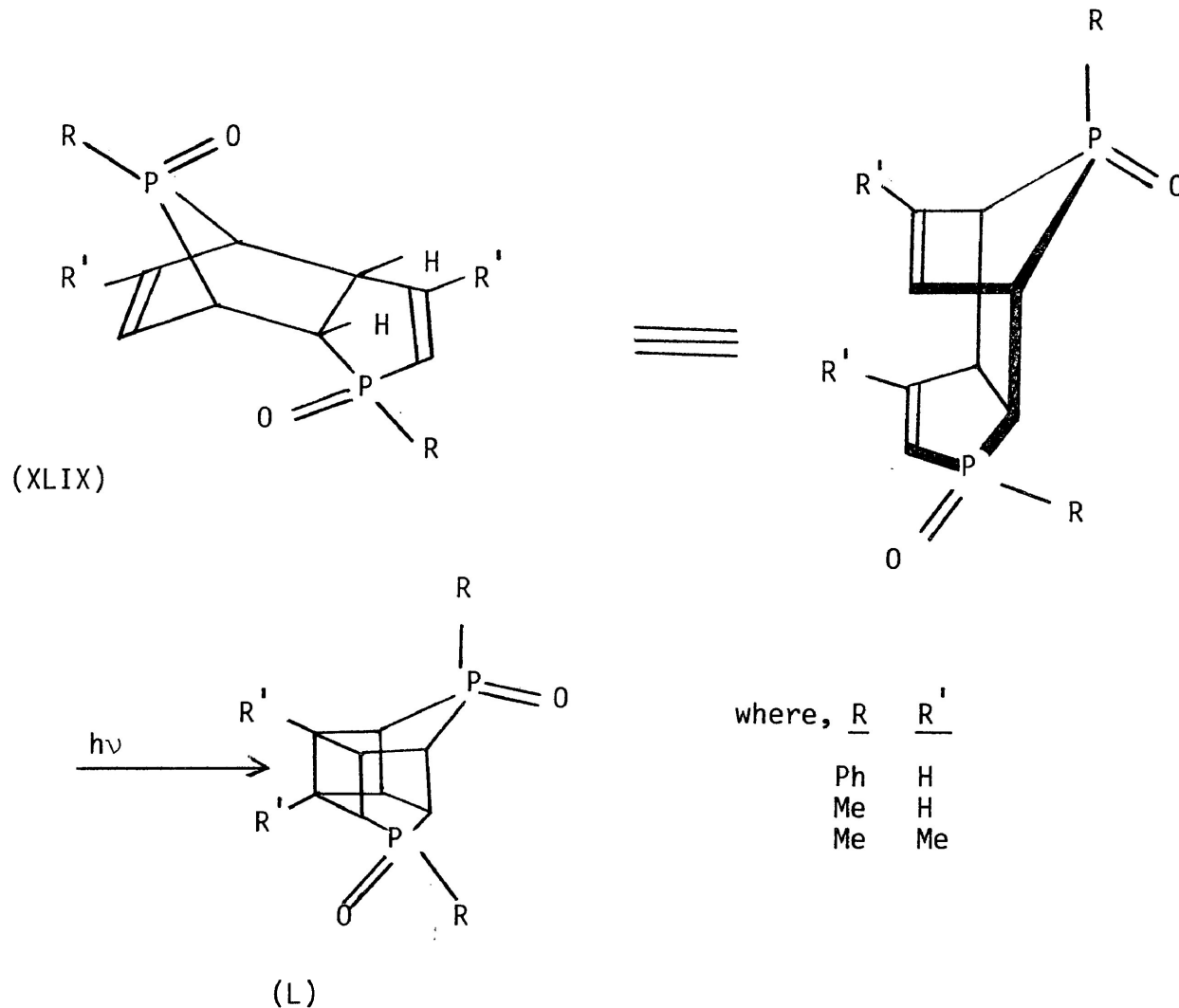
As mentioned a little earlier, many of these dimeric phosphole oxide and sulfide systems may be reduced to the corresponding phosphines using silane derivatives. In this connection, Quin et al. (112) made the first report of the synthesis of stable cyclic bisphosphines of the phosphole dimer type by the deoxygenation of phosphole oxide dimers with $HSiCl_3$ in the presence of pyridine

(Sequence LI→LII). These reactions are fairly general and will not be discussed further here.



(LI)                                                    (LII)
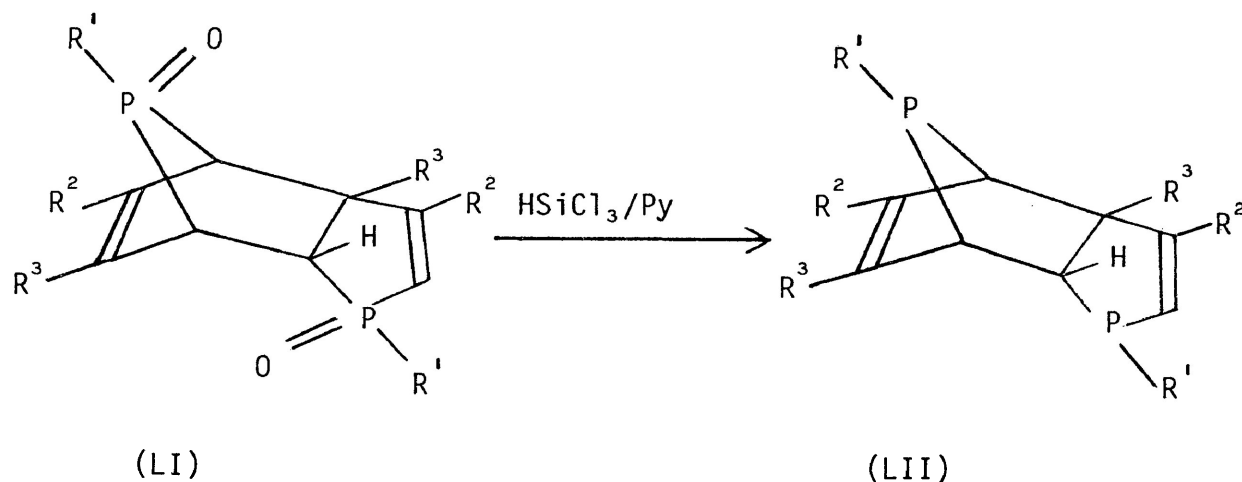
| where, | $R^1$ | $R^2$ | $R^3$ |
|--------|-------|-------|-------|
|        | Ph    | H     | H     |
|        | Ph    | Me    | H     |
|        | Me    | H     | H     |
|        | Me    | Me    | H     |
|        | Me    | Me    | Me    |

As mentioned in section 1.1, most of the phosphole dimers (and their oxide and sulfide derivatives) so far studied have endo configurations. However, Mathey et al. (12) recently reported the syntheses of phosphole sulfide dimers with the exo configuration (Sequence LIII→LV). The process involves the formation of stable phosphole dimer metal complexes (LIV) in which the phosphole dimers are also in the exo form. Subsequent sulfurization

of these complexes yields the <u>exo</u> dimeric phosphole sulfides (LV).



(LIII)　　　　　　　　(LIV)

(LV)
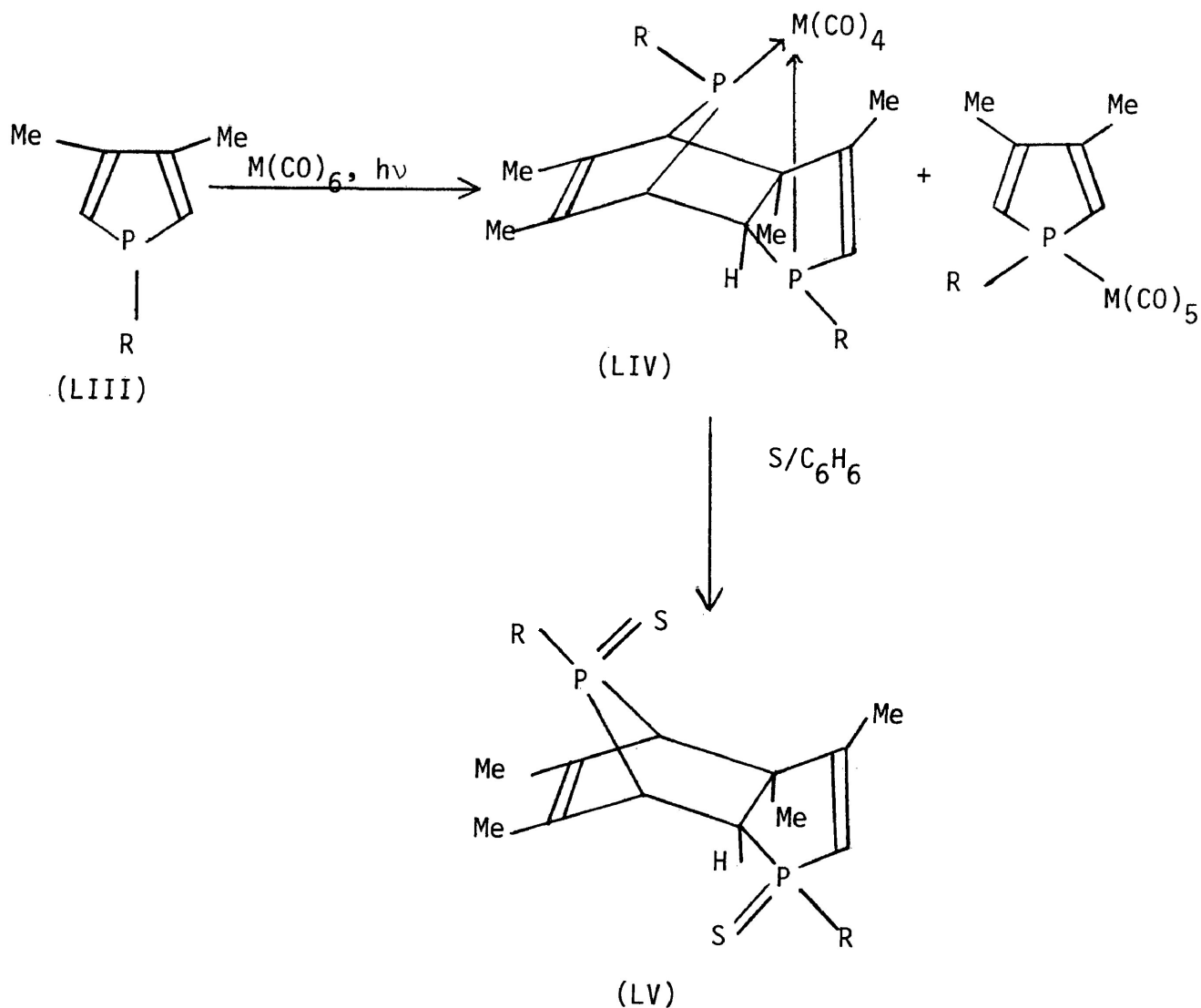
Quin <u>et al</u>. (113) also reported the <u>syn</u> to <u>anti</u> isomerization of some phosphole dimers. They found that in the presence of an alcohol, some <u>syn</u> phosphole dimers undergo inversion of configura-

tion at the bridging phosphorus atom to produce the corresponding <u>anti</u>
isomers (Sequence LII→LVI). A possible mechanism has been proposed (113).



$$(LII) \qquad\qquad (LVI)$$

$$(R^1 = Me, \ R^2 = H \text{ or } Me, \text{ and } R^3 = H)$$
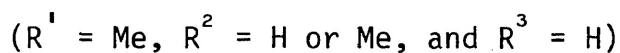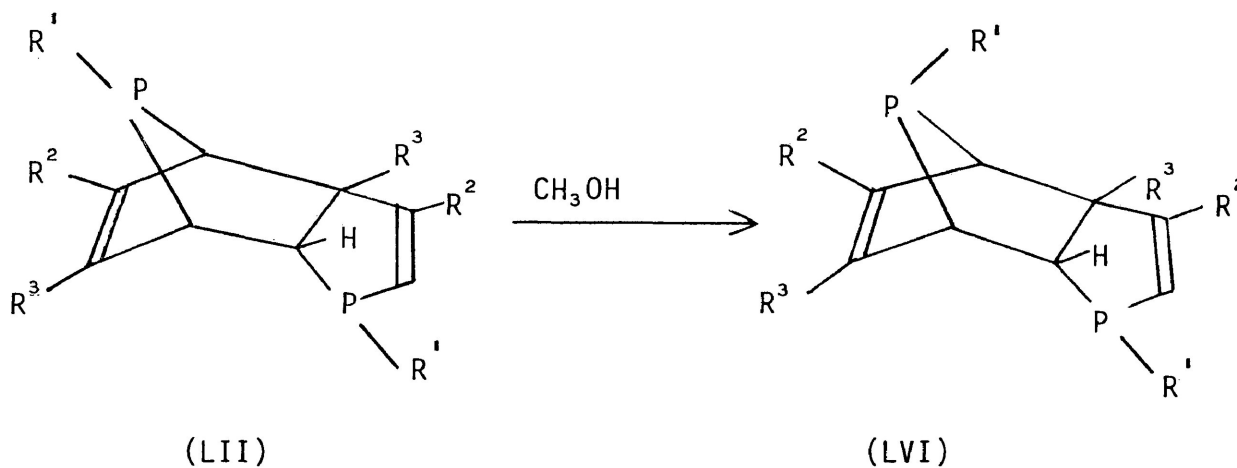
Before concluding this subsection, it should first be
mentioned that various other methods of synthesis of bisphosphines
also appear in the literature, but they are of limited application.
In general, it can be seen from the foregoing discussion of synthetic
approaches to bisphosphines that the method using organic dihalides,
has, perhaps, the widest range of application since it enables the
preparation of bisphosphines with backbones of a variety of chain
lengths. However, until now, probably the method using addition
to vinylphosphines derivatives has been the most extensively used
since the vast majority of bisphosphines so far studied contain

-PCH$_2$CH$_2$P- units. These are best prepared from vinylphosphine deri-
vatives.

1.5      $^{31}$P and $^{13}$C NMR spectroscopic studies of bisphosphines and
their metal complexes

$^{31}$P NMR spectroscopic studies have become an essential
part of research in organophosphorus chemistry since the technique
is one of the most important tools for the characterization of phos-
phorus containing compounds. As mentioned earlier, one of the
objectives of the present work was the synthesis of phosphino-
substituted phospholes (and 2-phospholenes). These would be new
types of bisphosphine and, since a number of such structures have
been synthesized in the present work and $^{31}$P NMR spectroscopy has
been used in their characterization, a brief discussion of $^{31}$P
spectra of bisphosphines in general should be made. A comprehensive
review of the topic is not, however, presented here. Emphasis is given
to the $^{31}$P spectra of unsymmetrical bisphosphines although those
of symmetrical bisphosphines are also included.

As one of the longer term objectives of the work initiated
by the study reported here was an investigation of the coordination
chemistry of phosphino-substituted phospholes, the $^{31}$P spectral
properties of bisphosphine-metal complexes in general are also
briefly discussed.

In addition to $^{31}$P spectroscopic studies, $^{13}$C NMR investigation of bisphosphines is the subject of considerable current interest because $^{31}$P-$^{13}$C coupling provides much additional structural information for these systems. Since $^{13}$C NMR data have also been used significantly in the present work, a very brief account of $^{13}$C spectroscopic studies of bisphosphines is given at the end of this section.

Symmetrical bisphosphines contain two chemically and magnetically equivalent phosphorus atoms and they will therefore give only one signal in a proton decoupled $^{31}$P spectrum. On the other hand, unsymmetrical bisphosphines contain two non-equivalent phosphorus atoms which will give rise to two signals which, if the chain linking the two P atoms is short, may be spin coupled. The $^{31}$P spectra of unsymmetrical bisphosphine derivatives are mostly first order in which the values of the chemical shifts ($\delta^{31}$P) and coupling constants ($J_{p-p}$) depend upon the nature of the substituents upon the two phosphorus atoms, the nature of the chain linking the two phosphorus atoms, and the oxidation states and hybridization of the phosphorus atoms.

Considering the structure-spectra relationships in various substituted phosphines it has been observed that a given substituent (alkyl or aryl) always makes a constant contribution to the $^{31}$P chemical shift of a phosphorus atom and, in this regard, Grim (114) assigned

a "Group Contribution" (GC) to each group which can be used to give a fairly accurate prediction of the actual $^{31}P$ chemical shift. Further details of Grim's GC values are not necessary for the purposes of the remaining discussion except that it should be mentioned that the concept of the GC works equally well for bisphosphines.

$^{31}P$ chemical shifts are also related to the C-P-C bond angles (115) and, generally, as the sizes of the groups on the phosphorus atoms increase, the C-P-C bond angle increases and the phosphorus signals move further downfield. However, it is interesting to note here that an extremely bulky group such as the neopentyl group brings about similar effects to those provided by the much smaller $CH_3$ group. It has been suggested (116) that in such cases, hyperconjugation of the $\alpha$-protons may occur and this could cause strong shielding. These substitution effects operate in the spectra of ditertiary bisphosphines as well.

$^{31}P$ chemical shifts are also affected by changes in the oxidation state of the phosphorus atoms. Thus the change from three-coordinate P(III) to four-coordinate P(V) causes strong deshielding (9). Several factors are involved here. For example, the lone pair which would provide strong shielding in tertiary phosphines is utilized in bond formation. In addition, the change in bond angles on going from P(III) to P(V) causes deshielding. Finally, the fourth atom may be electronegative (as in phosphine oxides) which also provides de-

shielding. On the other hand, five-coordinate P(V) is strongly shielded (9).

A more recently noticed factor in determining the $^{31}$P shift of bisphosphine complexes is the chelation effect. Thus, it has been observed that when a bisphosphine coordinates to a metal to give a chelate ring complex, the values of the chemical shifts and coupling constants change with the nature and magnitude of the change depending upon the nature of the metal and the size of the ring. The change in chemical shift of a phosphorus atom in a phosphine upon coordination to a metal is called the coordination shift and is defined as $\Delta = \delta^{31}$P coordinated $- \delta^{31}$P free ligand. A good linear correlation between the chemical shift of a free tertiary phosphine ($\delta F$) and the change in chemical shift upon coordination to a metal has been reported by Shaw et al. (117). Using the relationship $\Delta = A\delta F + B$, the coordination shifts of phosphines can be predicted for a given complex if several analogues are known for the calculation of the constants A and B. However, this relationship has been found not to be applicable to bisphosphine chelate complexes. In these cases, the magnitude of $\Delta$ largely depends upon the size and the number of chelate rings containing the phosphorus atoms. Such a contribution of the ring size is termed a ring contribution ($\Delta_R$) and is defined as the difference between the coordination shift ($\Delta$) of a cis-disubstituted phosphine complex (e.g. LVII) and the observed coordination shift of an equivalent phosphorus atom in a chelate

complex (e.g. LVIII).



Me        PPh$_2$Me

Pt

Me        PPh$_2$Me
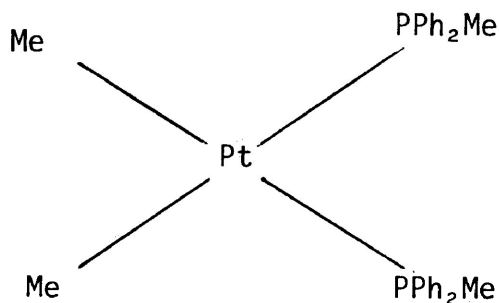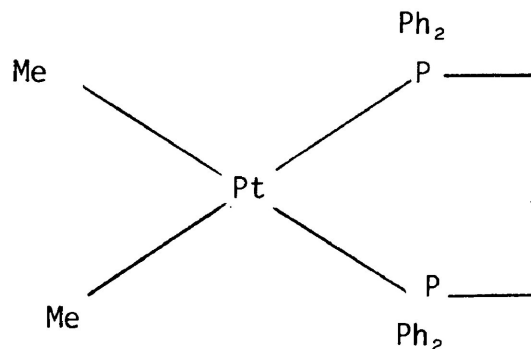
(LVII)

(LVIII)

It has been found that a four-membered ring provides maximum shielding to the P atoms whereas a five-membered ring provides maximum deshielding. A six-membered ring also provides some shielding but larger rings have no significant extra shielding or deshielding effects relative to the non-chelate complexes. The $\Delta_R$ ring conbribution to $^{31}$P NMR parameters of transition metal phosphorus chelate complexes has been discussed in detail elsewhere (118).

It should be noted here that a metal is not required in the ring for P atoms to show anomalous shifts (118). Thus, phosphole and phospholene oxides in which the P atom is in a five-membered ring exhibit $\delta^{31}$P at much lower field than do normal phosphine oxides.

A brief discussion of $^{31}$P spectral studies of various

types of bisphosphines and their metal complexes is made in the following subsections.

## 1.5.1    Bisphosphines containing symmetrical backbones

Quite a large number of both symmetrical and unsymmetrical bisphosphines and their metal complexes containing symmetrical backbones in between the phosphorus atoms have been synthesized and their $^{31}P$ spectra have been extensively studied. For example, Grim et al. (4) reported the $^{31}P$ spectra of the symmetrical bisphosphines $Ph_2P(CH_2)_n$-$PPh_2$ (n=1, 2 or 3) and their metal carbonyl (Cr, Mo or W) complexes. Significant variations in the $^{31}P$ chemical shifts of these bisphosphines were observed with the change in length of the backbone. The bisphosphine containing one backbone $-CH_2-$ unit was found to have maximum shielding ($\delta^{31}P= -23.6$) and that containing two such $-CH_2-$ units was found to have minimum shielding ($\delta^{31}P= -12.5$) in the series. Upon coordination to metals the chemical shifts of the bisphosphines $Ph_2P(CH_2)_nPPh_2$ moved downfield with the extent of the shift being dependent upon the nature of the metal. $Ph_2PCH_2PPh_2$ complexes have the lowest coordination shifts whereas $Ph_2PCH_2CH_2PPh_2$ complexes have the highest coordination shifts in the series which is in agreement with the fact that four-membered chelate rings provide maximum shielding and five-membered ring provide maximum deshielding (118).

$^{31}P$ spectra of symmetrical bisphosphines containing long

chain backbones, $Ph_2P(CH_2)_nPPh_2$ (n=6-12 or 16), have been studied (119) and it was observed that the $^{31}P$ chemical shifts are almost the same throughout the series. In a similar study, Clark et al. (87) found that the $^{31}P$ chemical shifts in the bisphosphines $(\underline{o}\text{-tolyl})_2P(CH_2)_n\text{-}P(\underline{o}\text{-tolyl})_2$ vary significantly when n=1-3, but remain almost the same when n=4, 6 or 8.

Other reports on the $^{31}P$ spectra of various symmetrical bisphosphines and their transition metal complexes (e.g. 118, 120, 121) appear in the literature. However, the results obtained are, in general, basically similar to those described above.

Grim et al. (2,3,93) also studied the $^{31}P$ spectra of a large variety of unsymmetrical bisphosphines of the type $Ph_2P(CH_2)_n\text{-}PR'R^2$ (n=1-3) and some of their Cr, Mo and W carbonyl complexes. It was found that in a given series of bisphosphines (containing the same number of $-CH_2-$ units) the $Ph_2P$-group has an almost constant chemical shift. The observed chemical shifts of the $R'R^2P-$ groups were also in good agreement with the calculated values from the group contribution (GC). $\delta^{31}P$ for the $R'R^2P-$ groups shifted to lower field with increasing size of substitutent groups as is the case with monophosphines. The only exceptions were again where the groups were very bulky (see earlier discussion).

Coupling constants ($^JP-P$) were very similar for a given

series of $Ph_2P(CH_2)_nPR'R^2$ (where n=constant and $R'$ and $R^2$ are varied) but the actual value depends upon whether n=1 or 2. No P-P coupling was observed for this series of bisphosphines where n is greater than 2 although significant $^3J_{P-P}$ couplings are known for other bisphosphine derivatives (112,113).

The $^{31}P$ signals of the ligands generally shift downfield when coordinated to a variety of metals although there are a few exceptions (in W complexes of $Ph_2PCH_2PR'R^2$). The coordination shifts $\Delta PPh_2$ and $\Delta PR'R^2$ are at maximum for the ligands $Ph_2PCH_2CH_2PR'R^2$ and are at a minimum for the ligands $Ph_2PCH_2PR'R^2$ indicating maximum deshielding in five-membered rings and maximum shielding in four-membered rings as already discussed. The coordination shifts are also found to decrease in the order Cr>Mo>W with the same ligand and this again is the expected trend (118). In most of the complexes, $J_{P-P}$ values were found to decrease in the order Cr>Mo>W.

$^{31}P$ spectra of various other unsymmetrical bisphosphines and their transition metal complexes have been reported elsewhere (e.g. 98, 103, 122-125). The results are faily straightforward and will not be discussed further here.

1.5.2      Bisphosphines containing unsymmetrical backbones

Syntheses and $^{31}P$ spectral studies of the unsymmetrical

bisphosphines $Ph_2P(CH_2)_nOPPh_2$ (n=1 or 2) and their metal complexes
were also carried out by Grim and his coworkers (4). The chemical shifts
of both P atoms of $Ph_2PCH_2OPPh_2$ are downfield from those of $Ph_2PCH_2CH_2OPPh_2$
and similar effects were also observed when these ligands were coordina-
ted to the carbonyls of Cr, Mo and W. Coordination shifts are again in
agreement with the fact that five-membered ring complexes generally show
greater $^{31}P$ downfield shifts than do six-membered ring complexes.
Coordination shifts also decrease in the order Cr>Mo>W. P-P coupling was
not observed in the spectrum of the free $Ph_2PCH_2CH_2OPPh_2$ because the
two phosphorus atoms are too far apart from each other for coupling.
However, the complexed ligand shows such coupling and, indeed, $J_{P-P}$
in the complexes of $Ph_2PCH_2CH_2OPPh_2$ are larger than those in the
corresponding complexes of $Ph_2PCH_2OPPh_2$. This is because in the
former complexes, coupling occurs solely through the metal centres
$(^2J_{P-P})$ whereas in the latter complexes, coupling occurs through
both the backbones $(^3J_{P-P})$ and the metal centres $(^2J_{P-P})$ $\underline{i.e.}$ $J_{P-P}$ =
$J^B_{P-P} + J^M_{P-P}$ (or $J_{P-P} = {}^3J_{P-P} + {}^2J_{P-P}$) where the coupling through the
backbone $(J^B_{P-P})$ is nearly the same as that of the free ligand but is
opposite in sign to the coupling through the metal centre $(J^M_{P-P})$.

Turning now to some very unusual bisphosphines containing
unsymmetrical backbones, it has been mentioned in an earlier subsection
that phosphole derivative dimers $(\underline{e.g.}$ XXXV) have interesting spectro-
copic properties. The most unexpected such property is that, in
such systems, the bridging phosphorus atom has an extraordinary down-

field shift compared with that of the more conventional 2-phospholene phosphorus atom. Several factors are involved here and these have been discussed in considerable detail elsewhere (9). In a recent report concerning syntheses and $^{31}P$ spectroscopic studies of some syn phosphole dimers where the two phosphorus atoms are tricoordinate (e.g. LII), Quin et al. (112) showed that the bridging phosphorus atom has an exceptionally large downfield shift ($\delta^{31}P$=100-120). This is greater than has ever been observed for a conventional tertiary phosphine containing three P-C bonds. On the other hand, the 2-phospholene phosphorus atom behaves much more normally and has $^{31}P$ chemical shift values varying from $\delta^{31}P$= -14 to $\delta^{31}P$=16. In these systems, the two P atoms are also coupled ($^{3}J_{P-P}$= ca. 25 Hz).

In a related study, Quin's group (113) also reported the spectroscopic properties of some anti phosphole dimers (e.g. LVI) and they observed a dramatic change in $^{31}P$ spectra upon isomerization from the syn to the anti form. For example, the $^{31}P$ spectrum of the syn isomer (LII, R$^{'}$=Me, R$^{2}$=R$^{3}$=H) shows the bridge P atom at $\delta^{31}P$=96.5 and the phospholene P atom at $\delta^{31}P$= -2.3 with $^{3}J_{P-P}$=24.4 Hz, while the $^{31}P$ spectrum of the anti isomer (LVI, R$^{'}$=Me, R$^{2}$=R$^{3}$=H) shows the bridge P atom at only $\delta^{31}P$=30.2 and the phospholene P atom at $\delta^{31}P$= -7.9. Equally surprising is the fact that the anti isomer shows no P-P coupling. Studies of this type of structure are clearly very interesting.

The only two types of phosphole dimer complexes reported
so far are those of Quin et al. (126) where the dimers have the
endo configuration and are not chelating and those of Mathey et al.
(12) where the dimers have the exo configuration and are therefore
chelating. Quin et al. (126) synthesized the phosphole dimer complexes
(LIX) and (LX) using the syn and anti isomers (LII) and (LVI) respectively
($R^1$=Me, $R^2$=$R^3$=H or $R^1$=$R^2$=Me, $R^3$=H). They observed that the $^{31}P$ spectra



(LIX)

(R = Me, $R^1$ = H or R = $R^1$ = Me,
X = Co(dmgH)$_2$ (CH$_3$))



(LX)
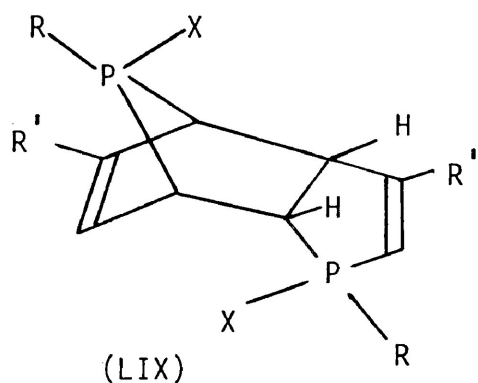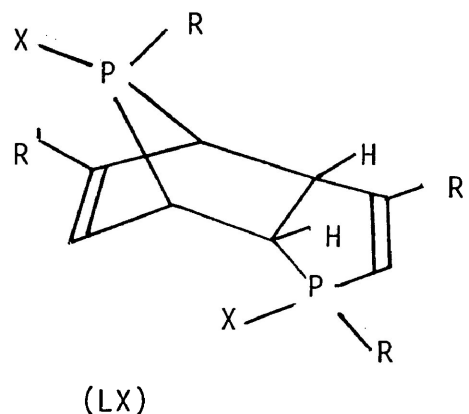
(R = Me, $R^1$ = H or R = $R^1$ = Me,
X = Co(dmgH)$_2$ (CH$_3$))

where, dmgH = [CH$_3$C-(=NOH)C(=NO)CH$_3$]$^-$

of the syn and anti complexes have a similar type of relationship to
that of the free syn and anti dimer isomers. In other words, the
bridging P atoms in the syn complexes (LIX) have large downfield
shifts compared with those in the anti complexes (LX). Similarly,

the <u>anti</u> complexes show no P-P coupling. In Mathey's complexes, (already briefly mentioned), the bridge phosphorus atoms also have very large downfield shifts ($\delta^{31}P$=135-193). The chemical shifts observed for the coordinated 2-phospholene P atoms in these complexes are in the range $\delta^{31}P$=31 to $\delta^{31}P$=77 and the $^3J_{P-P}$ values are 0-30 Hz.


1.5.3      <u>Bisphosphine derivatives (oxides and sulfides)</u>


We turn our attention now to oxides and sulfides of bis-phosphines rather than the free phosphine themselves. Since sulfide or oxide derivatives of bisphosphines are easily obtained by straightforward sulfurization or oxidation of the corresponding bis-phosphines (or obtained directly as intermediates in bisphosphine synthesis), a large variety of bisphosphine sulfides or oxides are known. Many of them have been used for complexation with metals. For example, Grim et al. (79) synthesized the bisphosphine mono or di-sulfides $Ph_2PCH_2P(S)R'R^2$, $Ph_2P(S)CH_2PR'R^2$, $Ph_2P(S)CH_2P(S)R'R^2$ and their metal complexes. The $^{31}P$ spectra of these bisphosphine derivatives and their complexes with Cr, Mo and W carbonyls were studied. In the $^{31}P$ spectra of these sulfides, the P atom attached to sulphur in the monosulfides show a downfield shift relative to the other tricoordinate P atoms. For $Ph_2P(S)$ and $Ph_2P-$, the chemical shifts are reasonably constant at $\delta^{31}P$=<u>ca.</u> 40 and $\delta^{31}P$=<u>ca.</u> -27 respectively. However, for $R'R^2P(S)-$ and $R'R^2P-$, the chemical shifts increase as expected with increasing sizes of $R'$ and/or $R^2$. An increase in $^JP-P$ is also observed as the bulkiness of the $R'$ and $R^2$

groups increases. On coordination to metals, the $^{31}$P signals of the monosulfide ligands are shifted downfield and the coordination shifts ($\Delta PR'R^2$) in the complexes of the ligands $Ph_2P(S)CH_2PR'R^2$ are much greater than those expected from four-membered chelate ring systems. This indicates that the thiophosphoryl group is bonded to the metal giving a deshielded five-membered ring. The value of $^JP-P$ decreases in the order Cr>Mo>W within the same series.

In a related study Grim et al. (78) also reported the $^{31}$P spectra of the bisphosphine mono-oxides $Ph_2P(O)CHRPPh_2$ and their complexes. The effects observed were similar to those observed for the corresponding sulfides discussed above.

Many phosphole oxide and sulfide dimers (e.g. XXXV, X=O or S) have been synthesized and their $^{31}$P spectra have also been extensively studied. As mentioned before for the corresponding phosphole dimers, the bridging phosphorus atom exhibits a $^{31}$P signal far downfield of that of the 2-phospholene oxide phosphorus atom and even more downfield than that of a similarly placed but much less strained phosphorus atom in a monocyclic 3-phospholene oxide system (LXI). Quin et al. (127) recently reported the $^{31}$P spectra of a number of phosphole oxide dimer derivatives. They found that the two phosphoryl $^{31}$P signals are well separated ($\Delta\delta^{31}$P=20-30) and the coupling constants are first order ($^3J$P-P=30-40 Hz). However,
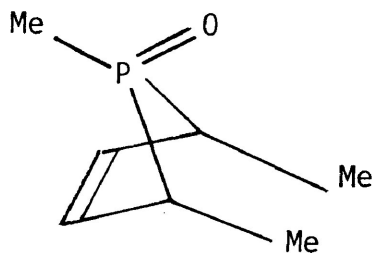
(LXI)

it is interesting to note that when the double bonds of the dimer skeleton are hydrogenated (as in, e.g. XLVIII), the chemical shifts of the phosphorus atoms become nearly identical and the $^{31}$P spectra become second order.

Finally, as mentioned in the previous subsection, Mathey et al. synthesized the exo phosphole sulfide dimers. These are the only known phosphole derivative dimers with the exo configuration. Their $^{31}$P spectra were reported and a striking difference between the $^{31}$P spectrum of the endo isomer (e.g. LXII) and that of the exo isomer (e.g. LV, R=Ph) was observed. Thus, the spectrum of the endo isomer (LXII) shows the bridge P atom at $\delta^{31}P=103$ and the phospholene P atom at $\delta^{31}P=57.6$ with $^{3}J_{P-P}=45$ Hz, whereas the spectrum of the exo isomer (LV, R=Ph) shows the bridge P atom at $\delta^{31}P=87.6$ and the phospholene P atom at $\delta^{31}P=52.4$ with $^{3}J_{P-P}\cong0$.
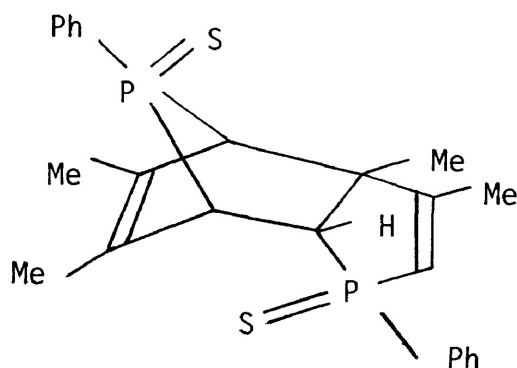
(LXII)

These observations, together with those of Quin on related phosphole derivative dimers, emphasize again that while $^{31}$P spectra in general are relatively predictable, numerous unexpected and hard to explain phenomena have been observed and phosphorus heterocycles are clearly worthy of much more extensive NMR studies.

In conclusion, from the foregoing discussion of $^{31}$P spectra of various types of bisphosphine and their derivatives, it is quite clear that, as mentioned at the beginning of this section, the $^{31}$P parameters of bisphosphines and their derivatives and complexes depend mostly upon the size (and hence the C-P-C bond angle) and the electronegativity of the substituents on phosphorus atoms, the length of the backbone joining the two phosphorus atoms, the oxidation states and hybridizations of the phosphorus atoms, and the ring size and the nature of the metal involved in coordination. Additonal, and as yet inexplicable, factors appear to operate in the

$^{31}$P spectra of both <u>exo</u> and <u>endo</u> phosphole dimers and their derivatives.

1.5.4      <u>$^{13}$C NMR spectral studies of bisphosphines and their metal complexes</u>

Prior to 1972, the $^{13}$C spectra of only a very few phosphorus compounds had appeared in the literature. During the past decade, however, the $^{13}$C spectra of quite a large number of phosphorus compounds have been studied and it is almost routine now to examine the $^{13}$C spectra of organophosphorus compounds in conjunction with their $^{31}$P spectra. Regarding compounds containing more than one phosphorus atom, there are only a few reports concerning the $^{13}$C spectra of bisphosphines and their metal complexes.

The underlying principles of the $^{13}$C spectroscopy of organophosphorus compounds in general and the $^{13}$C spectra of hetero-cyclic phosphorus compounds in particular have been discussed elsewhere (9,26) and only a very brief discussion of the nature of the $^{13}$C spectra of bisphosphines is presented here.

Symmetrical bisphosphines containing short linking chains of more than one carbon atom contain chemically equivalent P atoms which are magnetically non-equivalent as far as any carbon atom is concerned. This gives rise to second order AA'X spectra (87,120). In bisphosphines with much longer linking chains, the two P atoms become completely independent units from the point of view of the

C atoms and first order spectra are observed (119). Unsymmetrical bisphosphines with short linking chains, however, generally give the first order AMX type of $^{13}$C spectra (124). The chemical shift and coupling constants for a particular carbon atom in a bisphosphine depend upon its position with respect to the two phosphorus atoms. Thus, carbon atoms directly bonded to phosphorus atoms show downfield shifts compared with those which are not directly bonded. In this context, although it would be expected that the chemical shift values of bridging carbon atoms should decrease with increasing distance from the phosphorus atom, such a regular trend does not continue in the case of very long bridges (87,119). Also, in unsymmetrical bisphosphines, the signals due to the bridging carbon atoms become complicated by phosphorus-carbon coupling and signal overlap when the number of bridging carbon atoms is greater than three (124). The range of significant phosphorus-carbon coupling is usually limited to up to three bonds (119).

Considering briefly more unusual bisphosphine derivatives, dimeric phosphole oxides and sulfides (e.g. XXXV) give AMX spectra whereas some of their intramolecular [2+2] cyclo addition products (e.g. L) give rise to second order AA'X spectra (108) because of the presence of a $C_2$ axis of symmetry.

Regarding the $^{13}$C spectra of bisphosphine-metal complexes, only a very limited number of reports have appeared (12,120,126,128)

and no further discussion on this topic is made here.

The $^{13}C$ spectra of symmetrical bisphosphines are currently the subject of a detailed analysis in these laboratories (25).

1.6        Summary

It can be seen from the discussion outlined in sections 1.1 to 1.5 that bisphosphine derivatives are very interesting species from the point of view of their syntheses, their spectroscopic properties, their value as starting materials in the synthesis of phosphorus heterocycles, their coordinating ability, and the value of certain bisphosphine complexes in catalytic processes. Clearly, the availability of bisphosphine systems based upon the phosphole ring, also reviewed in this chapter, would open the way to new and possibly even more interesting aspects of both bisphosphine chemistry and phosphole chemistry.

The next chapter of this thesis therefore explores possible routes to such heterocyclic bisphosphines and, while the synthetic successes described therein are limited so far to a very interesting range of bisphosphine derivatives based upon the 2-phospholene system, the general approach holds some promise for the synthesis of phospholes with phosphorus-containing side chains.

RESULTS AND DISCUSSION

2.1          Introduction

As mentioned in the introductory chapter of this thesis, one of the more immediate aims of the present work was the synthesis of phosphino-substituted phospholes and the reasons for undertaking this work have also been explained in some detail.

Since heterocyclic bisphosphines containing one P atom in the ring and another P atom in the side chain (such as phosphino-substituted phospholes and their derivatives) are entirely different from the bisphosphines so far studied, the methods applicable for their synthesis would also be expected to be different from those described in section 1.4. Two possible routes for the construction of the phosphino-substituted phosphole ring system were considered for this work. The first one (Scheme 1) involves the introduction of a phosphino group at the 2-position of an already constructed phosphole ring system. This approach is based upon Mathey's observation (129) that the carbanion LXIV reacts with a variety of electrophiles to give, sometimes, 2-substituted phosphole sulfides. The second approach (outlined in general terms in Scheme 2) involves the introduction of a phosphino group into a phospholene system followed by aromatization to a phosphole system. This approach is based upon Quin's synthesis (31) of functionally substituted phospholes.

SCHEME 1



(LXIII)   (LXIV)   (LXVa)

(LXVb)   (LXVI)

## SCHEME 2



R' = H or Me
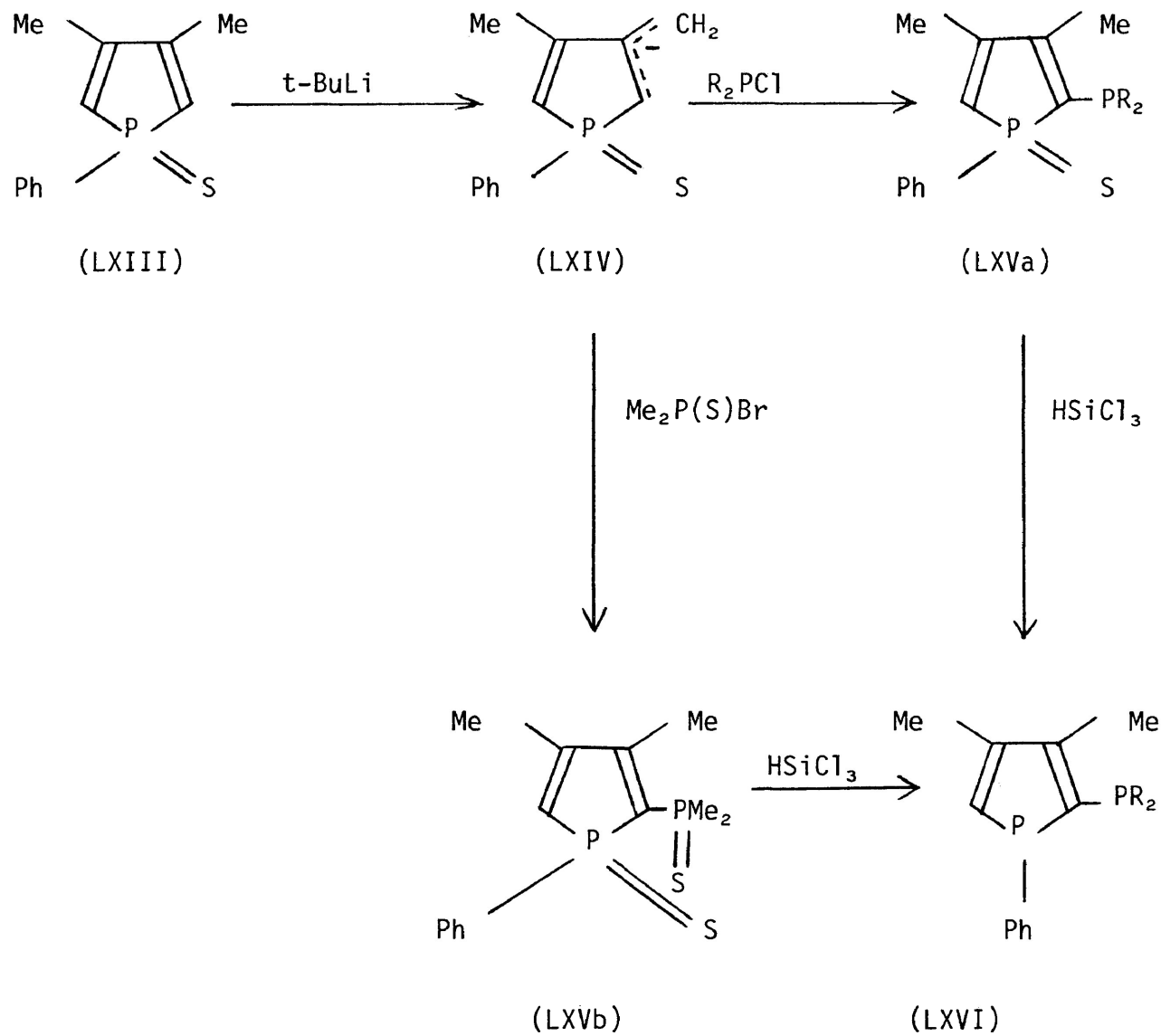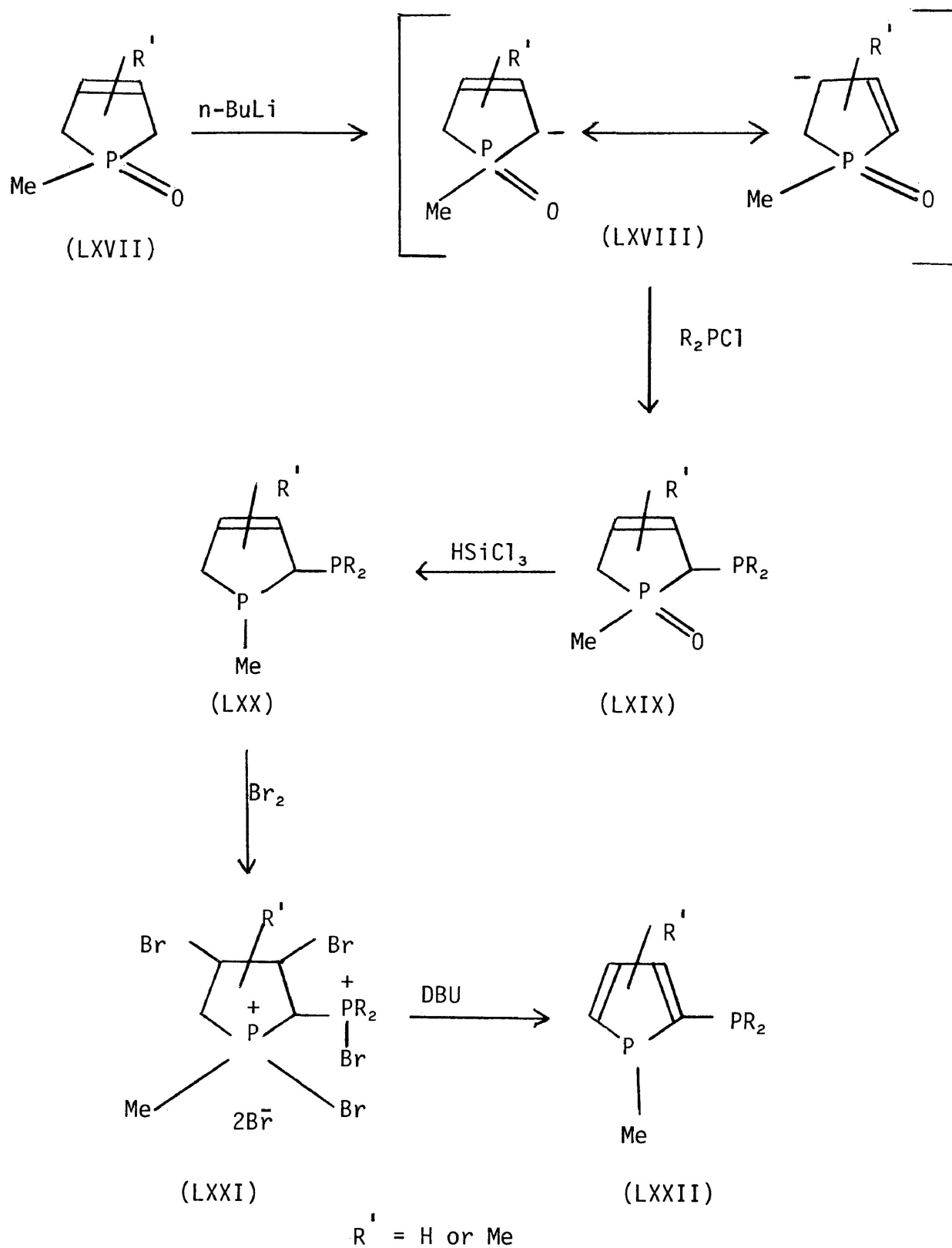
In the present work a variation of the second method was selected for two reasons.  First, the starting materials required (i.e. 3-phospholenes) are much more easily prepared in high yield than are phosphole derivatives such as LXIII.  They are also more stable and can be stored and handled easily.  Moreover, phospholenes and hence, possibly, phospholes with the desired substitution pattern can be constructed from easily available reactants.  The second reason for attempting this approach was that it had been observed previously in these laboratories (130) that although the first route shows some promise, the reactions are complex and serious purification difficulties are encountered.

It should be noted at the outset that in the work described in this chapter, several 2-diphenylphosphoryl-substituted 2-phospholene derivatives of the general structure desired were prepared and some most unexpected and potentially valuable reactions were encountered. In addition, these products show some interesting spectroscopic properties.  However, all attempts to convert these 2-diphenylphosphoryl-2-phospholene derivatives into the corresponding phospholes have so far been unsuccessful although the approach adopted does show some potential for this to be carried out.

These reactions are discussed in the following subsections and related reactions involving cyclic monophosphine derivatives also receive some attention.

## 2.2 Construction of the heterocyclic bisphosphine framework

The simple phospholene ring system itself can be readily constructed by the McCormack cycloaddition of conjugated dienes and phosphonous dihalides ($RPX_2$). This reaction has been thoroughly reviewed elsewhere (9) but the essentials are as outlined below. The cycloaddition initially gives highly reactive phospholenium salts (e.g. LXXIII) which, on subsequent hydrolysis, give 3- or 2-phospholene oxides (e.g. LXXIV or LXXV) depending upon the reaction conditions.

The cycloaddition is carried out by simply adding a conjugated diene and a phosphonous dihalide together at room temperature in the absence of moisture and leaving the mixture in the refrigerator for prolonged periods (days or weeks). The cycloaddition may be carried out using neat reagents or in the presence of a suitable hydrocarbon solvent. The adduct, which normally is formed as a filterable white crystalline solid, may be hydrolysed either by water or by $NaHCO_3$ or NaOH solution. This process is summarized in the sequence diene + $RPX_2$ → LXXIII → LXXIV and/or LXXXV.
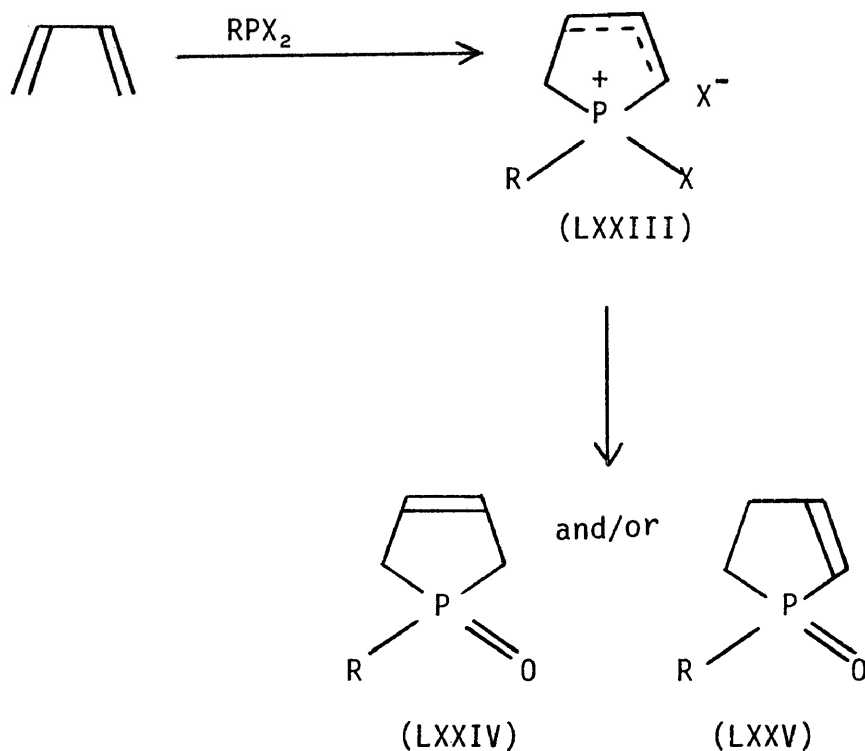
As mentioned above, the cycloaddition gives either a

3-phospholene oxide (e.g. LXXIV) or a 2-phospholene oxide (e.g. LXXV)

and which is formed depends upon the nature of the dihalide and the

reaction conditions during the hydrolysis stage. For example,

alkyl-$PCl_2$ usually give high yields of the 3-phospholene oxides,

aryl-$PCl_2$ give almost exclusively the 2-isomers and aryl-$PBr_2$ generally

give the 3-isomers. The 3-phospholene oxides formed in these reactions

may also be rearranged to the 2-isomers in the presence of a base un-

less they are stabilized by alkyl substituents on both of the $SP^2$

carbons. This is because of stabilization resulting from conjugation

of the double bond and the phosphoryl group in the 2-isomer. If the intermediate phospholenium adduct (e.g. LXXIII) is hydrolysed by adding water without controlling the high acidity or heat that develops, the product is largely or even exclusively the 2-isomer. On the other hand, if the hydrolysis is carried out by adding the adduct to a cold concentrated $NaHCO_3$ or diluted NaOH solution the product is normally exclusively the 3-isomer. The oxides are generally extracted by $CHCl_3$.

In the present work, the cycloaddition was carried out by treating 2,3-dimethyl-1,3-butadiene (LXXVI) with $PhPBr_2$. This diene was chosen because the phospholenium adduct is formed very rapidly in high yield and the product of adduct hydrolysis is exclusively the 3-pholene oxide which is easy to handle. The adduct (LXXVII) was hydrolysed by cold, concentrated $NaHCO_3$ solution and the synthesis is shown in the sequence (LXXVI) → (LXXVIII).



(LXXVI)          (LXXVII)          (LXXVIII)
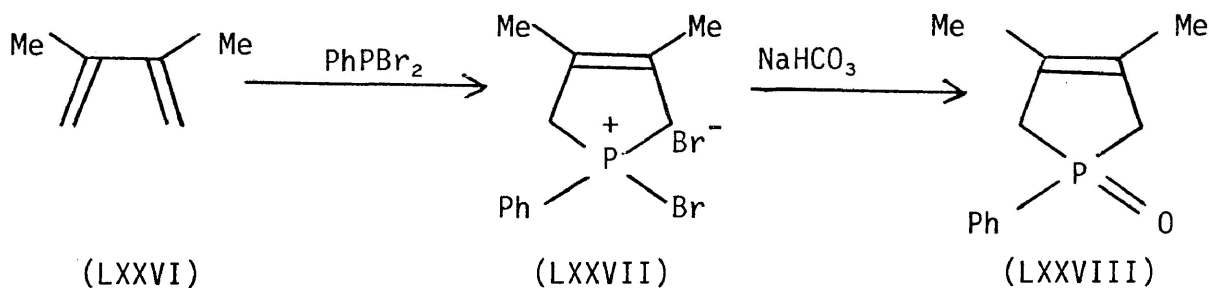
The compound gave a strong $^{31}$P NMR signal at $\delta^{31}$P = 46.3 which is very close to the literature (9) value of $\delta^{31}$P = 46.0. The compound is very hygroscopic and was therefore handled in a $N_2$-filled glove box. During drying of (LXVIII) under reduced pressure, its water content was checked from time to time by the IR spectrum. Since it was a known compound further characterization was not necessary.

Turning now to the introduction of the P containing side chain, 3-phospholenes form carbanions at the doubly-activated $\alpha$-position by the action of a strong base, usually n-butyllithium. These carbanions then react in a conventional manner with various electrophilic reagents to give either 2-phospholene or 3-phospholene derivatives or both (substituted at the 2-position or elsewhere) depending upon the substitution pattern of the starting 3-phospholenes (9). This method was applied in the present work to introduce a phosphorus-containing side chain at the 2-position of the parent 3-phospholene oxide LXXVIII by the route shown in the sequence (LXXVIII) → (LXXXI).

(LXXVIII)            (LXXIX)            (LXXX)
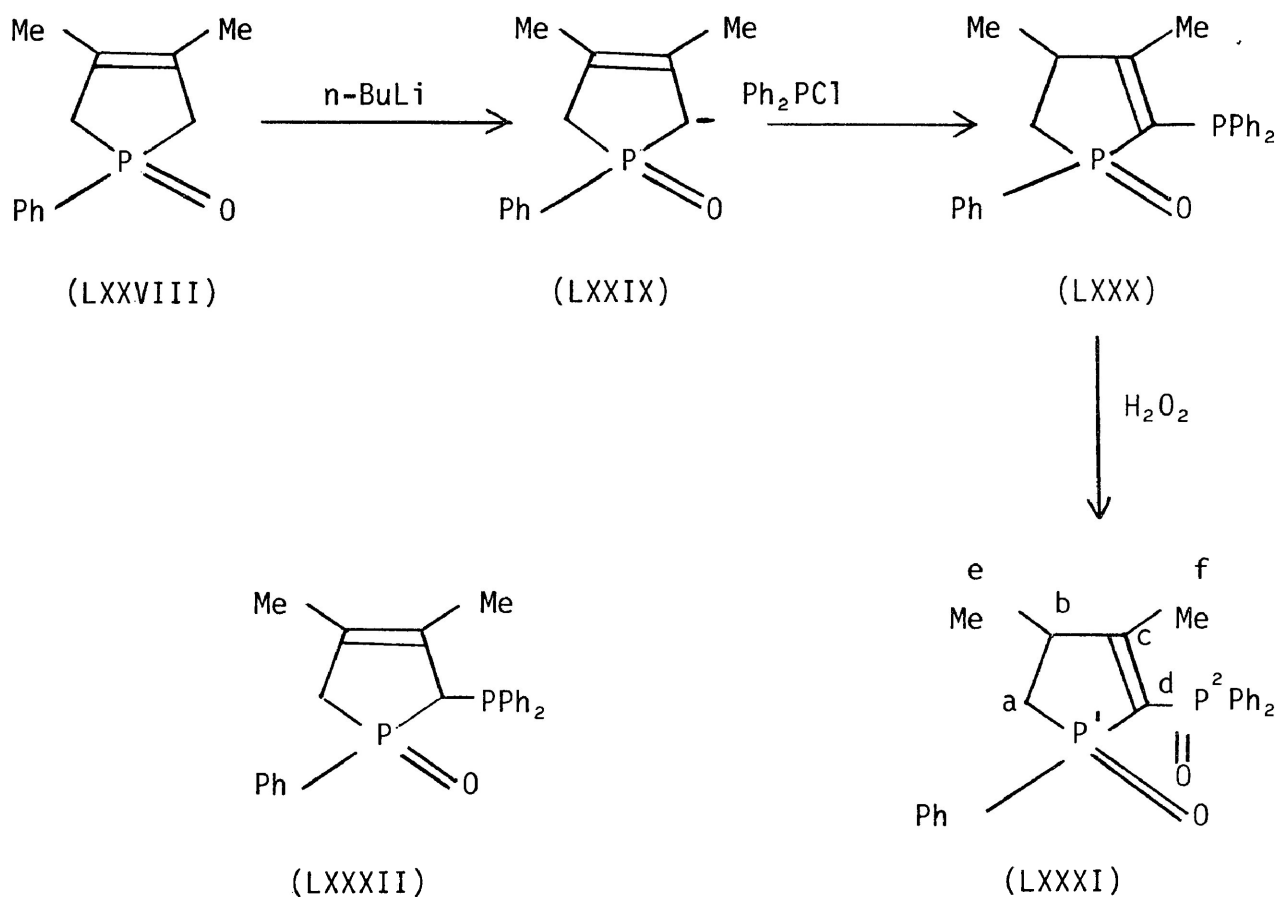
(LXXXII)                          (LXXXI)

Presumably the 3-phospholene derivative (LXXXII) is formed as an intermediate but rearrangement to the more fully conjugated system (LXXX) apparently occurs. This rearrangement may well be catalysed by the strongly basic conditions under which the reaction is carried out.

The anion (LXXIX) can be generated easily by the method described in the literature (31) and this reacts readily with $Ph_2PCl$ to give the 2-substituted phospholene oxide (LXXX) in good yield

although (LXXX) was not isolated from the viscous, complex product mixture. The ring system was, however, readily isolated as a solid in moderate yield in the form of the oxide (LXXXI) by oxidation of the reaction mixture in ethanol solution with $H_2O_2$. The compound could be crystallised directly from the reaction mixture but isolation was normally carried out by chromatographic methods.

Although there is a brief mention of this compound in one of Mathey's early papers (131), it was not well characterized in this report. In particular, the spectroscopic details given were very brief. The synthetic method was also somewhat different. However, in the present investigation the compound was characterized very thoroughly using ^{1}H, ^{31}P, and ^{13}C NMR and other physical methods and details of this characterization are given below.

The analytical data were in excellent agreement with the formulation $C_{24}H_{24}P_2O_2$ and the mass spectrum was also in agreement with the molecular weight of 406. The ^{31}P spectrum shows the ring P atom (P') as a doublet centred at $\delta = 58.08$ (typical (9) of 5-membered phosphorus heterocycles) while the side-chain P atom (P[2]) appears as another doublet centred at $\delta = 20.82$ with $^2J_{P-P} = 39.59$. The ^{31}P spectrum is, therefore, in agreement with the fact that the compound contains two coupled and non-equivalent phosphorus atoms one of which is in a five-membered ring. The ^{1}H NMR spectrum shows fifteen aromatic protons as a complex multiplet at $\delta = 6.70 - 8.25$ with the

ortho protons slightly downfield of the main multiplet, one tertiary proton as a broad hump at $\delta$ = 2.65 - 3.50 showing traces of fine structure, two methylene protons as a multiplet at $\delta$ = 1.57 - 2.65, three allyic methyl protons as a triplet centred at $\delta$ = 2.33 apparently coupled equally with both P atoms ($^4J_{P^1-H}$ = $^4J_{P^2-H}$ = 2.0 Hz) and partly obscuring the $CH_2$ multiplet, and three methyl protons as a doublet centred at $\delta$ = 1.40 ($^3J_{H-H}$ = 7.5 Hz). The tertiary hydrogen atom ($\delta$ = 2.65 - 3.50) should theoretically show up to 32 peaks (assuming only one stereoisomer is present and coupling occurs with only the ring P atom) but most of these should overlap with each other to give a broad hump as observed.

That this proton is coupled with both the adjacent methyl protons and the adjacent and non-equivalent methylene protons is evident from the fact that irradiation of either the methyl protons at $\delta$ = 1.40 or the methylene protons at $\delta$ = 2.11 causes changes in the tertiary proton hump so as to show increased fine structure. Similarly, irradiation of the tertiary proton signal at $\delta$ = 3.08 causes the methyl signal at $\delta$ = 1.40 to collapse to a singlet and also causes major changes in the $CH_2$ proton signal.

The non-equivalent ring methylene protons in the $^1H$ spectrum of (LXXXI) should theoretically appear as 16 signals (coupling with each other, the tertiary proton and the ring P atom) out of which 11 were observed while the rest were obscured by the signal of the

allylic protons. As mentioned above, irradiation of the tertiary pro-
ton brought some modification in this multiplet which indicates that
at least one of the methylene protons is coupled with the tertiary
proton. However, even with double irradiation, it was not possible
to assign the various coupling constants unambiguously because of the
band width of the decoupling field although the largest coupling
constant, which is <u>ca.</u> 15 Hz, is probably due to coupling with the
ring P atom (P').

Thus, both the $^{31}$P and the $^{'}$H spectra are in excellent
agreement with the proposed structure (LXXXI).

The structure should also be quite clear from the $^{13}$C
spectrum where both the $^{13}$C shifts and $^{31}$P - $^{13}$C couplings would give
important structural information. In particular, the structure
(LXXXI) should show $^{13}$C NMR signals for (a) two SP$^2$ carbons ($C_c$ and $C_d$),
each one appearing as a doublet of doublets as they will couple with
the two P atoms, (b) two primary SP$^3$ carbons, one of which ($C_f$) should
show a doublet of doublets as it will couple with the two P atoms,
while the other ($C_e$) should show a doublet through coupling with P',
(c) a secondary SP$^3$ carbon ($C_a$) which should appear as a doublet
of doublets, due to coupling with both P atoms, (d) a tertiary
SP$^3$ carbon ($C_b$) which should also appear as a doublet of
doublets, and (e) a complex multiplet for the aromatic carbon
atoms. The $^{13}$C spectrum of the compound was recorded and the chemical
shifts and coupling constants are: $\delta$ = 35.89, $^1J_{P'-C}$ = 68.36 Hz,

$^3J_{P^2-C}$ = 10 Hz for Ca; $\delta$ = 43.37, $^2J_{P'-C}$ = 7.33 Hz, $^3J_{P^2-C}$ = 13.42 Hz

for $C_b$; $\delta$ = 183.33, $^2J_{P'-C}$ = 21.97 Hz, $^2J_{P^2-C}$ = 2.44 Hz for $C_c$;

$\delta$ = 21.18 for $C_e$ (line broadened but no clear coupling with P'), and

$\delta$ = 19.15, $^3J_{P'-C}$ = 14.65, $^3J_{P^2-C}$ = 6.10 Hz for $C_f$. The signals

for the aromatic protons appear as a complex multiplet at $\delta$ = 127.15 -

135.50 and the signal of $C_d$ is obscured under these aromatic signals.

These $^{13}C$ spectral data are in excellent agreement with the expected

results and the structure given (LXXXI) is unambiguously confirmed.

It should be noted that some of the assignments in the $^{13}C$ spectrum

of (LXXXI) were made by analogy with the spectrum of the closely

related (LXXXIII) (26). The extreme downfield position of the

signal of $C_c$, typical of the C=C - P=O structural unit (9) is noteworthy.



(LXXXIII)
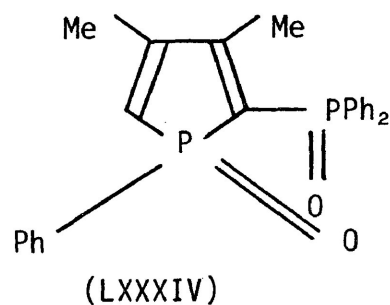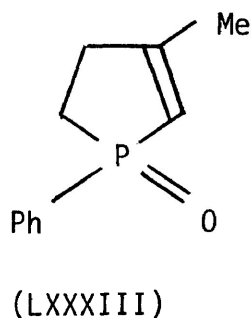


(LXXXIV)

In theory, four stereoisomers of the compound (LXXXI) are

possible since there are two chiral centres (ring P and C4). However,

the stereochemistry about the ring P-atom is fixed by the nature of

the starting material and therefore two stereoisomeric products could

be formed in the synthesis of (LXXXI). Rather surprisingly, only
one stereoisomer, as shown by the NMR spectra, appears to be formed
during the reaction. One might expect that the two stereoisomers
(if formed) would have very similar solubilities and might crystallize
together. However, the very clean $^{31}$P, $^{1}$H and $^{13}$C spectra showed
that no significant quantity of any other material was present.
Even a detailed chromatographic examination of the crude reaction
mixture revealed no trace of the other possible stereoisomer and the
synthesis therefore appears to be stereospecific or at least highly
stereoselective.

This reaction therefore appears to be a very easy and
stereoselective route to the framework of the desired heterocyclic
bisphosphine system. However, the fact that double bond migration
occurs during the reaction to give the 2-diphenylphosphoryl-2-phospholene
derivative (LXXXI) means that some modification of the originally
proposed route outlined earlier in Scheme 2 must be made. An allylic
bromination of (LXXXI) followed by dehydrobromination of the product
in an attempt to prepare the corresponding phosphole derivative
(LXXXIV) was therefore attempted and the interesting results obtained
in this series of reactions are outlined in the next subsection.

## 2.3 Attempted construction of a diphenylphosphoryl-substituted phosphole oxide ring using the 2-phospholene derivative (LXXXI)

As mentioned in the previous subsection, although the desired heterocyclic bisphosphine framework is readily constructed, the originally proposed approach to the phosphino-substituted phosphole system outlined in Scheme 2 had to be modified because the double bond in this framework (LXXXI) is in the wrong position for the later stages of Scheme 2 to be carried out. The modified route chosen is shown in the proposed sequence (LXXXI) → (LXXXV) → (LXXXIV). This is a photochemically induced allylic bromination of (LXXXI) followed by endocyclic dehydrobromination of the product (LXXXV).
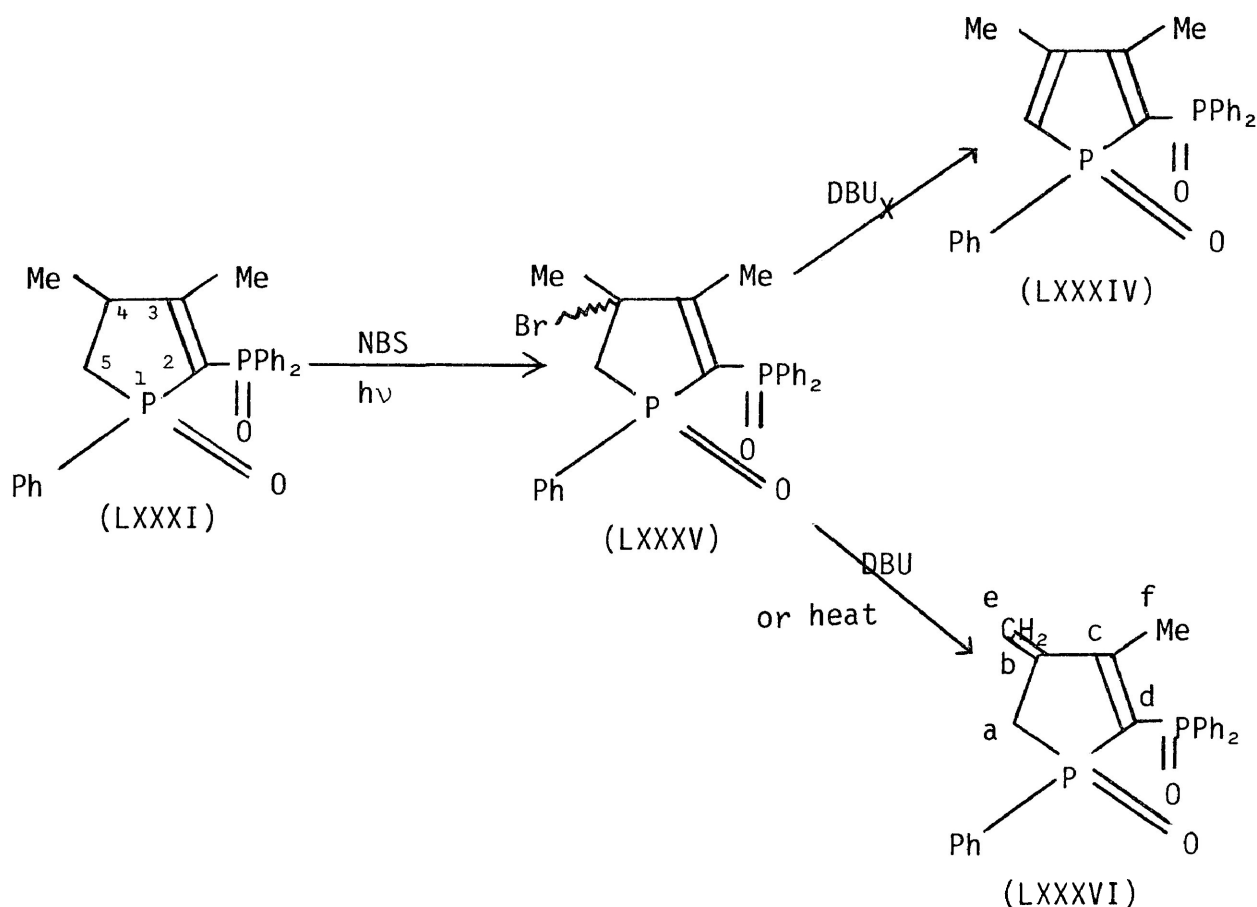
The route was chosen on the basis that the compound
(LXXXI) contains a tertiary hydrogen atom at C4 and, since the
abstraction of a tertiary hydrogen during a free radical halogenation
is easier than that of secondary or primary hydrogens, (LXXXI) should
undergo photochemical bromination easily at C4 to give (LXXXV).
Furthermore, the hydrogen atoms at C5 of (LXXXV) are reasonably acidic
and, therefore, dehydrobromination of (LXXXV) should readily occur
between C4 and C5 yielding the phosphole system (LXXXIV). As will
be seen shortly, the allylic bromination of (LXXXI) is easily
achieved but the dehydrobromination of (LXXXV) leads to (LXXXVI)
rather than (LXXXIV).

N-Bromosuccinimide (NBS) is very effective reagent
for allylic bromination of alkenes (132) and, therefore, it was
selected for the bromination of (LXXXI). The desired bromination
occurs very smoothly in the presence of UV radiation (high pressure
mercury lamp) to give (LXXXV) in excellent yield although it took
some time to establish the optimum conditions for this. Reliable
analytical data have not been obtained because (LXXXV) is of very
limited stability even at room temperature. However, there is more
than enough spectroscopic and chemical evidence that (LXXXV) is
formed in this photobromination. For example, there is sufficient
thermal stability for the compound to show the expected molecular ion
peaks at m/e=484 ($^{79}$Br) and 486 ($^{81}$Br) in the mass spectrum although the peaks
are quite weak. Furthermore, the compound (LXXXV) has been unambigu-

ously characterized by the usual $^1$H and $^{31}$P NMR techniques although it should be noted that the spectra are a little more complex (particularly the $^1$H spectrum) than those of the precursor (LXXXI) because (a) two stereoisomers are formed in unequal amounts (as would be expected) and (b) the compound is thermally unstable. Nevertheless, both the $^{31}$P and the $^1$H spectra are quite consistent with the existence of two stereoisomers of (LXXXV).

The $^{31}$P NMR spectrum shows two sets of two doublets of unequal intensity. The major isomer shows a doublet centred at $\delta$ = 48.90 (ring P) and a second doublet at $\delta$ = 20.78 (side-chain P) with $^2J_{P-P}$ = 35.4 Hz. The minor isomer shows a similar pattern with one doublet centred at $\delta$ = 51.12 (ring P) and the other at $\delta$ = 20.66 (side-chain P) with $^2J_{P-P}$ = 35.4 Hz. The chemical shifts of the ring P atoms are typical (9) of five-membered phosphorus heterocycles in both cases and $^2J_{P-P}$ is similar to that observed for (LXXXI).

In theory, the $^1$H NMR spectrum of an individual isomer of (LXXXV) should show a narrow doublet of doublets for the allylic methyl protons because of their unequal coupling with the two P atoms ($^4J_{P-H}$ in each case), a narrow doublet ($^4J_{P'-H}$) for the other methyl protons, a complex multiplet for the non-equivalent methylene protons because of coupling with each other as well as the two P atoms, and a complex multiplet for the aromatic protons. The $^1$H spectrum of the product actually obtained shows the allylic methyl protons as a very

closely spaced multiplet centred at $\delta$ = 2.47 which appears to be

two superimposed triplets of unequal area, the other methyl protons

as two singlets of unequal area at $\delta$ = 2.06 and 2.12, the ring

methylene protons as a broad and complex multiplet at $\delta$ = 2.25 - 3.50,

and the aromatic protons as another complex multiplet at $\delta$ = 6.77 -

8.25. The signals of the methylene protons and the C4 methyl protons

are shifted downfield (as would be expected from the inclusion of

bromine in the structure) compared with those of similar protons in

(LXXXI). These $^1$H NMR results are in excellent agreement with those

expected for a mixture of two stereoisomers of (LXXXV). It should

be noted that, as with the precursor (LXXXI), the allylic methyl

protons couple equally with the two P atoms in <u>both</u> stereoisomers

($^4J_{P^1-H}$ = $^4J_{P^2-H}$ = <u>ca.</u> 2 Hz). Similarly, as with (LXXXI), the other

methyl protons in both stereoisomers of (LXXXV) do not couple with

either P atom.


Thus, both the $^{31}$P and the $^1$H spectra confirm the pro-

posed structure (LXXXV) and the presence of two stereoisomers in un-

equal quantities.


Turning now to the dehydrobromination step, the dehydro-

bromination of (LXXXV) occurs very readily with both DBU (1,8-diaza-

bicyclo[5.4.0]undec-7-ene) and gentle heating in the absence of other

reagents and this also offers powerful supporting evidence that the

product of the reaction of (LXXXI) with NBS is indeed (LXXXV).

Since the dehydrobromination by gentle heating gives a purer product,

the reaction was normally carried out by this process.  As is so

often the case in phosphorus heterocyclic chemistry the reaction did

not follow the expected course and, instead of the expected product

(LXXXIV), the isomer (LXXXVI) was obtained in moderate yield.  Again

the structure of this product has been confirmed by analytical data

(excellent agreement), the mass spectrum (m/e 404 as expected for

(LXXXIV) or (LXXXVI))and the usual NMR spectra.


The $^{31}P$ spectrum shows the ring P atom (P') as a doublet

centred at $\delta$ = 48.22 (as expected (9) for a 5-membered phosphorus

heterocycle) while the side-chain P atom (P$^2$) appears as another

doublet centred at $\delta$ = 22.18 with $^2J_{p-p}$ = 33.5 Hz.  The $^{31}P$ spectrum is,

therefore, in agreement with the fact that the compound, like the

precursors (LXXXI) and (LXXXV), contains two coupled and non-equivalent

phosphorus atoms, one of which is in a five-membered ring.


The $^1H$ NMR spectrum shows fifteen aromatic protons as a

complex multiplet at $\delta$ = 6.78 - 8.25 with the ortho protons (as is

usual in arylphosphine oxides) slighly downfield of the main multiplet,

each of the exocyclic non-equivalent olefinic protons as a very

closely spaced multiplet centred at $\delta$ = 5.48 and $\delta$ = 5.75 respectively,

two ring methylene protons as a multiplet consisting mainly of three

broadened peaks of unequal area at $\delta$ = 2.75 - 3.37, and the three

allylic methyl protons as a triplet centred at $\delta$ = 2.46 apparently

coupled equally with both P atoms ($^4J_{P^1-H}$ = $^4J_{P^2-H}$ = 2.0 Hz) as is

the case in the spectra of (LXXXI) and (LXXXV).


The signals of the two olefinic protons are slightly

different in appearance with the higher field signal split into at

least five peaks and the lower field signal split into at least six

peaks of unequal intensities. These splittings could be due to

coupling of the exocyclic olefinic protons with each other, with the

nearby non-equivalent ring methylene protons and, possibly, with the

ring P atom. That the couplings are primarily with the methylene

protons was confirmed by double resonance techniques. Thus, irradia-

tion of the ring methylene protons at $\delta$ = 3.0 changes each olefinic

signal into a narrow doublet of two slightly broadened peaks ( J =

ca. 2 Hz in each case). The small residual coupling could be due

to coupling of the olefinic protons with each other but the near

equivalence in area of each peak in the remaining doublets suggests

that coupling with ring P is more likely.


The two non-equivalent ring methylene protons should

theoretically appear as 8 signals (coupling with each other and the

ring P atom) or a much larger number of signals if, as shown above,

coupling with the exocyclic olefinic proton occurs. However, as already

noted, they appear as a narrow multiplet which consists largely of a broad singlet and a broad and not properly resolved doublet with all three main peaks of unequal area. This is presumably because the two protons are so similar in chemical shift that highly distorted and deceptively simple signals are observed.

Irradiation at the midpoint between the two olefinic proton signals ($\delta = 5.6$) causes some changes in the methylene proton signals. This again confirms that the ring methylene protons are coupled with the olefinic protons.

Thus, both $^{31}P$ and $^{1}H$ spectra are in excellent agreement with the proposed structure (LXXXVI) and totally inconsistent with the alternative structure (LXXXIV).

This structure allows fairly easy prediction of the $^{13}C$ spectrum of the compound. The spectrum of (LXXXVI) should show $^{13}C$ NMR signals for four $SP^2$ carbon atoms ($C_b$, $C_c$, $C_d$ and $C_e$) in which $C_b$, $C_c$ (well downfield because of the presence of the $C = C - P = O$ unit as mentioned earlier) and $C_d$ should show doublets of doublets as they will couple with the two P atoms while $C_e$ should show a doublet (somewhat upfield of the aromatic signals) as it would be expected to couple with only the ring P atom. In addition, the spectrum should show one primary $SP^3$ carbon ($C_f$) which should appear as a doublet

of doublets as it will couple with both of the P atoms and a secondary $SP^3$ carbon $(C_a)$ which should again appear as a doublet of doublets due to coupling with both of the P atoms. A complex multiplet for the aromatic protons would also be expected.

The $^{13}C$ spectrum of the compound, entirely consistent with the above predictions, was recorded and the chemical shifts and coupling constants are: $\delta = 34.65$, $^1J_{P'-C} = 72.33$ Hz, $^2J_{P^2-C} = 3.97$ Hz for $C_a$; $\delta = 144.45$, $^2J_{P'-C} = 10.85$ Hz, $^3J_{P^2-C} = 17.29$ Hz (or _vice versa_) for $C_b$; $\delta = 170.86$, $^2J_{P'-C} = 14.24$ Hz, $^2J_{P^2-C} = 3.39$ Hz for $C_c$; $\delta = 116.74$, $^3J_{P'-C} = 15.26$ Hz, $^4J_{P^2-C} = 0$ Hz for $C_e$ and $\delta = 15.85$, $^3J_{P'-C} = 14.04$ Hz, $^3J_{P^2-C} = 5.49$ Hz for $C_f$. The signals for the aromatic protons appear as a complex multiplet at $= 127.38 - 135.58$ and the signals of $C_d$ are obscured by these aromatic signals. These $^{13}C$ spectra results are in excellent agreement with the expected results and the structure (LXXXVI) is therefore unambiguously confirmed.

The formation of (LXXXVI) instead of the expected (LXXXIV) by dehydrobromination of (LXXXV) might be due to internal strain in (LXXXIV) created by steric interactions between the two methyl groups and perhaps also involving the side-chain $Ph_2P = 0$ group. Such strain has been used to explain unusual spectra in structurally related 3,4-dimethylphospholes (16) and it should also be noted that several structurally related phosphole oxides and

sulfides such as (LXXXVII) (133) and (LXXXVIII) (134) prefer the

exo methylene structures shown although the sulfide (LXXXVIII) can

exist in either the exo methylene form shown or the isomeric phosphole

sulfide (134). Most simple phosphole oxides and sulfides, however,

rapidly dimerize in the same manner as cylopentadiene.



(LXXXVII)                    (LXXXVIII)
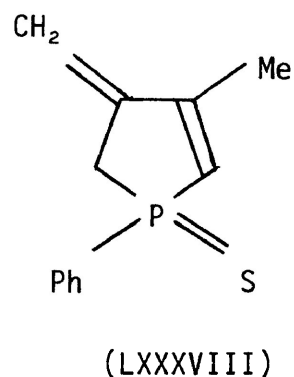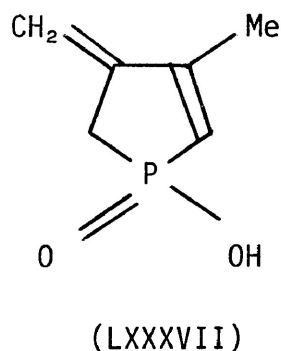
As the construction of the desired phosphoryl-

substituted phosphole oxide system (LXXXIV) has not been achieved by

the route outlined above, a further reaction was considered which

might have solved the problem. This involved reduction of the dioxide

(LXXXVI) to give (LXXXIX) on the assumption that if the phosphole (XC)

isomeric with (LXXXIX) had significant aromatic character, the de-

localization energy in XC might provide sufficient driving force for

the isomerization (LXXXIX) → (XC) to occur.
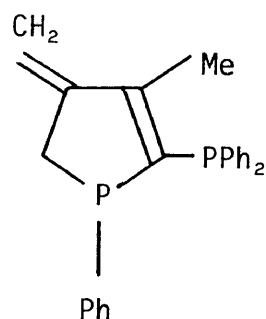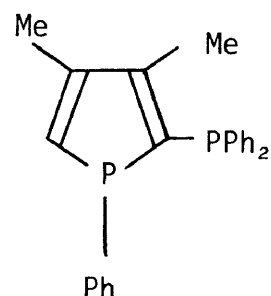
(LXXXIX)                    (XC)

The results of this study are outlined below.

The route initially attempted is shown in the sequence (LXXXVI) → (LXXXIX) → (XC). However, reductions using the large excess of trichlorosilane usually used for these reactions were found to give complex mixtures in which, clearly, considerable hydrogenation of the system had occurred and neither (LXXXIX) nor (XC) could be isolated. The amount of trichlorosilane used (in the presence of pyridine) was therefore decreased until it was only in slight excess but still a mixture of at least three components was obtained. Thus, the $^{31}$P spectrum of the crude mixture shows mainly

three sets of doublets of doublets of unequal intensities. The major

component shows signals at $\delta$ = 1.12 and $\delta$ = 25.0 for the ring P atom

and the side chain P atom respectively with $^2J_{\underline{P}-\underline{P}}$ = 59.7 Hz. These
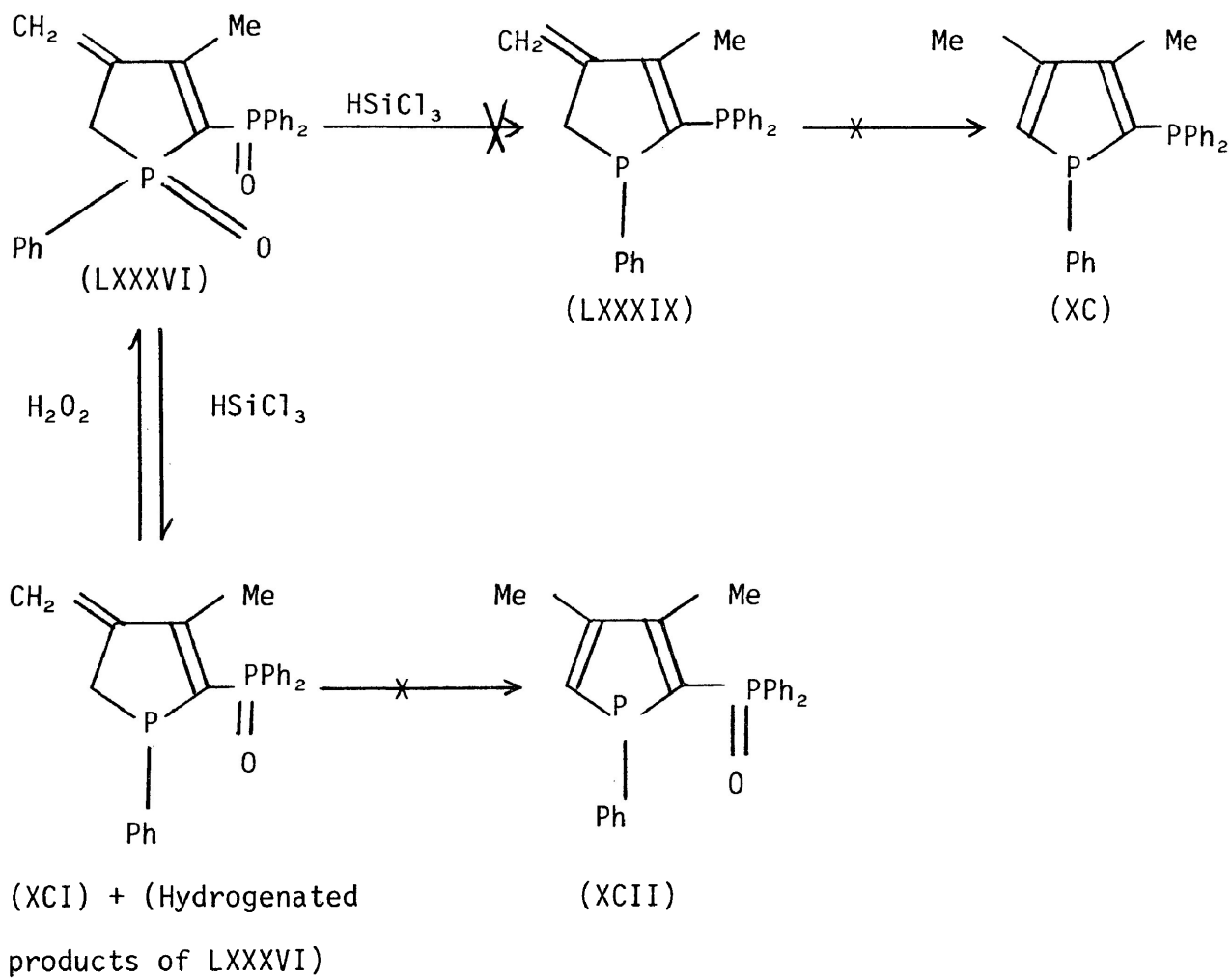


chemical shift values for the major component indicate that the

ring P = O group of (LXXXVI) has been reduced whereas the side chain

P = O group has not. That only one of the two P = O groups is reduced

is confirmed by the low voltage mass spectrum of the crude reduction

mixture which shows molecular ion peaks at m/e = 388 (major) and

390 (minor) corresponding to the loss of one oxygen (m/e 388) and

loss of one oxygen together with addition of $H_2$ (m/e 390) respectively.

A strong peak at m/e = 201 in the mass spectrum at 80 eV shows that

the $Ph_2P$ = O unit is still intact and, therefore, it is the ring P = O

of (LXXXVI) which is reduced as indicated by the $^{31}P$ spectrum. A

second component (much less intense $^{31}P$ spectrum) shows a similar

pattern with ring and side-chain P signals at $\delta$ = -16.5 and +31.10

respectively with $^2J_{P-P}$ = 74.20 Hz, although the possibility of ring

cleavage cannot be excluded yet for this product. However, reoxida-

tion of this material, discussed later, showed from the $^{31}P$ spectrum

of the product that the five-membered ring is indeed still intact.

A third and much less significant component is present with all four

very weak peaks of the doublet of doublets in the $\delta$ = 13 - 15.5 range.

Purification of the mixture by column chromatography was not

successful because all three main components have the same $R_f$ value

under a variety of conditions.

In an attempt to identify at least some of the components,

the mixture was re-oxidized. Oxidation of the mixture by $H_2O_2$ gave

another complex mixture which could be chromatographically separated

to some extent and which yielded only one component in pure form. The $^{31}$P spectrum and other characteristics of this pure fraction are identical with those of the exo methylene compound (LXXXVI). That this is the framework of the major product obtained from the trichloro-silane reduction of (LXXXVI) seems highly likely since, in the crude reoxidized mixture, the oxide (LXXXVI) is clearly the major component as shown by the $^{31}$P spectrum. That the exo methylene group is still intact in the HSiCl$_3$ reduced mixture is shown by the $^1$H spectrum of that mixture which clearly shows such an exo methylene group as two very narrow multiplets at $\delta$ = 5.25 and 5.43 (slightly upfield of the similar multiplets in the spectrum of LXXXVI as would be expected from ring P = O reduction). Integration confirms that about 50% of the mixture consists of this compound which, on the basis of this and the other evidence cited, appears to be (XCI).

The hydrogenated material present (as shown by the mass spectrum) in the crude reduction mixture could not be identified and, since these products are of no great importance to the investigation described here, further attempts to isolate and characterize them were not undertaken. The one point that should be made here is that double bond reductions in phospholene oxides by HSiCl$_3$ or HSiCl$_3$/Py appear to be rare although trichlorosilane has frequently been used for reduction of less hindered double bonds in more conventional systems (135). There is, however, one such example in fused-ring phospholene chemistry where 1,4-hydrogenation of a dienoid system has

been observed (136).

That the side chain phosphoryl group of (LXXXVI) does
not undergo trichlorosilane reduction whereas the the ring phosphoryl
group is reduced in a conventional manner is worthy of brief comment.
Such a difference in the reactivity of the two phosphoryl groups towards
trichlorosilane is presumably largely due to differences in the bond
strengths of the P = O unit although steric factors might also play
a part. The differences in bond strength at first sight would be due
to the fact that the ring phosphoryl group may be regarded as essentially
dialkylaryl substituted whereas the side chain P = O group has some-
thing like a diarylalkyl pattern. However, one might expect (by
analogy with other systems in the literature (137)) higher, not lower,
P = O bond energies as the number of alkyl groups on the P = O group
increases relative to the number of aryl groups. It is therefore
possible then that conventional steric effects exert some influence and/or
the constraint of a five-membered ring is important here.

Returning now to the basic theme of this reaction, the
2-pholene structure (XCI) which is apparently formed in the
reduction of (LXXXVI) is potentially capable of isomerization to
the phosphole system (XCII). However, this was not observed and could
not be made to occur and one must infer that this phosphole probably
has little if any aromatic character - possibly because of the 3,4-
disubstitution steric effects referred to earlier.

At this point in the investigation then, it seemed briefly that the synthetic approach used so far could not be further extended although it is clearly of considerable use in constructing the desired molecular framework. A similar approach based upon a phosphole system which does not contain 3- and 4-substituents appeared to be the next step to be tried. However, while these results were being thoroughly analysed, a curious and potentially very useful spontaneous oxidation of (LXXXVI) was observed which offered another possible route to phosphine-substituted phospholes. This is discussed in the next subsection.

## 2.4  Spontaneous and controlled oxidations of (LXXXVI)

Several preparations of (LXXXVI) were carried out in order to accumulate a reasonably large quantity for further studies. However, after the product of each preparation had been stored for some time, it was observed that the compound undergoes a slow decomposition to give a new compound which was later characterized as (XCIII). The reaction is, therefore, a spontaneous and very surprising oxidation which can also be carried out more quickly under more precisely controlled conditions as will be seen later. This slow, spontaneous oxidation occurs even in the solid state in the dark at low temperatures (refrigerator) and, under these conditions, almost complete conversion of (LXXXVI) into (XCIII) occurs in about two months.
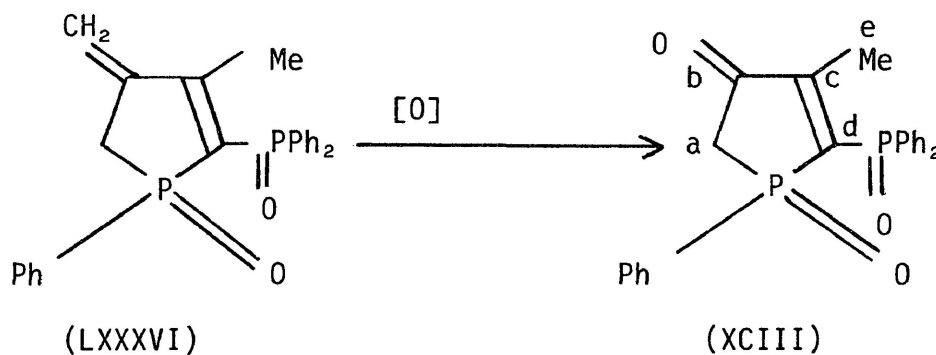
As stated above, the product of this oxidation has been unambiguously characterized by various analytical and spectroscopic methods. The C and H analyses, carried out on very freshly prepared samples in these laboratories, are in excellent agreement with the proposed structure. Good P analyses, carried out commercially elsewhere, were more difficult to obtain since the compound is somewhat hygroscopic. In addition, the mass spectrum shows a molecular ion peak at m/e 406 which is two atomic mass units more than the precursor (LXXXVI). Furthermore, the IR spectrum (liquid film) shows a strong and sharp C = O stretching vibration at 1710 cm$^{-1}$.

The $^{31}P$ spectrum of the compound is rather interesting in that it shows the ring P atom (P') as a doublet centred at the unusually highfield value of $\delta$ = 32.50 while the side chain P atom (P$^2$) appears as another doublet centred, as expected, at $\delta$ = 21.64 with $^2J_{P-P}$ = 24.7 Hz. Thus, the compound, like its precursors, contains two coupled non-equivalent phosphorus atoms. It should be noted here that one would normally expect (9) the ring P atom of a 2-phospholene oxide of this general type to resonate at around $\delta$ = 50 or at even lower field. However, similar anomalous shifts have been observed for a few other 2-phospholene oxide derivatives. For example, $^{31}P$ shifts of $\delta$ = 32.0 and $\delta$ = 29.2 have been observed for (XCIV) (9) and (XCV) (136) respectively.
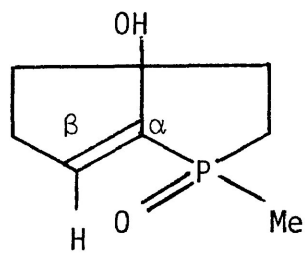
(XCIV)
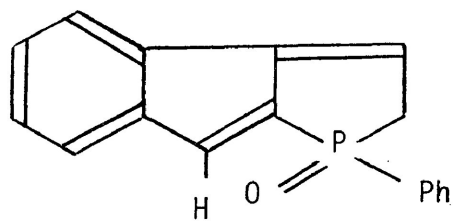
(XCV)
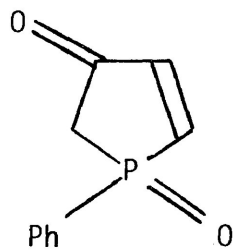
(XCVI)

The unusually highfield $^{31}$P shifts of these structures (XCIV) and (XCV) are thought (136) to be due to the shielding effect originating from an eclipsing C - H interaction at the unsaturated β-carbon with the P atom. However, such an interaction is absent in the structure (XCIII). Moreover, the structures (XCIV) and (XCV) are fused-ring systems with an exocyclic double bond at the α-position whereas (XCIII) is a monocyclic compound with no such α exocyclic un- saturation. From an electronic point of view, the compound (XCIII) might be expected to show an even more downfield shift than its precursor (LXXXVI) because of the presence of the conjugated, electron- withdrawing carbonyl group at C4. The reasons for the unusally highfield $^{31}$P shift of the ring P atom of the ketone (XCIII) are, therefore, at this time, obscure although it should be noted that in a recent paper (138) concerning 4-oxo-2-phospholenes, the structur- ally related compound (XCVI) shows a $^{31}$P shift of δ = 36.4. This point will be considered again later.

Returning now to the structural proof, the $^{1}$H NMR spectrum of the compound shows fifteen aromatic protons as a complex multiplet at δ = 6.75 - 8.25 with the <u>ortho</u> protons slightly downfield of the main multiplet, the two ring methylene protons as a multiplet at δ = 2.65 - 3.30 and the three allylic methyl protons as a triplet centred at δ = 2.35 coupled equally with both of the P atoms ($^{4}J_{P'-H}$ = $^{4}J_{P^2-H}$ = 2.0 Hz). The two non-equivalent ring methylene protons could theoretically appear as up to 8 signals as they may couple with

each other and the ring P atom. Long-range coupling with $P^2$ could also conceivably occur. However, they appear as a narrow multiplet (slightly broader than that in the precursor LXXXVI) which consists of two broad singlets, two other singlets of very low intensity and a broad and not properly resolved doublet with all of the peaks of unequal area. Other peaks may perhaps be obscured by the more intense broad signals observed. Detailed assignments of $\delta'H$, $J_{P-H}$ and $J_{H-H}$ therefore cannot be made although the location of the centre of the multiplet and the integration are entirely consistent with the proposed structure.

It can be seen, then, that the $^{31}P$ and the $^1H$ spectra of the product of the spontaneous oxidation of (LXXXVI) are in excellent agreement with the proposed structure (XCIII).

As with other structures discussed earlier, the $^{13}C$ spectrum expected for (XCIII) can easily be predicted. Thus, the structure would be expected to show signals for three $SP^2$ carbons ($C_b$, $C_c$ and $C_d$), each of which should appear as a doublet of doublets as they should all couple with both of the P atoms. These signals would have quite large downfield shifts because of the presence of the $O = C - C = C - P = O$ unit. $C_b$ would be expected to give the most downfield signal. The spectrum should further show one primary $SP^3$ carbon ($C_e$) as a doublet of doublets as it should couple with both of the P atoms, a secondary $SP^3$ carbon ($C_a$) as a doublet of doublets

because of its coupling with both of the P atoms and the aromatic

protons as a complex multiplet in the usual position for such

signals. In the $^{13}$C spectrum of the compound actually recorded,

$C_a$ appears as a doublet centred at $\delta$ = 38.26 with $^1J_{P'-C}$ = 75.19.

In this instance, unlike the precursors (LXXXI) and (LXXXVI), $^3J_{P^2C}$ =

0 Hz. The carbon atom of the carbonyl group, $C_b$, appears as a

triplet (centred at the expected position of $\delta$ = 196.00) because

of identical coupling with both of the P atoms ($^2J_{P'-C}$ = $^3J_{P^2-C}$ =

20.14 Hz). Similarly, $C_c$ also appears as a triplet centred at $\delta$ = 166.44

with $^2J_{P'-C}$ = $^2J_{P^2-C}$ = 2.69 Hz and such a shift is typical of $\beta$-carbon

atom in the C = C - P = O unit as mentioned earlier. The remaining ring

carbon atom $C_d$ appears as a doublet of doublets centred at $\delta$ = 149.52

with $^1J_{P'-C}$ = 73.86 Hz and $^1J_{P^2-C}$ = 63.11 Hz (or _vice versa_). The

corresponding C atom in the two precursors (LXXXI) and (LXXXVI) could

not be observed because of masking by the aromatic signals. However,

in the case of XCIII, the inductive effect of the C = O group  shifts

the signal into an observable region. $C_e$ appears as the usual doublet

of doublets centred at $\delta$ = 13.23 with $^3J_{P'-C}$ = 13.43 Hz and $^3J_{P^2-C}$ =

5.37 Hz while the aromatic protons appear as a complex multiplet at

the normal position of $\delta$ = 126.5 - 133.2. The $^{13}$C spectral results

obtained are entirely consistent with the postulated structure and,

therefore, the structure (XCIII) is unambiguously confirmed.

It should be noted here that while during the purification

of the freshly prepared exocyclic methylene compound (LXXXVI) by

column chromatography, the compound was usually obtained in a pure form, it was occasionally observed that trace amounts of another material contaminated this precursor of (XCIII). This contaminant was not the 4-oxo-2-phospholene (XCIII) as might be expected but was yet another oxidation product of the exo methylene compound (LXXXVI). Discussion of this new oxidation product will be deferred until a little later as it is much more easily prepared by a controlled oxidation reaction.

Since the conversion of the exo methylene compound (LXXXVI) into the ketone (XCIII) by spontaneous oxidation takes an unusually long time, a controlled and more rapid reaction would be desirable. Such a reaction is also desirable from the point of view of establishing the mechanism of this most unexpected oxidation. In considering possible mechanisms, a free-radical process seemed likely because of the conditions under which the spontaneous reaction occurs.

Initial experiments were carried out by treatment of (LXXXVI) in ethanol or chloroform with hydrogen peroxide. However, it was observed that although $H_2O_2$ does indeed oxidize (LXXXVI), complete conversion into the ketone (XCIII) takes ca. 20 - 25 days at room temperature. No significant change in the rate of oxidation was observed at higher temperatures. Clearly, this process is too slow and represents little advantage over the spontaneous reaction. Also, it provides

little mechanistic information.

Since the reaction could be free-radical initiated as mentioned earlier, it was decided to expose (LXXXVI) to oxygen in the presence of an efficient radical initiator such as AlBN (azobisiso-butyronitrile) under a variety of conditions. It was found that under a slow stream of air, AlBN not only catalyzes the oxidation of (LXXXVI) to the ketone (XCIII) relatively rapidly (48 hours) in benzene at 70°C (moderate yield), but also yields two isomeric epoxides characterized as (XCVIIA) and (XCVIIB) (good yield). The overall reaction is shown in the sequence (LXXXVI) → (XCIII) + (XCVIIA) + (XCVIIB).

This result confirms that the reaction is indeed free radical catalysed and the nature of the three products obtained suggests



(LXXXVI)          (XCIII)          (XCVIIA) (major)

                                   (XCVIIB) (minor)
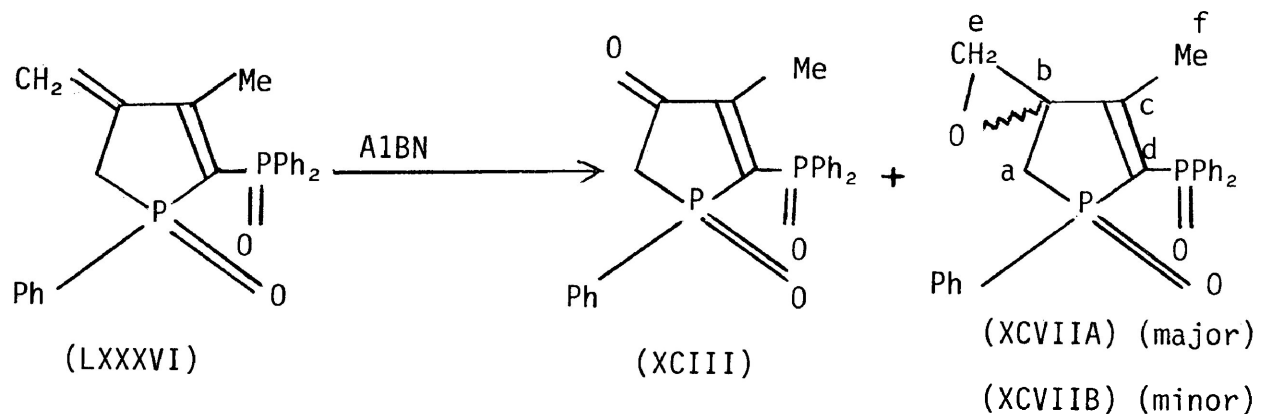
a possible mechanism for the reaction as there are several precedents for this type of oxidation in unsaturated hydrocarbon chemistry (139). This possible mechanism will be considered again after the isolation and structural proof of the two epoxides have been considered. It should also be noted in passing that the two epoxides (XCVIIA) and (XCVIIB) are apparently the first reported spiro-oxirano phosphorus heterocycles although other ring-fused epoxides of five-membered phosphorus heterocycles are well known (9,138).

The crude mixture of the ketone and the two epoxides obtained from the AlBN catalysed oxidation of (LXXXVI) is easily purified by column chromatography (see Experimental section). The ketone is eluted first, followed by the minor epoxide isomer. The major epoxide is retained quite strongly by the column. The maximum yields obtained are 26% for the ketone and 28% and 10% respectively for the major and minor epoxides. The two epoxides have been well characterized by the usual analytical and spectroscopic techniques although the actual stereochemistry of each stereoisomer about $C_4$ of the ring relative to the orientation of the P = O group has not been established. The two epoxide stereoisomers have considerably different melting points, significant differences in their $^{31}P$ spectra and some minor differences in their $^1H$ and $^{13}C$ spectra. They both give excellent C, H and P analyses for the proposed formulation and the mass spectrum in each case confirms the molecular weight as 420.

Considering first the major epoxide stereoisomer
(XCVIIA), the $^{31}P$ spectrum shows the ring P atom (P') as the usual
doublet centred at $\delta$ = 46.5 and the side chain P atom (P$^2$) as
another doublet centred at $\delta$ = 20.27 with $^2J_{P-P}$ = 31.65 Hz. The
two coupled and non-equivalent P atoms observed in the spectra of the
various precursors of this compound are therefore clearly present.
The chemical shift of the ring P atom is also much more typical of a
5-membered phosphorus heterocycle than is the case in the spectrum of
the ketone (XCIII).


The $^1H$ NMR spectrum of this major epoxide (XCVIIA) shows
fifteen aromatic protons as a complex multiplet at $\delta$ = 6.70 - 8.25 with
the _ortho_ protons, as is common in the spectra of arylphosphine oxides,
slightly downfield of the main multiplet. The two non-equivalent
methylene protons of the oxirano (epoxide) ring occur as a doublet of
doublets, characterstic of an AB pattern, centred at $\delta$ = 3.21 with
$^2J_{H-H}$ = 5.0 Hz. The chemical shifts of these two protons are $\delta$ = 3.17
and $\delta$ = 3.28 respectively and neither of these protons is coupled with
either of the P atoms. The two phospholene ring methylene protons appear
as a narrow multiplet at $\delta$ = 2.27 - 2.82 quite similar in appearance to
that observed in the spectra of the related structures (LXXXVI) and
(XCIII). Finally, the three allylic methyl protons are observed as a
triplet centred at $\delta$ = 2.10 apparently coupled equally with the two
P atoms ($^4J_{P'-H}$ = $^4J_{P^2-H}$ = 2.0 Hz) as is the case in the spectra of
other diphenylphosphoryl substituted 2-phospholene-1-oxide derivatives

so far discussed. As is also the case with the other 2-phospholene-1-oxides discussed earlier, the two phospholene ring protons can not be assigned individual shifts or H-H or P-H coupling constants. The reasons for this have been discussed earlier.

Both the $^{31}$P and the $^1$H spectra of this major epoxide product are, therefore, in excellent agreement with the proposed general structure (XCVII) for the two possible epoxides.

The $^{13}$C spectrum of the compound was recorded and is again entirely consistent with the proposed general structure according to the principles outlined for similar structures earlier in this chapter. The observed chemical shifts and coupling constants are: $\delta$ = 33.83, $^1J_{P'-C}$ = 70.80 Hz, $^2J_{P^2-C}$ = 3.66 Hz for $C_a$; $\delta$ = 63.65, $^2J_{P'-C}$ = $^3J_{P^2-C}$ = 20.14 Hz for $C_b$; $\delta$ = 175.64, $^2J_{P'-C}$ = 11.60 Hz, $^2J_{P^2-C}$ = 3.05 Hz for $C_c$; $\delta$ = 53.19, $^3J_{P'-C}$ = 3.05 Hz, $^4J_{P'-C}$ = 0 Hz for $C_e$; and $\delta$ = 13.45, $^3J_{P'-C}$ = 14.03 Hz, $^3J_{P^2-C}$ = 5.49 Hz for $C_f$. The aromatic protons appear as the usual multiplet at $\delta$ = 123.86 - 138.62 and the signals of $C_d$ are obscured by the aromatic signals.

Considering now the minor stereoisomer (XCVIIB), the $^{31}$P spectrum shows the usual pattern with the ring P atom (P') as a doublet centred at $\delta$ = 43.93, which is on the low side of the range generally observed for 5-membered phosphorus heterocycles of this type,

and the side chain P atom as another doublet centred at $\delta$ = 21.61 with $^2J_{P-P}$ = 31.34 Hz. The significant difference between the $^{31}P$ spectrum of this isomer and that of the major isomer (XCVIIA) discussed earlier is noteworthy.

The $^1H$ spectrum of (XCVIIB) is quite similar to that of (XCVIIA). It shows fifteen aromatic protons as a complex multiplet at $\delta$ = 6.67 - 8.32 with the ortho protons, as usual, slightly downfield of the main multiplet. The two non-equivalent methylene protons of the oxirane ring occur as a doublet of doublets (with the AB pattern observed for the major isomer (XCVIIA)) with shifts of $\delta$ = 3.17 and 3.24 respectively ($^2J_{H-H}$ = 5.5 Hz). As with the major isomer, no P - H coupling is observed in these signals. The 2-phospholene ring methylene protons appear as a multiplet of at least 8 signals at $\delta$ = 2.20 - 3.00 (with the exact shifts and coupling constants not assignable for the reasons outlined earlier), and, finally, the three allylic methyl protons are observed as a triplet centred at $\delta$ = 2.12 ($^4J_{P'-H}$ = $^4J_{P^2-H}$ = 2.0 Hz).

The biggest difference between this $^1H$ spectrum and that of the major isomer (XCVIIA) is the coupling pattern exhibited by the ring methylene protons.

The $^{31}P$ and the $^1H$ spectra, therefore, fit the proposed

general structure (XCVII) very well and this assignment of structure is confirmed by the $^{13}C$ spectrum which should be, and is, similar to that of the major isomer. The $^{13}C$ spectrum shows $C_a$ as a doublet of doublets centred at $\delta$ = 34.60 with $^1J_{p'-C}$ = 67.82 Hz and $^2J_{p^2-C}$ = 3.39 Hz. $C_b$ also appears as a doublet of doublets centred at $\delta$ = 62.35, as would be expected from its attachment to oxygen, with $^2J_{p'-C}$ = 23.05 and $^3J_{p^2-C}$ = 18.99 Hz (or _vice versa_). $C_c$ appears as a further doublet of doublets centred at $\delta$ = 175.60, the usual downfield position for such carbon atoms, with $^2J_{p'-C}$ = 11.53 Hz and $^2J_{p^2-C}$ = 2.71 Hz. In addition, the spectrum shows $C_e$ as a doublet centred at $\delta$ = 52.52 with $^3J_{p'-C}$ = 3.39 Hz. As is the case with the major isomer this carbon atom is not coupled with the side chain P atom. Finally, $C_f$ appears as the expected doublet of doublets centred at $\delta$ = 13.49, with $^3J_{p'-C}$ = 13.90 Hz and $^3J_{p^2-C}$ = 5.4 Hz, while the aromatic carbon atoms appear as a complex multiplet at the usual location of $\delta$ = 127.5 - 134.55. Again, as is usually the case, the signals of $C_d$ are obscured by these aromatic signals. Thus, the $^{13}C$ spectra of the major and minor epoxide stereoisomers (XCVIIA) and (XCVIIB) are almost, but not quite, identical.

These two epoxides can be made much more easily and quickly by the conventional oxidation of (LXXXVI) with m-chloro-perbenzoic acid (MCPBA) which is quite frequently used (138) in such oxidations. Again, there is a stereochemical preference for what has been described as the major stereoisomer but this epoxidation seems

to be less selective than the A1BN catalysed reaction yielding 38% of the major isomer and 22% of the minor isomer.

The actual stereochemistries about C4 of these two stereoisomeric epoxides were not determined partly because the problem was not directly relevant to the main theme of this thesis and partly because the equipment required was not readily available to this author. However, it might be possible to establish the two stereochemistries by dipole moment studies since the stereoisomer in which the oxygen atom of the oxirane ring and the oxygen atom of the ring $P = O$ group are on the same side of the ring should have the higher dipole moment. However, the substitution pattern of the system is quite complex and X-ray crystallographic studies may be necessary.

Before leaving this discussion of the two epoxides, one further point should be made. Thus, a little earlier in this discussion, it was noted that the freshly isolated 4-methylene compound (LXXXVI) was sometimes contaminated with an oxidation product which was not the ketone (XCIII). This contaminant proved to be the minor epoxide just discussed.

Turning now to the mechanism of the oxidation, it is undoubtedly an oxidation by molecular oxygen catalysed by a free radical initiator. In the case of the solid state reaction, the initiator

remains unknown but, in solution, AlBN readily acts as an initiator.

The mechanism is therefore probably basically the same as that of the

autoxidation of styrene which has been discussed in detail elsewhere

(139). The radical catalysed oxidation of styrene is very complex

but the main pathway appears to be addition of $O_2$ to the radical

initiator to give $RO_2$· which then adds to the terminal methylene

group of styrene to give $Ph\overset{\bullet}{C}HCH_2OOR$. This reacts with more $O_2$ and then

more styrene to give a polyperoxide radical which then cleaves and

"unzips" to give benzaldehyde, formaldehyde and styrene oxide. Further

details are available elsewhere and will not be given here. However,

the probable mechanism as it applies to the oxidation of (LXXXVI) is

illustrated in condensed form in Scheme 3.


This reaction sequence shows that in the decomposition

of the polyperoxide radical, the first cleavage occurs at the end of

a polymeric chain. This chain end portion gives the major and

minor epoxides (styrene oxide in the case of styrene). The remainder

of the polyperoxide chain then "unzips" to give the ketone (XCIII)

and formaldehyde although attempts to detect formaldehyde were not

made. The epoxide ring closure may occur either from the same side

of the phospholene ring as the P = O group giving the cis isomer or

from the opposite side of the ring giving the trans isomer. Assuming

that the oxygen of the ring phosphoryl group lies above the plane of

the ring, the epoxide ring closure might be electronically favoured

from the opposite side of the ring because of electrostatic repulsions

SCHEME 3
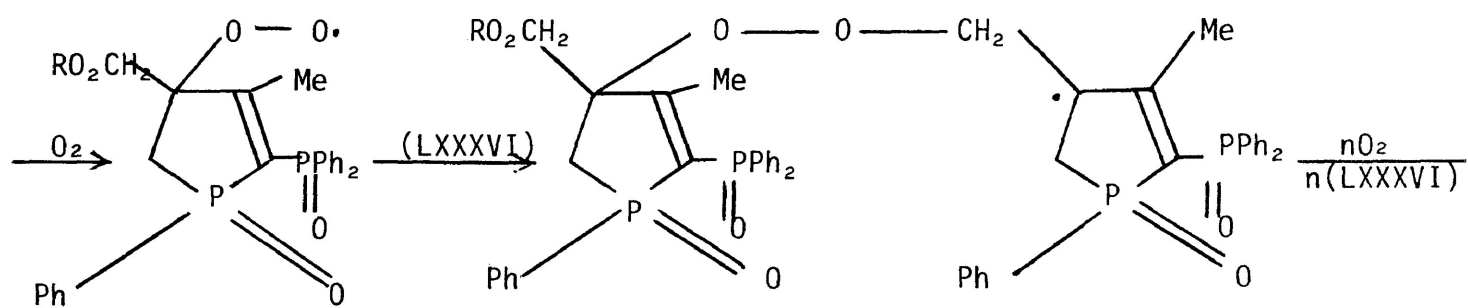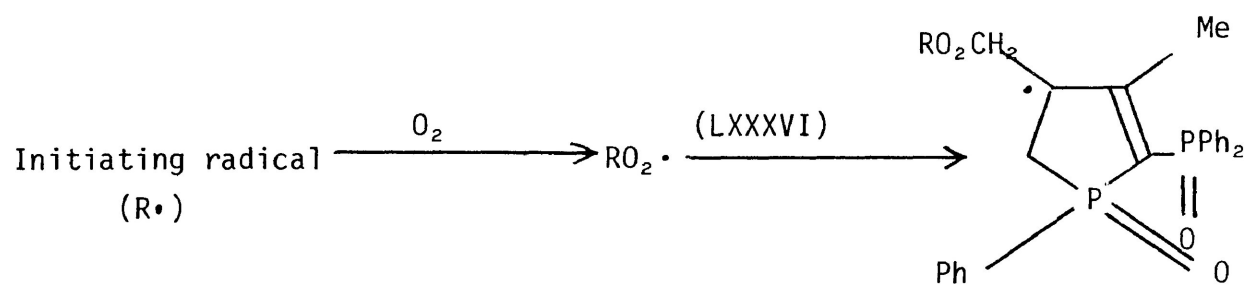
SCHEME 3 continued...



Polyperoxide radical



RO· + nHCO +

(XCIII)          (XCVII)
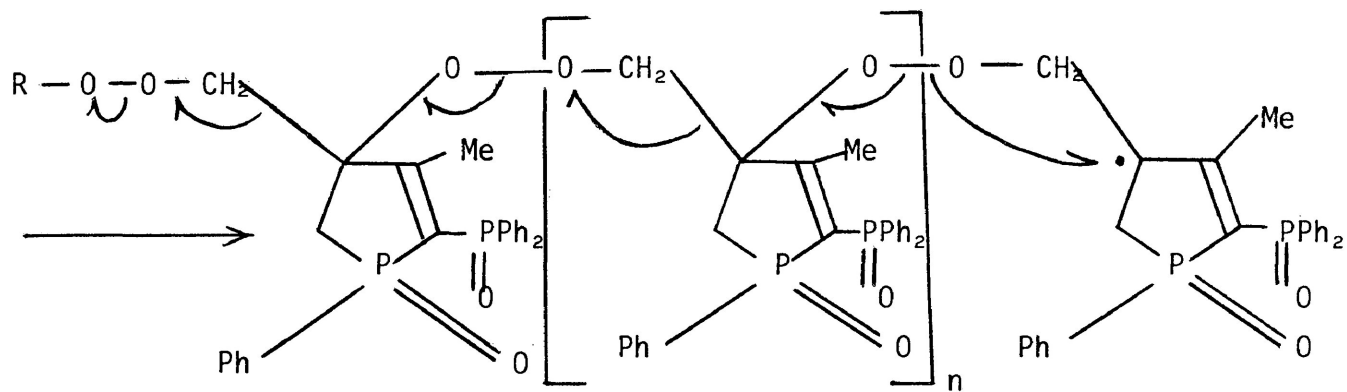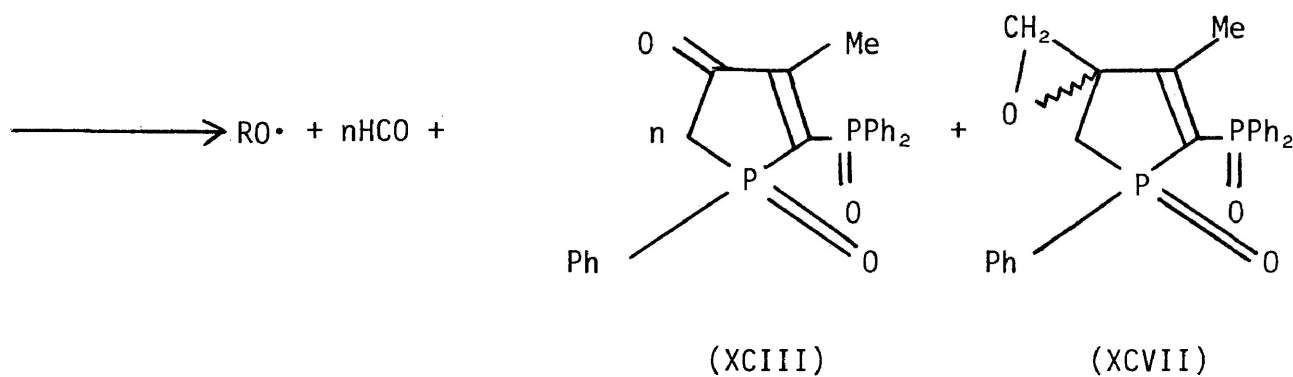
between the two negative oxygen atoms. On the other hand, since the phenyl group is bulkier than the oxygen of the ring phosphoryl group, the epoxide ring formation might be sterically favoured from the same side of the ring as the P = O group. In any case, ring closure to give an epoxide would not be equally likely from either side of the ring and this is observed since the two isomers are formed roughly in the ratio 3:1. For epoxide ring formation, the same arguments apply to the MCPBA oxidation of (LXXXVI). However, this reaction is stereospecifically cis addition of oxygen (from the point of view of the double bond) which proceeds via a rigid, cyclic transition state. Thus, while similar steric and electronic arguments would apply they would not necessarily do so to the same extent and a different product ratio would be observed as is the case.

During the spontaneous oxidation of (LXXXVI), the ketone (XCIII) is the only product isolable. This suggests that , in the proposed pathway outlined in Scheme 3, the polyperoxide radicals formed have long chains because there are few initiating radicals present and, since cleavage of each chain gives only one epoxide molecule, but many ketone molecules, the ratio of ketone to epoxide formed is high. In this case it is so high that epoxide formation is not observed. On the other hand, the AlBN catalysed oxidation always gives the ketone and the epoxides in moderate yields. If the mechanism proposed above is correct, this indicates that during the AlBN catalysed oxidation, relatively short chain polyperoxide radicals are formed. Indeed, this

might well be expected as there are many initiating radicals present. As the polyperoxide chains are short, the ratio of the ketone formed to epoxide formed should be relatively small and, as is observed, reasonable amounts of the two possible epoxides should be formed.

However, if the polyperoxide radical chains contain more than three or four units, the yield of the ketone should be higher than that of the epoxides if the postulated mechanism is followed exactly but it is observed that the AlBN catalysed oxidation of the 4-methylene compound (LXXXVI) gives the epoxides in higher yield than the ketone. In this connection, it was stated earlier that the mechanism of oxidation is complex in that there are several competing reactions and it should be mentioned here that Mayo et al. (140,141) also reported higher yields of epoxides than aldehydes in the radical catalysed oxidations of 2-butene and cyclooctene. This is thought to be due to the fact that if and as aldehydes or ketones accumulate in such a reaction mixture, another reaction in which the co-oxidation of the aldehyde or ketone product with the alkene starting material results in the formation of additional epoxide products, becomes of importance. This may well be the case in the AlBN catalysed oxidation of (LXXXVI).

Also mentioned earlier, the spontaneous oxidation of (LXXXVI) occurs even in the dark and at low temperatures. This indicates that the reaction is not activated photochemically or thermally. The

nature of the radical initiator for this spontaneous oxidation is not yet known but it seems likely that it is carried right through the synthesis and purification of (LXXXVI) and originates from the synthesis of the bromo compound (LXXXV) which does involve radical reactions.

Returning now briefly to the original aims of this project, although the formation of the ketone (XCIII) from the exo methylene compound (LXXXVI) was quite unexpected, this compound (XCIII) apparently has much potential as a precursor to a variety of phosphole derivatives such as (XCVIII), (XCIX) or (C) which could be derived from (XCIII) by various reductive processes. However, the oxidation

(XCVIII)                    (XCIX)                    (C)
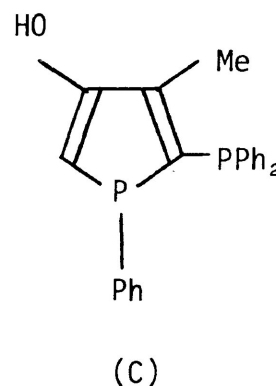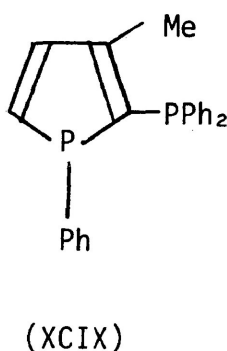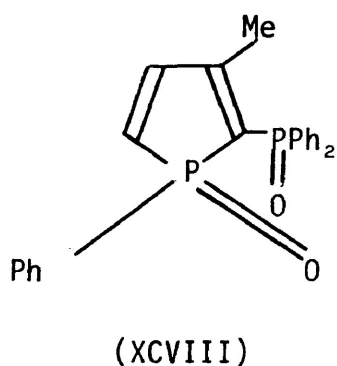
reaction is intrinsically interesting and is also potentially useful, if general, for the synthesis of a variety of 4-oxo-2-phospholenes

which have received attention recently (138). Since a number of 4-methylene-2-phospholene derivatives related to (LXXXVI) have appeared in the literature over the years, it seemed worthwhile to digress from the original objectives for a short investigation of the generality of this reaction. The results of this brief study are outlined in the next subsection.

2.5        Possible generality of the free-radical oxidation of the exocyclic double bond in 4-methylene-2-phospholene derivatives

As has been noted elsewhere (138), 4-oxo-2-phospholene derivatives (e.g. XCVI) containing a chiral tetracoordinate phosphorus atom have some potential (142,143) as chiral reagents in a variety of heterocyclic syntheses. Such compounds have been prepared (and resolved)(138) by a three-step procedure from the corresponding 3-phospholene derivatives although details of this synthesis will not be given here. The relationship of the 4-oxo-compound (XCIII) to these 4-oxo-2-phospholene oxides therefore raised the question of whether the free-radical catalysed oxidation of the 4-methylene-2-phospholene oxide (LXXXVI) could be extended to 4-methylene-2-phospholene oxides in general thereby providing an alternative route to the potentially valuable 4-oxo-compounds.

As mentioned in the previous subsection, several 4-methylene-2-phospholene derivatives have been reported in the

literature and, with the above idea in mind, the 4-methylene-2-
phospholene sulfide (LXXXVIII) was selected for an attempted
AlBN catalysed oxidation. This compound was selected for two
reasons. First, it can be prepared relatively easily and the
immediate precursor (CI) was already available in our laboratories.
Second, as well as going some way towards establishing the generality,
or otherwise, of the desired reaction, the feasibility of the oxida-
tion in a 2-phospholene sulfide system rather than a 2-phospholene
oxide system would also be established.

The known compound (LXXXVIII) has been prepared from
the isomeric phosphole sulfide (CI) according to the literature pro-
cedure (134). However, while the structure of this compound is not
in doubt, full spectroscopic characterization was not given in the
earlier report and is therefore given here.



(CI)                    (LXXXVIII)
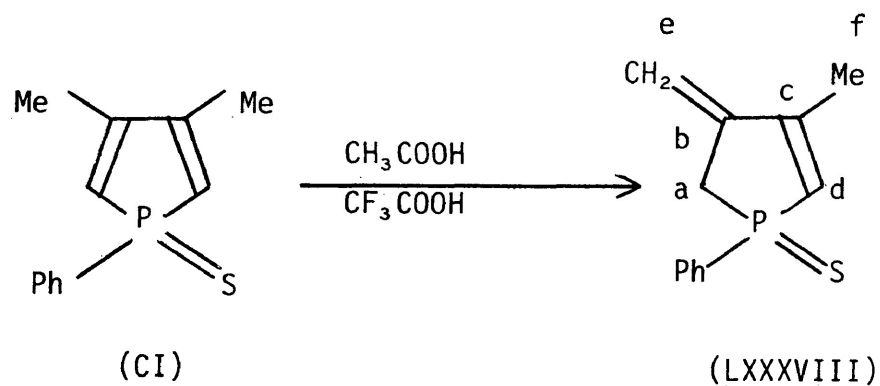
The $^{31}$P spectrum of the compound shows a sharp singlet at $\delta$ = 48.94 (lit. $\delta$ = 47.50). This chemical shift is, as mentioned earlier, typical of 5-membered phosphorus heterocycles of this general type.

The $^1$H spectrum shows five aromatic protons as a complex multiplet at $\delta$ = 7.20 - 8.12 with the _ortho_ protons slightly down-field of the main signal, one ring olefinic proton as a doublet of two slightly broadened peaks centred at $\delta$ = 6.07 with $^2J_{P-H}$ = 25 Hz, each of the exo cyclic non-equivalent olefinic protons as a very closely spaced multiplet centred at $\delta$ = 5.27 and $\delta$ = 5.42 respectively, two ring methylene protons as a narrow multiplet consisting mainly of two broadened peaks of unequal area at $\delta$ = 3.0 - 3.32 and three allylic methyl protons as a triplet centred at $\delta$ = 2.13 apparently coupled equally with the P atom and the ring olefinic proton ($^4J_{P-H}$ = $^4J_{H-H}$ = 1.5 Hz). That each of the peaks of the ring olefinic proton doublet is broadened is consistent with coupling with the allylic methyl protons as suggested above. The signals of the exocyclic olefinic protons are slightly different from each other in multiplicity with the higher field signal split into at least four peaks and the lower field signal into at least five peaks of unequal intensities. Since the splitting patterns of these signals are very similar to those of the similar type of protons in the 4-methylene compound (LXXXVI), it seems likely that by analogy with the spectrum of (LXXXVI), this fine structure is due to coupling of these protons

mainly with the ring methylene protons and, to some extent, either with the P atom or to each other. The signals due to the two non-equivalent ring methylene protons are very similar in appearance to those of the related 2-phospholene derivatives (LXXXVI) and have been (XCIII) discussed in detail earlier.

The observed $^{13}C$ chemical shifts and coupling constants for this compound are entirely consistent with the proposed structure (LXXXVIII). The signals observed are: $\delta$ = 40.37, $^{1}J_{P-C}$ = 59.0 Hz for $C_a$; $\delta$ = 145.55, $^{2}J_{P-C}$ = 9.49 Hz for $C_b$; $\delta'$ = 156.60, $^{2}J_{P-C}$ = 12.89 Hz for $C_c$; $\delta$ = 112.99, $^{3}J_{P-C}$ = 13.56 Hz for $C_e$; and $\delta$ = 16.35, $^{3}J_{P-C}$ = 16.95 Hz for $C_f$. The spectrum also shows the aromatic carbons as a complex multiplet at $\delta$ = 123.92 - 135.06 and the signals of $C_d$ are, as usual, obscured by the aromatic signals. The $^{13}C$ spectral results are therefore in excellent agreement with those which would be predicted and, indeed, are quite similar to those observed for (LXXXVI) if the couplings due to the additional side-chain P atom in the later are ignored. The structure (LXXXVIII) is, therefore, unambiguously confirmed.

In addition, the analytical data are in excellent agreement with the formula $C_{12}H_{13}PS$ and the mass spectrum shows the molecular ion at the expected value of m/e 220.

Considering now the AlBN catalysed oxidation of (LXXXVIII),

it has been found that this compound undergoes the desired oxidation

under similar reaction conditions to those employed in the oxidation

of (LXXXVI) to give the ketone (CII) in moderate yield (30%) with

little evidence for the formation of the epoxides (CIV) corresponding

to (XCVIIA) and (XCVIIB). The reaction therefore seems cleaner

than that of (LXXXVI). However, quite unexpectedly, another ketone



(LXXXVIII)          (CII)          (CIII)

+

A trace of an

unidentified product

(CIV)
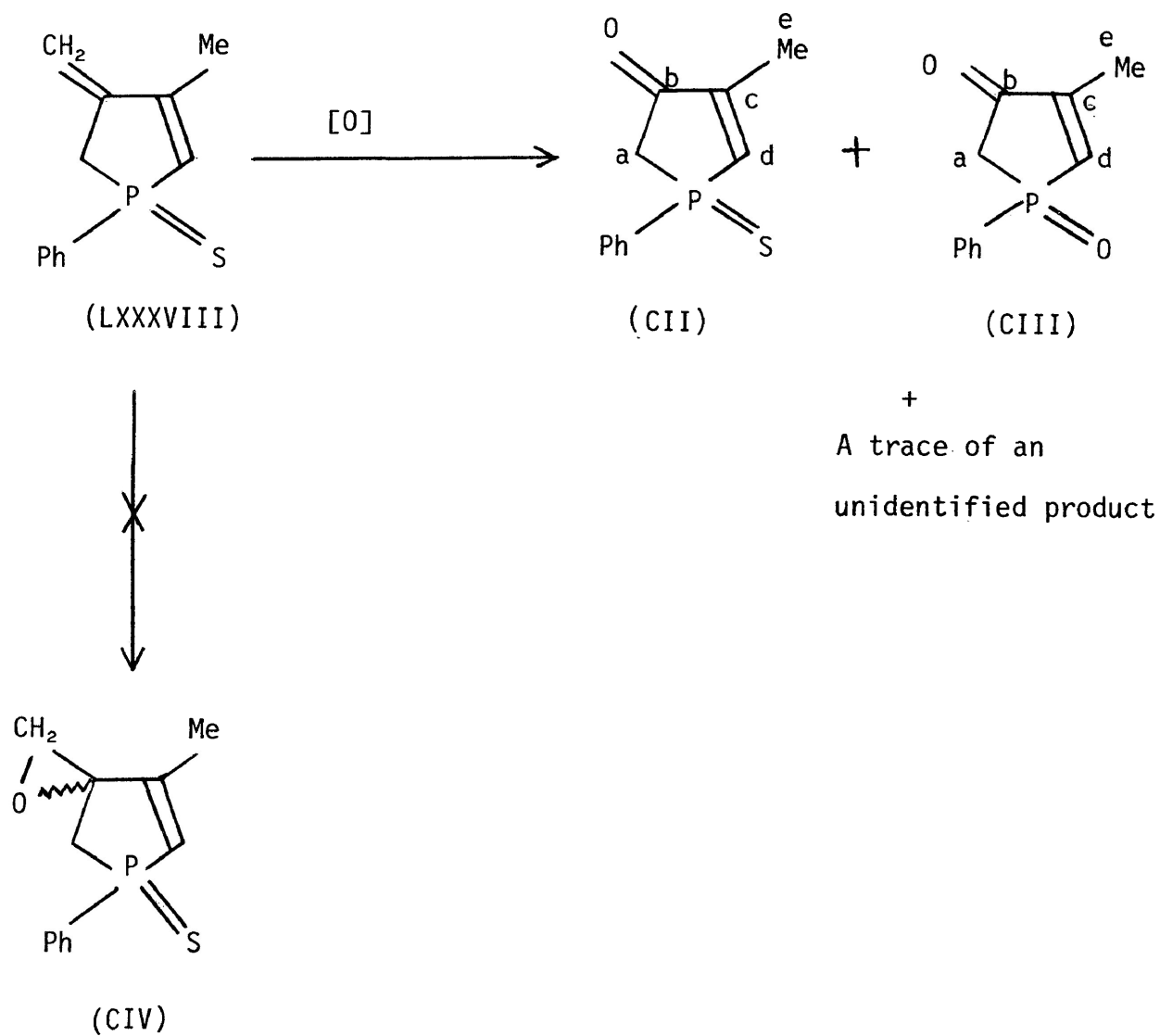
characterized as (CIII), has been isolated from the above reaction

mixture in relatively low yield (10%). Both of these new compounds

have been characterized by the usual analytical and spectrocopic

studies. C and H analytical data for both very freshly prepared com-

pounds are good but reliable P analyses (carried out commercially

elsewhere) were difficult to obtain because of the hygroscopic nature

of these compounds. The mass spectra of the 4-oxo compounds (CII)

and (CIII) showed molecular ion peaks at the expected values of m/e

222 and m/e 206 respectively.


The IR spectrum of the compound for which the 4-oxo-2-phospholene

oxide structure (CII) has been postulated shows a sharp C = O stretching

vibration at 1708 cm$^{-1}$ and the $^{31}$P spectrum shows a sharp singlet

at $\delta$ = 31.98 which is very close to that of the ring P atom of (XCIII).

This unusually highfield location for the $^{31}$P signal of such 4-oxo-

therefore seems to be general.


The $^1$H spectrum of this product shows five aromatic protons

as a complex multiplet at $\delta$ = 7.35 - 8.12, the ring olefinic proton

as a doublet of quartets (because of coupling with the P atom and

the allylic methyl protons) centred at $\delta$ = 7.18 with $^2J_{P-H}$ = 19.5 Hz

and $^4J_{H-H}$ = 1.5 Hz, the two ring methylene protons as a narrow

multiplet at $\delta$ = 2.75 - 3.30 as observed for such protons in related

structures discussed earlier, and the three allylic methyl protons

as a doublet of doublets apparently coupled unequally with the P atom

and the ring olefinic proton with $^4J_{P-H}$ = 2 Hz and $^4J_{H-H}$ = 1.5 Hz. The ring olefinic proton signals appear at much lower field than those of the similar proton in the precursor (LXXXVIII) as would be expected because of the presence of the electron-withdrawing carbonyl group.

The $^{13}C$ spectrum of the compound was recorded and is in excellent agreement with the proposed structure. The chemical shifts and coupling constants observed are: $\delta$ = 43.50, $^1J_{P-C}$ = 60.35 Hz for $C_a$; $\delta$ = 198.69, $^2J_{P-C}$ = 16.31 Hz for $C_b$; $\delta$ = 154.47, $^2J_{P-C}$ = 3.30 Hz for $C_c$; $\delta$ = 145.14, $^1J_{P-C}$ = 67.81 for $C_d$ and $\delta$ = 13.63, $^3J_{P-C}$ = 14.92 Hz for $C_e$. The spectrum also shows the aromatic carbons as a complex multiplet at $\delta$ = 128.0 - 132.73. As with the related compound (XCIII), the presence of the carbonyl group causes the ring carbon atom $C_d$ signal to shift to lower field where it may be observed free of interference from the aromatic carbon atom signals.

The spectroscopic data for the other ketone for which the structure postulated is (CIII) are very similar to those of (CII). Thus, the IR spectrum shows a sharp carbonyl vibration at 1710 cm$^{-1}$ and an additional P = O peak, not present in the spectrum of (CII), appears at 1215 cm$^{-1}$. The $^{31}P$ spectrum shows a sharp singlet at $\delta$ = 30.71 which is very close to the chemical shifts of the ring P atoms of the other two ketones (XCIII) and (CII) already discussed. Again, the unusually highfield location of this signal should be noted.

The $^1$H spectrum is also very similar to that of (CII) and shows the five aromatic protons as a complex multiplet at $\delta = 7.38 - 7.92$, the ring olefinic proton as a doublet of quartets centred at $\delta = 7.24$ with $^2J_{P-H} = 15.0$ Hz and $^4J_{H-H} = 2.0$ Hz, the two ring methylene protons as the usual narrow multiplet at $\delta = 2.5 - 3.3$ (slightly broader than observed for (CII)) and the three allylic methyl protons as a triplet centred at $\delta = 2.13$ coupled equally with the P atom and the ring olefinic protons ($^4J_{P-H} = {}^4J_{H-H} = 2.0$ Hz). The only significant differences from the spectrum of (CII) are the lower field location of the ring olefinic proton (because of the neighbouring P = O group ) and the fact that in the spectrum of (CIII), the methyl protons appear as a triplet.

The $^{13}$C spectrum should be very similar to that observed for (CII) and this is the case. The chemical shifts and the coupling constants are: $\delta = 37.94$, $^1J_{P-C} = 74.60$ Hz for $C_a$; $\delta = 196.97$, $^2J_{P-C} = 6.70$ Hz for $C_b$; $\delta = 158.42$, $^2J_{P-C} = 6.10$ Hz for $C_c$; $\delta = 143.71$, $^1J_{P-C} = 83.41$ Hz for $C_d$ (now observable as in the cases of (XCIII) and (CII)) ; and $\delta = 13.71$, $^3J_{P-C} = 15.6$ Hz for $C_e$. The spectrum also shows the aromatic carbons as a complex multiplet at $\delta = 129.05 - 133.00$. The structure (CIII) is, therefore, unambiguously confirmed.

The formation of the ketone (CIII) during the oxidation of the 4-methylene-2-phospholene sulfide (LXXXVIII) clearly results from the replacement of sulfur of (CII) by oxygen. In view of the

fact that the reaction was carried out under a constant flow of air for a considerable time (ca. 36 hours), such a replacement is not unexpected but whether it is due to a radical catalysed process or is simply a conventional oxidation was not investigated.

By analogy with the mechanism suggested in Scheme 3 for the corresponding reaction with (LXXXVI), the AlBN catalysed oxidation of (LXXXVIII) should also yield the two possible isomeric epoxides (e.g. CIV). The formation of such epoxides has not, however, been detected with any certainty although a trace of another product, which was found to contain only one type of phosphorus atom ($\delta$ = 49.79), has been isolated. The $^1$H spectrum of this product showed that it was heavily contaminated with hydrocarbon-like materials and, because of the very small quantity obtained, isolation and purification of this compound was not further pursued. The insignificant amount of the epoxide formed (if any) indicates that either the polyperoxy chains formed during the reaction are very long and/or that the other processes (mentioned earlier) which can lead to epoxide production are only minor pathways in this particular reaction.

The successful oxidation of the 4-methylene compound (LXXXVIII) into the ketones (CII) and (CIII) indicates, therefore, that the exocyclic double bond at C4 of a 2-phospholene oxide or sulfide derivative can be readily oxidized to an oxo group by molecular oxygen in the presence of AlBN as a catalyst. Since the two 4-methylene-2-

phospholene derivatives (LXXXVI) and (LXXXVIII) which undergo
this reaction differ considerably in substitution pattern, it is
highly probable that the reaction is general and a further route to
4-oxo-2-phospholene oxides or sulfides is therefore now available.
Two examples of a reaction are not, however, sufficient to prove
generality and other examples would be desirable. With this in mind,
another 4-methylene-2-phospholene oxide (LXXXVII) was selected from
the literature for A1BN catalysed oxidation. Because of time
limitations and because of the need to make one or two further attempts
at the synthesis of 2-phosphino-substituted phosphole derivatives
based upon the approach outlined earlier in this chapter, only pre-
liminary steps in the synthesis of (LXXXVII) could be taken. These
are reported in a later sub-section. Meanwhile, the next subsection
reports the interesting results of an investigation of the 4-oxo-2-
phospholene derivative (XCIII) as a possible source of 2-phosphino-
substituted phosphole derivatives.


2.6        Attempted construction of a 2-diphenylphosphoryl-
           substituted phosphole oxide ring using the 4-oxo-
           2-phospholene derivative (XCIII)


        The 4-oxo-2-phospholene derivative (XCIII), as mentioned
in subsection 2.4, could be a potential precursor for 2-diphenyl-
phosphoryl- or 2-diphenylphosphinophosphole derivatives and it appeared
to this author that there are two ways in which this transformation
could be brought about. The first of these involves reduction of the

carbonyl group to the corresponding secondary alcohol which would
then be dehydrated to give the desired phosphole oxide system
according to the sequence (XCIII) → (CV) → (XCVIII). The second
approach involves reduction of the ring P = O bond of (XCIII) followed



(XCIII)                    (CV)                    (XCVIII)



(CVI)
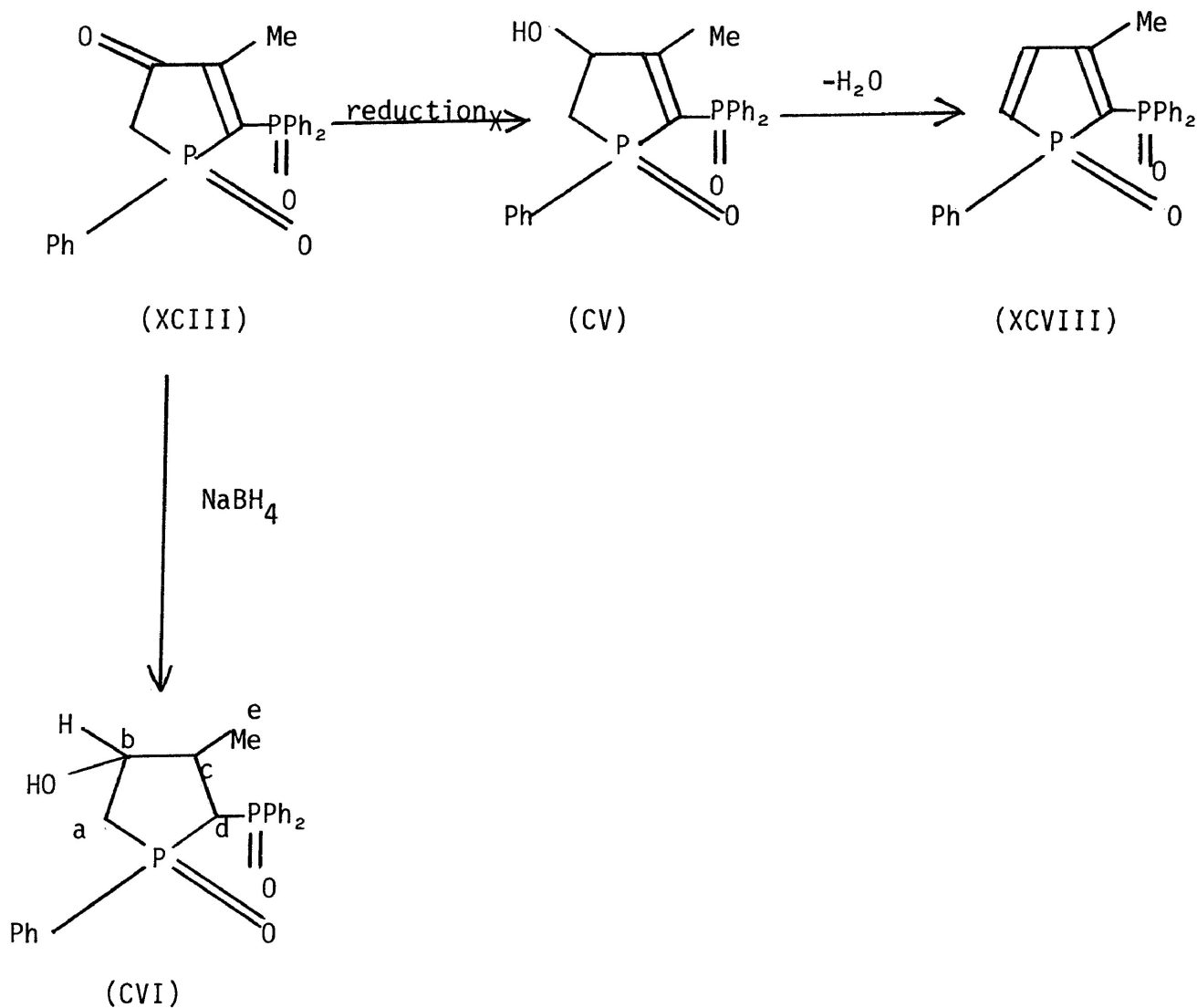
by possible tautomerization of the resulting 4-oxo-2-phospholene
to give the corresponding 4-hydroxylphosphole although it was
realized that such a tautomerization is unlikely unless the phosphole
which would be produced has very considerable aromatic character.
The results of these two studies will now be considered.

The first route was chosen on the assumption that the
C = O group of (XCIII) could be reduced by a suitable reducing agent to
give the alcohol (CV) without affecting the ring double bond. This
alcohol, on subsequent dehydration, would give the diphenylphosphoryl
substituted phosphole derivative (XCVIII) which, since the steric
effect of 3,4-disubstitution on the ring which has complicated these
reactions so far has now been removed, would be unlikely to adopt
an exocyclic double bond structure at C3.

9-BBN (9-Borabicyclo[3.3.1]nonane) has been reported (144)
to be a very good reagent for the selective reduction of a C = O
group in $\alpha,\beta$-unsaturated carbonyl compounds. The compound (XCIII)
was, therefore, treated with a 0.5 M solution of 9-BBN in dry THF
under $N_2$ according to the literature procedure (144). However, a very
complex mixture of products was obtained as shown by the $^{31}P$ spectrum
of the crude material. Repeated attempts to isolate pure components
from this crude mixture were not successful.

The inability of 9-BBN to reduce the C = O group of

(XCIII) selectively could perhaps be due to the fact that the ring

and/or side-chain P = O groups compete with the oxygen atom of the

carbonyl group for the electron deficient boron atom of 9-BBN and

reductions, possibly involving ring cleavage in certain instances,

could occur at at least three sites in the molecule. However, the

$^{31}P$ spectrum of the crude product mixture is so complex that it is not

possible to make any definitive comment on what actually happens

during the reaction. Other reducing agents therefore had to be

considered.

Another reducing agent which has been successfully used

for the selective reduction of a C = O group in $\alpha,\beta$-unsaturated

carbonyl compounds is DlBAL-H (Diisobutylaluminium hydride)(145).

Since the reduction of (XCIII) into (CV) was not achieved using 9-BBN,

DlBAL-H (1M solution in hexane) was therefore tried using the

published procedure (145). Again, as in the case of 9-BBN, this

reaction yielded a complex mixture from which isolation of pure components

was not possible. As with 9-BBN, the complicating factor is

probably the three sites in (XCIII) which could undergo reduction.

Since these two attempted reductions of (XCIII) to (CV)

were not successful some other reducing agent had to be found. In

this connection, although $NaBH_4$ is not particularly good as a selective

reducing agent, there are reports in the literature (146,147) which

show that it can occasionally be used successfully for the reduction

of a C = O group in $\alpha,\beta$-conjugated systems under very mild conditions. Furthermore, P = O groups are normally unaffected by $NaBH_4$. The ketone (XCIII) was therefore treated with $NaBH_4$ in 95% ethanol at low temperatures according to the published procedure (146) and it was found that the ketone (XCIII) undergoes reduction very smoothly to give an alcohol as indicated by the IR spectrum. Thus, this product shows a broad -OH vibration at 3200 - 3400 $cm^{-1}$ and the C = O peak present in the spectrum of precursor (XCIII) is absent in the spectrum of the product. The product mixture is much less complex than that obtained with 9-BBN and D1BAL-H and the $^{31}P$ spectrum of the crude material shows only two main sets of doublets of doublets of unequal intensities (one strong, one relatively weak) along with some other minor peaks. The various spectra of the pure product isolated from this mixture will be discussed shortly. Purification was easily effect by dry column chromatography and only one component was obtained in the pure form. This has been characterized as the saturated alcohol (CVI) and not the desired unsaturated alcohol (CV). The first evidence that this is the case was provided by the mass spectrum which showed a molecular ion peak at m/e 410 which corresponds to the addition of four hydrogen atoms to the starting material (XCIII).

The pure compound isolated is a colorless solid with a sharp melting point and it has been well characterized by analytical and spectroscopic methods. Thus, the C and H analyses (carried out

in these laboratories) and the P analysis (carried out commercially elsewhere) are in excellent agreement with the proposed structure.

The $^{31}$P spectrum of the compound shows the ring P atom (P$^1$) as a doublet centred at $\delta = 60.05$, which is well within the range normally observed for 5-membered phosphorus heterocycles and is somewhat downfield of the ring P atoms in the various products described so far in this thesis. The side-chain P atom (P$^2$) also appears as a doublet centred at $\delta = 31.59$ ($^2J_{p-p} = 2.2$ Hz) with the low coupling constant presumably a result of the change in hybridization at $C_d$ which would greatly change the angular relationships between the two P atoms. This chemical shift for the side-chain P atom signal is also significantly downfield from those observed so far for the side-chain P atoms in the various 2-pospholene oxide precursors in which the chemical shifts have been found to be around $\delta = 20.0$. Such a downfield shift for the signals of both the ring and the side-chain P atoms is presumably due to the hydrogenation of the ring double bond (which will be unambiguously proved shortly) at the position $\alpha$ to the P(IV) atom since a C = C bond adjacent to a P(IV) atom normally (but not always) produces a shielding effect (9). This is because the d-orbitals share some of the electron density on the $\alpha$-carbon and in general an increase in d-orbital utilization produces shielding.

It should be mentioned here in passing that this type

of downfield shift for a side-chain P atom has also been observed for a similar kind of P atom in one of the uncharacterized components obtained from the trichlorosilane reduction of the 4-methylene compound (LXXXVI). This provides further evidence that, during the trichlorosilane reduction of (LXXXVI), a considerable amount of ring hydrogenation also occurs.

The $^1$H spectrum of the compound shows the fifteen aromatic protons as a complex multiplet at $\delta = 6.80 - 7.95$, the range being slightly upfield from the aromatic proton signals in the various 2-phospholene oxides precursors. The hydroxyl hydrogen atom appears as a doublet centred at $\delta = 6.12$ ($J = 8.75$ Hz) which is at unexpectedly low field for an alcoholic hydrogen. However, the fact that the hydrogen is indeed alcoholic has been confirmed by addition of $D_2O$ which causes the signal to vanish completely. Such a downfield shift of the alcoholic hydrogen might be explained by intramolecular or intermolecular H-bonding with the ring (or side-chain) P = O group. The relatively low frequency range (3200 - 3400 $cm^{-1}$) for the OH vibration observed in the IR spectrum of the compound is another indication of H-bonding.

The tertiary hydrogen at C4 appears as a doublet of multiplets centred at $\delta = 4.38$ ($^3J_{P-H} = 27.0$ Hz) and the ring

methylene protons are observed as a narrow multiplet at $\delta$ =
2.9 - 3.41 which consists of eight peaks of unequal area apparently
indicating that they are coupled with the ring P atom and the C4
tertiary proton. The two tertiary protons at C2 and C3 appear
as a multiplet at $\delta$ = 2.42 - 2.77 which consists of mainly five
peaks some of which are broad indicating that more peaks are ob-
scured by these observed signals. Finally, the methyl protons appear
as a doublet centred at $\delta$ = 1.28 apparently coupled only with the
adjacent tertiary proton ($^3J_{H-H}$ = 7.0 Hz). These methyl protons
appear well upfield from the allylic methyl protons in the various
2-phospholene oxide precursors as would be expected.

Several double resonance $^1$H experiments have been
carried out to verify the couplings among the different protons.
Thus, irradiation at the middle of the hydroxyl proton doublet
brings changes only at the signals of the C4 tertiary proton.
Therefore, the hydroxyl proton is coupled with the C4 tertiary
proton ($^3J_{H-H}$ = 8.75 Hz). Such coupling between two protons through
an oxygen at atom is quite often not observed in alcohols (e.g.
ethyl alcohol) and the compound is therefore clearly free of
acidic or basic impurities. This coupling was confirmed by
further irradiation at the middle of the C4 tertiary proton doublet
of multiplets which causes the hydroxyl proton doublet to collapse
to a singlet. During this particular irradiation, the multiplets
of the ring methylene protons and the C2 and C3 protons also undergo

some changes. Thus, the tertiary proton at C4 is coupled with the
ring P atom ($^3J_{P-H}$ = 27.0 Hz), the hydroxyl proton ($^3J_{H-H}$ = 8.75
Hz), the ring methylene protons and the C3 proton. Coupling with
the C2 proton is very unlikely. Further double irradiation experi-
ments confirmed the remainder of the suggested coupling pattern.

The $^{31}P$ and the $^1H$ spectra are therefore in excellent
agreement with the proposed structure (CVI) and this structure
is further supported by the $^{13}C$ spectrum in which the coupling
patterns of certain carbon atoms are quite interesting when compared
with those of the unsaturated precursors. Thus, $C_a$ appears as a
doublet centred at $\delta$ = 39.31 with $^1J_{P'-C}$ = 66.46 Hz. As in the
precursor (XCIII), $^3J_{P^2-C}$ = 0 Hz. Similarly, $C_c$ also appears as
a doublet centred at $\delta$ = 44.11 with $J_{P-C}$ = 8.81 Hz ($^2J_{P'-C}$ or
$^2J_{P^2-C}$) and $C_d$ appears as a doublet of doublets, as would be
expected, centred at $\delta$ = 49.59 with $^1J_{P'-C}$ = 61.37 Hz, $^1J_{P^2-C}$ =
48.83 Hz (or _vice_ _versa_). The signals of $C_b$ are obscured by the
solvent ($CDCl_3$) signals and this is indicated by some extra multipli-
city (not properly resolved) of the solvent signals. Because of
solubility problems, the spectrum could not be recorded in any other
deuterated solvent.

Turning now to stereochemical aspects of the reduction,
in theory, 16 stereoisomers of the compound (CVI) are possible since

there are four chiral centres (ring P, C2, C3 and C4). However, since the stereochemistry about the ring P atom is fixed throughout the reduction, 8 stereoisomers could, in theory, be produced in this synthesis of (CVI). Rather surprisingly, however, only one stereoisomer (as shown by the various spectra) was isolated and the reduction therefore apparently shows considerable selectivity although, as mentioned earlier in this subsection, the $^{31}$P spectrum of the crude NaBH$_4$ reduction product shows another relatively weak doublet of doublets at $\delta$ = 47.04 and $\delta$ = 30.55 respectively with $^2J_{P-P}$ = 6.05 Hz. These shifts and the coupling constant indicate that this component could be another stereoisomer. The compound could not be isolated in pure form because it is retained so strongly by the chromatographic column used for purification that it is eluted in impure form only with methanol. No further attempts at the isolation and purification of this obviously minor component were made.

The various reductions described above were repeated many times under different conditions but absolutely no indication of selective reduction of the carbonyl group of (XCIII) was obtained. An alternative route was therefore considered for one last attempt at construction of a 2-diphenylphosphino-substituted phosphole derivative. This involved the reduction of the P = O groups of the ketone (XCIII) by trichlorosilane to give (CVII) on the assumption that if the phosphole (C), isomeric with (CVII), had significant aromatic character, the resonance energy in (C) might provide

sufficient driving force for the isomerization of (CVII) to (C). It was recognized, of course, that this was something of a "long-shot" because, in keto-enol equilibria, the equilibrium normally lies far on the keto side. However, in exceptionally favourable cases where enolization can give an aromatic ring (e.g. cyclohexadienone→phenol), the enol form is favoured. One such case in phosphorus heterocyclic chemistry is the $\lambda^3$-phosphorin (CX)(148).



(XCIII)     (CVII)     (C)

(CVIII)     (CIX)     (CX)
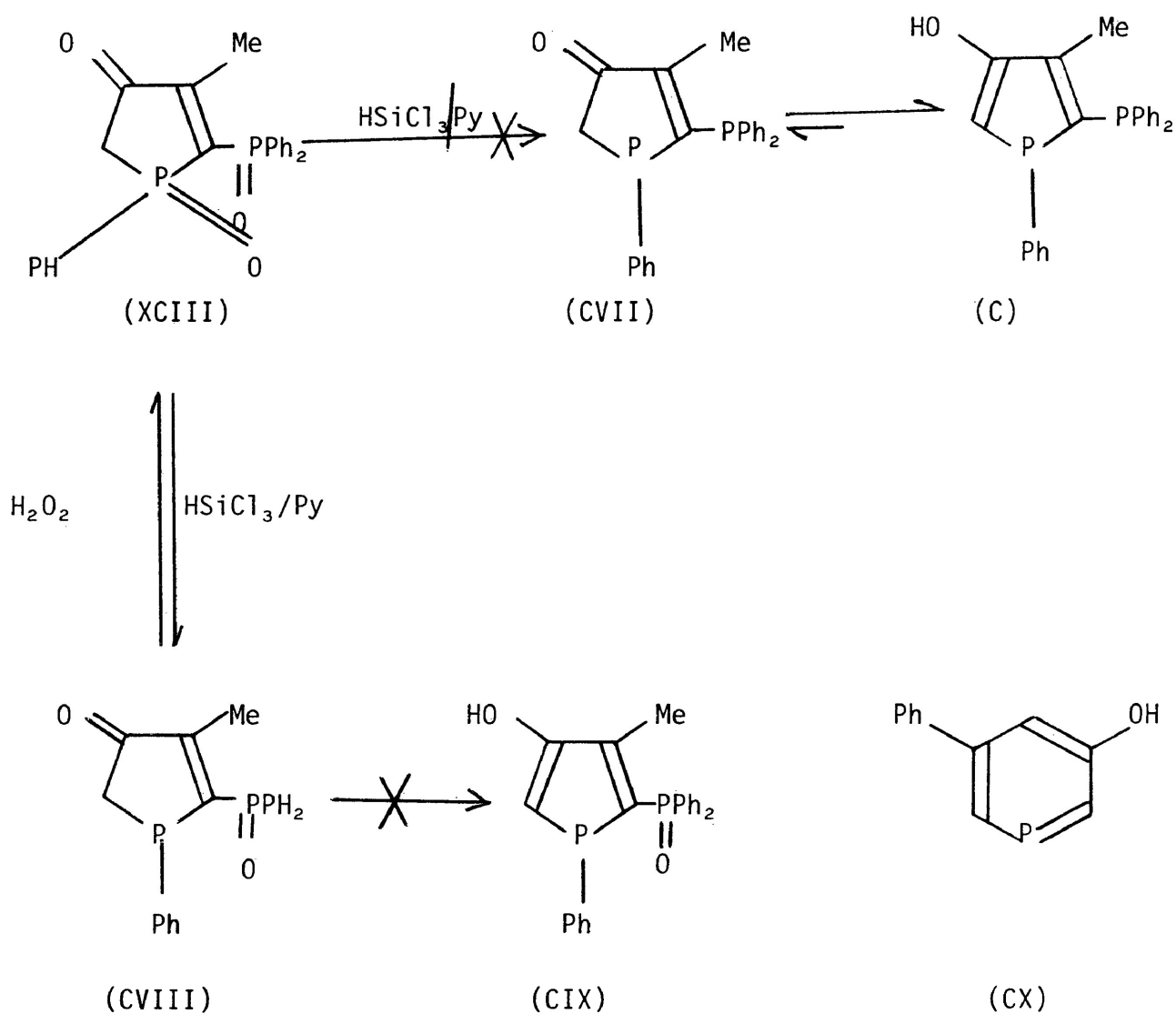
It was found that, using only a slight excess of trichlorosilane (in the presence of pyridine), the ketone (XCIII) undergoes reduction smoothly to give a new compound which was later characterized as the 4-oxo-2-phospholene (CVIII). The reaction was repeated varying the amount of trichlorosilane but the same result was obtained. Thus, the trichlorosilane reduction of (XCIII) occurs in a similar manner to the trichlorosilane reduction of the 4-methylene compound (LXXXVI) in that it is the ring P = O group which is the most sensitive to reduction. In this case, no ring hydrogenation was detected and the reduction appears to be very clean.

Analytical data were not obtained for this compound because the reaction was done on a very small scale, the product is a viscous liquid from which it is difficult to remove the last traces of solvent and the compound is somewhat hygroscopic like the other 4-oxo-compounds already discussed. However, it was well characterized spectroscopically. Thus, the IR spectrum of the compound shows a strong and sharp C = O stretching vibration at 1710 $cm^{-1}$ showing that the carbonyl group is unaffected by the reduction. The $^{31}P$ spectrum shows the ring P atom (P') as a doublet centred at $\delta$ = -28.44 and the side-chain P atom as another doublet centred as usual at $\delta$ = 23.70 with $^2J_{P-P}$ = 51.2 Hz. These chemical shift values are similar to those observed in the spectrum of (XCI),

and indicate that the ring P = O group has been reduced whereas the side-chain P = O group is not. It should also be noted that the ring P resonance is upfield of that of (XCI) which again illustrates the strong shielding effect of the 4-oxo-group. The mass spectrum shows a molecular ion peak at m/e = 390 which is also in agreement with the fact that only one of the P = O groups is reduced and that no hydrogenation has occurred. The probable reasons for the differences in reactivity of the two P = O groups towards trichlorosilane have already been outlined in the discussion of the trichlorosilane reduction of (LXXXVI).

The $^1$H spectrum is also in agreement with the proposed structure. It shows the fifteen aromatic protons as a complex multiplet at $\delta$ = 6.5 - 8.05 and the two ring methylene protons as a multiplet at $\delta$ = 2.23 - 2.75 consisting of eight peaks of unequal intensities of the general form which would be expected (see earlier discussion of similar structures). The three allylic methyl protons appear as a very narrow doublet of doublets centred at $\delta$ = 2.15 apparently coupled unequally with the two P atoms ($^4J_{p^1-H}$ = 2.0 Hz, $^4J_{p^2-H}$ = 2.25 Hz or _vice versa_). The chemical shifts of all the protons are slightly upfield from those of similar protons of the precursor (XCIII) as would be expected because of the loss of one P = O oxygen atom.

The structure of the compound has been finally confirmed by reoxidation with $H_2O_2$ which regenerates the ketone (XCIII) in quantitative yield.

However, while the successful reduction of (XCIII) to give (CVIII) is of interest, isomerization of (CVIII) to give (CIX) was not observed and one must conclude that, as in the case of (XCI), this isomeric phosphole has little if any aromatic character.

This reaction concluded this author's investigation of this route to five-membered heterocycles containing both ring and side-chain phosphorus atoms. The route is obviously quite satisfactory generally for compounds of the thesis title type but the particular structural type in which the five-membered heterocycle is the fully unsaturated phosphole ring is not readily attainable by this route and some modification of the approach is required. Further reference to this will be made shortly.

Only one topic now remains to be discussed. Thus, it was mentioned earlier that further studies towards establishing the generality of the A1BN catalysed oxidation of 4-methylene-2-phospholenes were started but not completed. These are reported briefly in the next subsection.

2.7    Further studies directed towards establishing the generality of the oxidative cleavage of the 4-methylene double bond in 4-methylene-2-phospholene derivatives

The importance of establishing beyond doubt the generality of the AIBN catalysed oxidation of an exocyclic double bond in 4-methylene-2-phospholene derivatives has already been discussed in subsection 2.5. After the successful such oxidation of the second of these 4-methylene compounds (LXXXVIII), the generality of this AIBN catalysed oxidation seemed highly likely but it was decided to attempt to verify further the general applicability of the above oxidation using the 4-methylene compound (LXXXVII). This compound was chosen for extension of these studies because its synthesis is apparently straightforward and the reagents required for the synthesis are easily available. It should be remembered here, however, that this work was started while various aspects of the main theme of the thesis were still under investigation. This additional study therefore could not be completed because of time limitations but some new information, in particular the synthesis of the previously uncharacterized (CXI), was acquired.
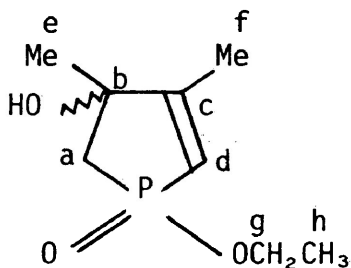


(CXI)

The original method used by Mathey et al. (133) for the synthesis of this 4-methylene compound (LXXXVII) is shown in Scheme 4 and the starting material, i.e. 1-ethoxy-3,4-dimethyl-3-phospholene 1-oxide (CXIII), is easily prepared according to the sequence (LXXVI) → (CXII) → (CXIII).



(LXXVI)          (CXII)          (CXIII)
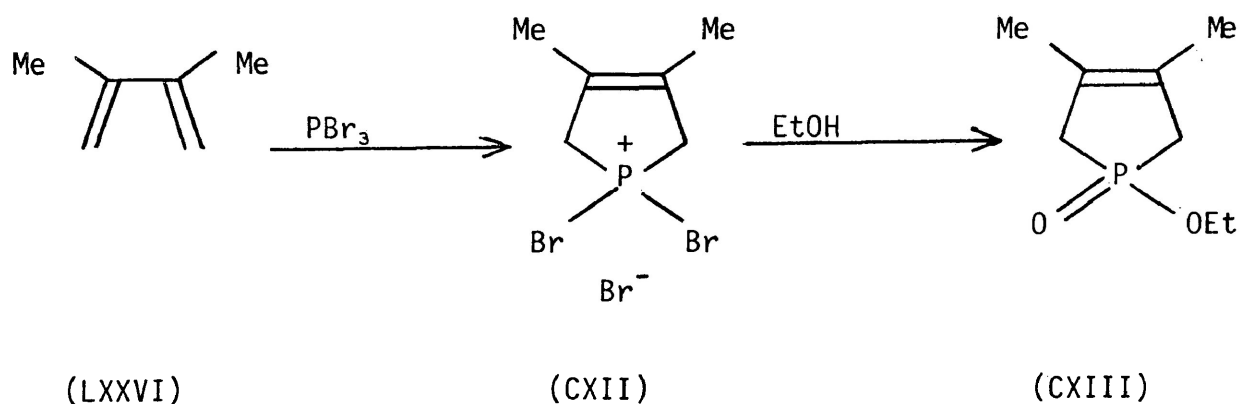
The adduct (CXII) was prepared by this author in the usual manner by McCormack cycloaddition of 2,3-dimethyl-1,3-butadiene and $PBr_3$ in n-hexane. The adduct is very hygroscopic and was, therefore, handled in a $N_2$-filled glove box. The adduct (CXII), on alcoholysis

in the presence of triethylamine at low temperatures, gives the 3-phospholene oxide derivative (CXIII). This compound was obtained as a colorless solid after purification by dry column chromatography. The compound has been known for some years (9) but, for the sake of having complete information available, a full $^{31}P$ and $^{1}H$ spectroscopic characterization was carried out.

The $^{31}P$ spectrum of the compound shows a sharp signal at $\delta = 68.84$ and the $^{1}H$ spectrum of the compound is entirely consistent with the structure (CXIII). Thus, the two ethoxy methylene protons appear as a doublet of quartets centred at $\delta = 4.09$ as would be expected because these protons couple with the P atom ($^{2}J_{P-H} = 9.0$ Hz) and the adjacent methyl protons ($^{3}J_{H-H} = 7.0$ Hz). The four ring methylene protons appear superficially as a doublet centred at $\delta = 2.44$ and the main coupling is with the P atom ($^{2}J_{P-H} = 13.0$ Hz).

However, the peaks are broad and there is evidence of some additional coupling and the pattern may be a rather simplified form of the pattern observed for similar non-eqivalent ring methylene protons in similar structures discussed earlier. The six allylic methyl protons appear as a narrow doublet centred at $\delta = 1.74$ with $^{4}J_{P-H} = 1.75$ Hz and, finally, the three ethoxy methyl protons are observed as a triplet centred at $\delta = 1.36$ with $^{3}J_{H-H} = 6.0$ Hz.

SCHEME 4



(CXIII)     n-BuLi     (CXIV)     $O_2$ / $H^+$     (CXV)

$-H_2O$
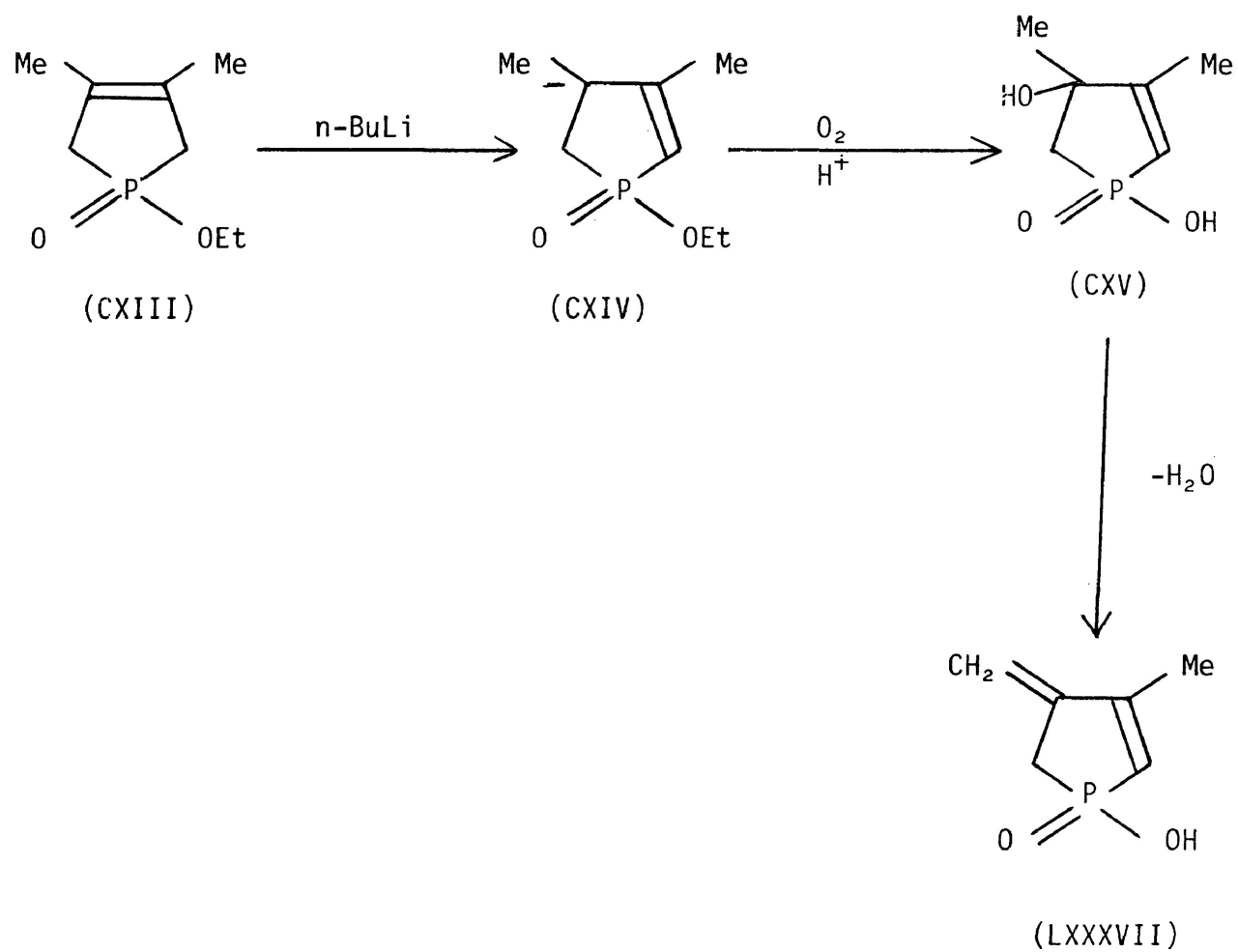
(LXXXVII)

The 3-phospholene oxide derivative (CXIII) was then used in an attempted synthesis of (LXXXVII) according to the published procedure (133)(Scheme 4). However, the $^{31}P$ spectrum of the crude product shows two sharp signals of almost equal area very close to each other at $\delta$ = 61.59 and $\delta$ = 60.99 respectively. The crude product is, therefore, a mixture of two components. Both shifts indicate the P atom of a P = O group in a five-membered ring. However, purification by dry column chromatography yields only one component in pure form which has been characterised as (CXI) and not (LXXXVII) obtained by Mathey (133). It should be mentioned here that the two components of the crude product mixture have very similar $R_f$ values and only very careful collection of the fractions from the column gave one of the components in pure form. The second component was always contaminated with the first when eluted from the column.

The compound (CXI) is a colorless solid with a sharp melting point. It has been characterized by the usual analytical and spectroscopic methods and the C, H and P analyses are in excellent agreement with the formula $C_8H_{15}PO_3$. The mass spectrum shows the expected molecular ion peak at m/e = 174.

The $^{31}P$ spectrum of the pure compound isolated from the product mixture shows a sharp signal at $\delta$ = 61.40 and this

chemical shift is in the range normally observed (9) in 2-phospholene oxide systems.

The $^{1}$H spectrum shows the ring olefinic proton as a doublet of quartets (signals of similar pattern have already been observed for ring olefinic protons in (CII) and (CIII)) centred at $\delta$ = 5.68 with $^{2}J_{P-H}$ = 19.0 Hz and $^{4}J_{H-H}$ = 1.25 Hz. The hydroxyl hydrogen appears as a broad singlet at $\delta$ = 4.44 and the ethoxy methylene protons appear as a doublet of quartets, somewhat better resolved than those of its precursor (CXIII), centred at $\delta$ = 4.05 with $^{2}J_{P-H}$ = 9.0 Hz and $^{3}J_{H-H}$ = 7.0 Hz. The two ring methylene protons appear, rather suprisingly in view of their potential non-equivalence, as a sharp doublet centred at $\delta$ = 2.16 with $^{2}J_{P-H}$ = 14.0 Hz and the three allylic methyl protons are observed as a doublet of doublets centred at $\delta$ = 2.0 because of coupling with the P atom and the olefinic proton ($^{4}J_{P-H}$ = 1.75 Hz, $^{4}J_{H-H}$ = 1.0 Hz, or vice versa). The three other methyl protons attached to the ring appear as a singlet at $\delta$ = 1.48 and, finally, the three ethoxy methyl protons occur as a triplet centred at $\delta$ = 1.31 with $^{3}J_{H-H}$ = 7.0 Hz.

The $^{13}$C spectrum of the compound is also entirely consistent with the proposed structure and the spectrum shows each carbon atom as a doublet as would be expected because of P-C coupling. The observed chemical shifts and coupling constants are: $\delta$ =

40.26, $^1J_{P-C}$ = 91.56 Hz for $C_a$; δ = 168.63, $^2J_{P-C}$ = 24.41 Hz for $C_c$; δ = 119.07, $^1J_{P-C}$ = 123.43 Hz for $C_d$; δ = 28.37, $^3J_{P-C}$ = 6.78 Hz for $C_f$ and δ = 61.45, $^2J_{P-C}$ = 6.1 Hz for $C_g$. Finally, the doublets of $C_e$ and $C_h$ are so close to each other that it is not possible to make a definite assignment. However, the chemical shifts of these two carbon atoms are δ = 16.65 and 15.26 and the coupling constants are $^3J_{P-C}$ = 6.11 and 22.38 Hz respectively. The signals of $C_b$ are obscured by the solvent signals as is the case for the alcohol (CVI) mentioned earlier.

Thus, the $^{31}$P, the $^1$H and the $^{13}$C spectra are in excellent agreement with the structure (CXI) and, therefore, the structure is unambiguously confirmed.

As mentioned earlier, the crude product was a mixture of two components. The $^1$H spectrum of the crude product resembles the $^1$H spectrum of (CXI) superimposed on another spectrum of a similar pattern. This clearly indicates, as does the $^{31}$P spectrum, that two stereoisomers of the same basic structure are obtained during the reaction.

Although the synthesis of the desired 4-methylene compound (LXXXVII) was not immediately successful, the intermediate compound (CXI) obtained could possibly be dehydrated to give a related 4-methylene compound (CXVI). However, as mentioned earlier, time
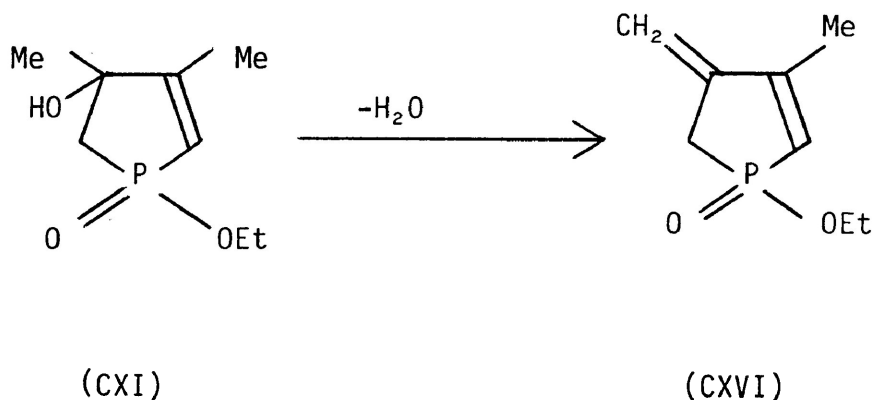
limitations dictated that further investigations on the synthesis
of either (LXXXVII) or (CXVI) and the feasibility of the AlBN
catalysed oxidation of these compounds could not be carried out.

One last point should be mentioned here and that is
that in Mathey's synthesis of (LXXXVII) (133) outlined in Scheme 4,
the structure isolated here and characterized as (CXI) is probably
the immediate precursor of (CXV). It would seem then that Mathey
used somewhat more acidic conditions which prevented the isolation
of (CXI) (and, for that matter CXV, because of acid catalysed
dehydration) in his experiments.

## 2.8    Conclusions

The approach investigated and reported here is excellent for the synthesis of a variety of 2-phosphoryl substituted 2-phospholene derivatives. However, the scheme originally proposed for the synthesis of phosphine-substituted phospholes is clearly unsuitable for such systems if they contain substituents at both the 3- and 4-positions. On the other hand, the approach may well work for phosphine-substituted phospholes having either only one or no substitutent at the 3- or 4-position.

4-Methylene-2-phospholene derivatives seem to be particularly susceptible to free radical catalysed oxidations and there is some evidence for the general nature of the conversion of an exocyclic double bond at C4 of a 2-phospholene derivative to an oxo group by AlBN catalysed oxidation. This could offer a useful alternative route to the synthetically useful 4-oxo-2-phospholene oxide system.

It appears also that trichlorosilane is particularly useful for the selective reduction of a ring phosphoryl group in a 2-phosphoryl substituted 2-phospholene oxide system.

Most of the reactions encountered in this study are

either stereospecific or stereoselective.

Finally, the $^{13}$C spectra of these various 2-phosphoryl-
2-phospholene derivatives are of interest because of the complex
array of long-range couplings they exhibit while the shielding effect
of a 4-oxo group in the 2-phospholene system is worthy of further
study.

## 2.9 Suggestions for further work

The present work has clearly indicated possibly fruit-
ful areas for further investigation. For example, the selective
reduction of the C = O group of the 4-oxo-2-phospholene derivative
(XCIII) should, as mentioned earlier, be attempted using a wider
range of suitable reducing agents at lower temperatures and with
different molar ratios and rates of addition. In this connection,
LiAlH$_4$ has been found (147) to be a better selective reducing agent
for such groupings than NaBH$_4$ in certain reactions.

In addition, it would be useful, to attempt the synthesis
of the as yet unknown 4-methylene-2-phospholene derivative (CXVI)
and the known (LXXXVII) for further studies of the generality of
the AlBN (or other radical) catalysed oxidation which was discussed
extensively in subsection 2.4. This AlBN catalysed oxidation may

further be extended to other known 4-methylene-2-phospholene
derivatives such as (CXVII) (9).
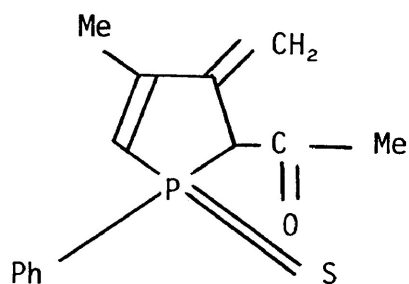


(CXVII)

Although this is a minor point, attempts could be made
to establish the stereochemistries of the epoxide stereoisomers
(XCVIIA) and (XCVIIB) by the methods already mentioned in sub-
section 2.4.

The final and perhaps most important of these suggestions
is that synthesis of 2-phosphino-substituted phospholes containing
either only one substituent or no substituents at the 3- or 4-
positions (e.g. LXXII) should be pursued as outlined in Scheme 2.
The procedure may, however, have to be modified because delocalization
of the negative charge in the anionic precursor (LXVIII) could cause
the P-containing side chain to be introduced at the 2- or 4-position

of the phospholene ring.  However, separation and purification
of structures of this type by dry column chromatography has
proved to be very effective with such mixtures and separation
problems could be minimal.  It should be mentioned here that this
author made a brief and preliminary attempt at the synthesis of
the phosphoryl substituted phospholene oxide system  (CXVIII)
and successfully obtained a crude solid product, the $^{31}$P spectrum
of which showed that it was a mixture of at least two compounds with
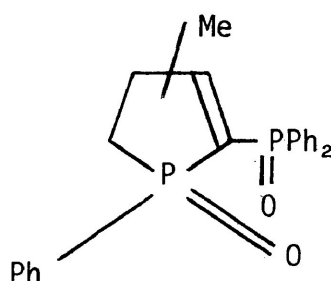


(CXVIII)

chemical shift and coupling constant values typical of the ring and
side-chain P = 0 groups observed in the spectra of systems already
discussed.  This approach therefore shows some promise.

These studies should not, of course, be limited to
phosphino-substituted five-membered heterocycles and extension to
six-membered phosphorus heterocycles is perfectly feasible.  For

example, it has been established (149) that $\lambda^3$-phosphorins
react readily with phenyllithium to give anions which then react
with electrophiles to give either $\lambda^5$-phosphorins  or ring
addition    $\alpha$ to the P atom.  A typical such sequence leading to
(CXXI) and (CXXII) is shown below and, clearly the process might be
modified to give compounds of type (CXXIII).
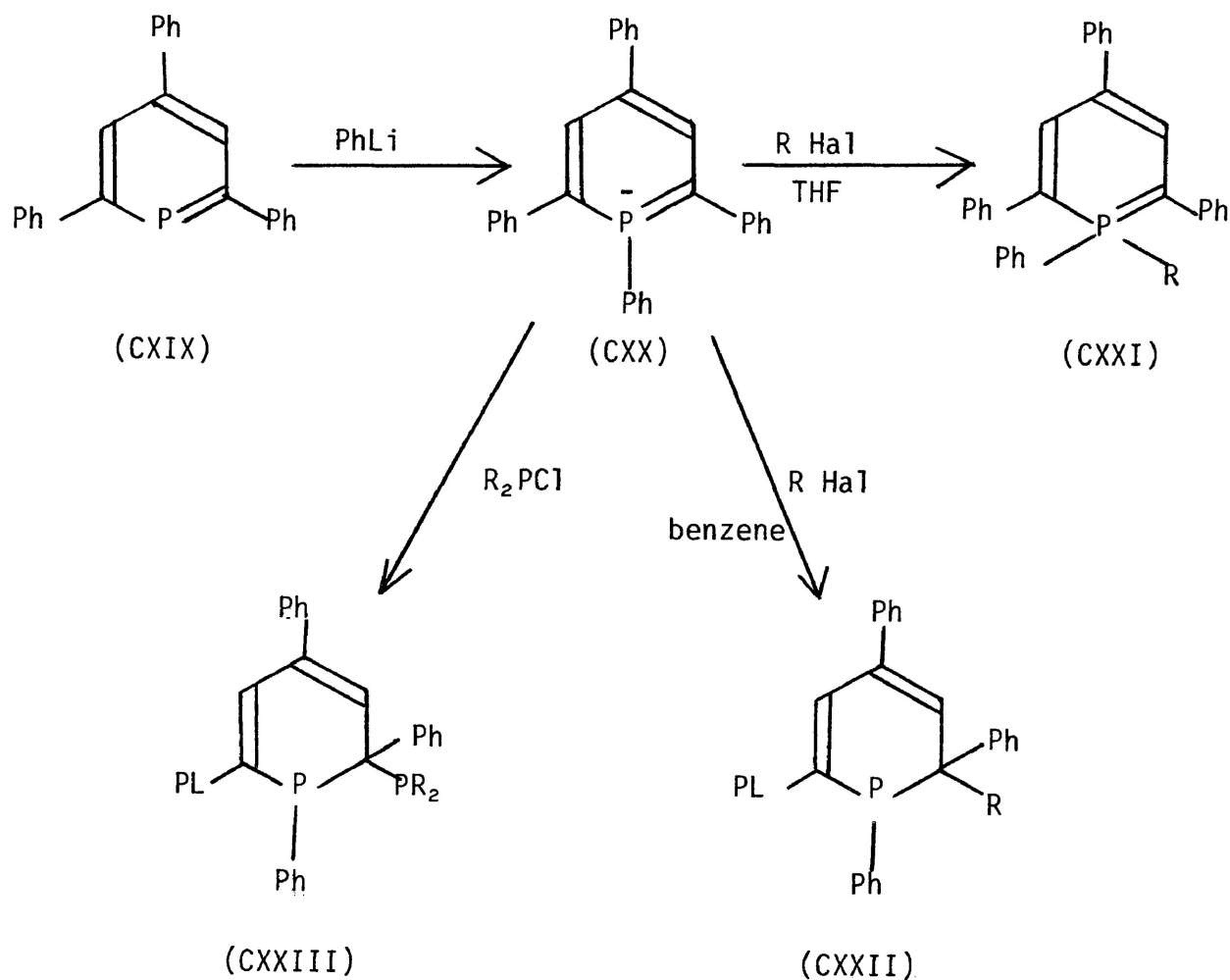
## EXPERIMENTAL

3.1     Materials

Trichlorosilane was obtained from Matheson Coleman
and Bell Chemicals and was used without further purification. Tri-
fluoroacetic acid and N,N,N',N'-Tetramethylethylenediamine (TMEDA)
were obtained from Eastman Organic Chemicals and the TMEDA was
purified by distillation. The rest of the reagents used in the
present work were obtained either from the Aldrich Chemical Company
Incorporated or from BDH Chemicals Limited and were used without further
purification except for N-bromosuccinimide (NBS) which was
crystallised from water before use.

Benzene, methylene chloride and tetrahydrofuran (THF)
were dried by heating under reflux over $CaH_2$, $P_2O_5$ and $LiAlH_4$
respectively followed by distillation in previously dried glassware.

All solvents used for column chromatography were
laboratory grade and were distilled in order to remove all grease
and involatile materials.

Nitrogen (Canadian Liquid Air Ltd.) was dried by pass-
ing it through self-indicating silica gel.

3.2          Physical measurements and instrumental procedures

All air-sensitive samples were properly protected from atmospheric hydrolysis or oxidation during weighing and data collection. Certain operations were carried out in a nitrogen-filled glove box.

Infrared spectra of the samples were recorded on a Beckman IR-4250 spectrophotometer as Nujol mulls or as liquid films pressed between NaCl plates. The spectra were calibrated with a polystyrene reference film.

A Bruker WP-80 multinuclear Fourier-transform instrument equipped with an automatic temperature control device (B-VT 1000) was used to record $^1H$, $^{31}P$ and $^{13}C$ spectra at 80 mHz, 32.3 mHz and 20.1 mHz, respectively. The chemical shifts for the $^1H$ and $^{13}C$ spectra were measured relative to internal tetra-methylsilane (TMS) using deuterated chloroform as solvent and frequency lock. The $^{31}P$ chemical shifts were measured relative to external 85% $H_3PO_4$ using chloroform as solvent and with $D_2O$ as the frequency lock. In practice, however, the direct use of $H_3PO_4$ in routine NMR measurements was avoided. $D_2O$, enclosed in a central capillary tube, was used as the external frequency lock and the position of the $H_3PO_4$ signal was determined relative to $D_2O$.

The position of the $H_3PO_4$ signal against the $D_2O$ reference was found to be 2800 Hz and the chemical shifts of the $^{31}P$ signals were calculated relative to this frequency using the following relationship:

$$\delta P = \frac{\text{Frequency observed} - 2800}{32.3}$$

The $D_2O$ was sealed in a thin capillary coaxially fitted to the $^{31}P$ NMR sample tube through a vortex plug. The advantage of this method is that weak signals produced by dilute samples could be measured without the saturation problems generated by a strong $H_3PO_4$ signal. This is particularly useful for sparingly soluble samples where pulsing for long periods becomes necessary. All spectra were recorded at room temperature and $^{31}P$ and $^{13}C$ spectra were recorded in the proton decoupled mode. All chemical shifts are regarded as positive if downfield from the reference signal.

Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-7 double focussing mass spectrometer using a direct heated inlet system.

Microanalytical data for carbon and hydrogen were acquired on a Perkin Elmer model 240 Analyser in these laboratories with $V_2O_5$ used as a combustion aid for samples where combustion was

incomplete under normal conditions. Phosphorus analyses were carried out commercially by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

Column chromatography was carried out using silica gel (specially prepared for dry column chromatography), obtained from ICN Pharmaceuticals, Inc., K & K Laboratories Division, as adsorbent. Thin layer chromatography was carried out using a variety of adsorbents of TLC grade spread upon microscope slides.

## 3.3 Syntheses

The detailed procedures for the preparations of the various compounds synthesized in the present work are described in the following subsections. Analytical and $^{31}$P NMR only data are given. Other NMR data are discussed at length in the Results and Discussion section. The $^{31}$P chemical shifts $\delta P^{1}$ and $\delta P^{2}$ correspond to the locations of the signals of the ring and side-chain phosphorus atoms respectively for the phosphoryl-substituted phosphorus heterocyclic systems.

### 3.3.1    Dibromophenylphosphine

Phosphorus tribromide (406.05 g., 1.5 moles) was added slowly from a pressure equalizing dropping funnel to magnetically stirred dichlorophenylphosphine (268.5 g., 1.5 moles) at room temperature under a slow stream of dry nitrogen. After the last portion of $PBr_3$ had been added, the reaction mixture was heated at 100 - 200°C for 2 hours. The initial fractions up to b.p. 175°C were then distilled from the mixture at atmospheric pressure. The residual mixture was distilled under reduced pressure with a free flame to give dibromophenylphosphine (316.10 g., 78.63%); b.p. 124°C/9 Torr (lit. (150) b.p. 126 - 128°C/11 Torr); $^{31}P$ NMR (Neat): $\delta P$ = 153.35 (lit. (150) value $\delta P$ = 152 ±1).

### 3.3.2    3,4-Dimethyl-1-phenyl-3-phospholene 1-oxide (LXXVIII)

A 250 ml three-necked flask was flushed with dry nitrogen for 30 minutes. 2,3-Dimethyl-1,3-butadiene (14.3 g., 0.175 moles) and dibromophenylphosphine (46.0 g., 0.17 moles) were then mixed together in the flask which was immediately stoppered and stored in the refrigerator. When the mixture had solidified (2-3 days) it was removed from the refrigerator and was ground into powder under dry $N_2$. The powder was quickly added to an ice-cold saturated solution of $NaHCO_3$ with vigorous stirring. The resulting aqueous

solution was extracted with $CHCl_3$ (4x150 ml) and the combined

chloroform extracts were dried over anhydrous $Na_2SO_4$. After

concentrating the solution first in the rotary evaporator and then

using a vacuum pump (2 Torr) a solid was obtained which was crushed

under $N_2$ in the $N_2$-filled glove box and further dried under reduced

pressure for 48 hours to give (LXXVIII) (26.0 g., 74.24%); $^{31}P$ NMR

$\delta P = 46.3$ (lit. (9) $\delta P = 46.0$). This known compound was not

further characterized and was used directly for the next step in the

synthetic sequence.


3.3.3    3,4-Dimethyl-2-diphenylphosphoryl-1-phenyl-2-phospholene
         1-oxide (LXXXI)


A solution of 3,4-dimethyl-1-phenyl-3-phospholene 1-

oxide (LXXVIII) (10.38 g., 0.05 moles) in dry THF (75 ml) was

added slowly over a period of 45 minutes to a stirred solution of

1.6 M n-BuLi (40 ml, 0.064 moles) in dry THF (30 ml) at -75°C

under dry nitrogen. The resulting dark-red solution was stirred at

-75°C for 30 minutes. Chlorodiphenylphosphine (16.3 g., 0.073 moles)

was then added over a period of 20 minutes to give a bright-red

solution which was stirred at the same temperature for a further 3

hours. The temperature of the solution was then raised to -20°C

and dil. HCl (1.0%) was added slowly until the solution was neutral.

In this step, the colour changed from red to pale-yellow. Water

(25 ml) was added to increase the volume of the aqueous layer and

the solution was then transferred to a round-bottomed flask for removal of the THF by a rotary evaporator. The remaining aqueous layer was extracted with $CH_2Cl_2$ (3x50 ml) and the combined $CH_2Cl_2$ extracts were washed with 5% $K_2CO_3$ solution (3x50 ml). The solution was further washed with water (3x50 ml) and then dried over anhydrous $K_2CO_3$. After concentrating the solution in a rotary evaporator, the residue was dried under reduced pressure (oil pump) to give a yellow viscous liquid (22.8 g.).

The viscous liquid so obtained was dissolved in absolute ethanol (50 ml) and then treated with 30% $H_2O_2$ (ratio 2 drops of $H_2O_2$/1.0 g. of the viscous liquid). The solvent was again removed on a rotary evaporator and the residue was dried under reduced pressure as before. The resulting viscous liquid was dissolved in $CHCl_3$ (100 ml), washed with water (3x50 ml) and dried over $Na_2SO_4$. The viscous liquid obtained after removal of the $CHCl_3$ was treated with ether to precipitate a filterable solid (4.85 g.). This was recrystallised from acetone-water to give the pure desired product (LXXXI) 3.5 g., 17.15%); m.p. 236 - 239°C (lit. (131) m.p. 253°C); $^{31}P$ NMR: $\delta P' = 58.08$, $\delta P^2 = 20.82$, $^2J_{P-P} = 39.59$ Hz.

Analysis

Calcd. for $C_{24}H_{24}P_2O_2$: C, 70.94, H, 5.91; P, 15.27

Found: C, 70.85; H, 5.97; P, 15.18

### 3.3.4    4-Bromo-3,4-dimethyl-2-diphenylphosphoryl-1-phenyl-2-phospholene 1-oxide (LXXXV)

A solution of 3,4-dimethyl-2-diphenylphosphoryl-1-phenyl-2-phospholene 1-oxide (LXXXI) (3.0 g., 0.008 moles) in dry $CH_2Cl_2$ (50 ml) was flushed with dry $N_2$ to remove oxygen. The solution was placed in a 100 ml three-necked flask and then irradiated by a high pressure mercury lamp (Hanovia 654A10) under dry nitrogen. N-Bromosuccinimide (2.22 g., 0.012 moles) was added slowly, as a solid, to the above solution over a period of 15 minutes. After completion of the addition, the mixture was stirred and irradiated at room temperature under nitrogen for a further one hour. It was then transferred to a separatory funnel, extra $CH_2Cl_2$ (50 ml) was added to increase the volume and the solution was washed with water (8x50 ml). The organic layer was dried over anhydrous $Na_2SO_4$ and the solvent was removed carefully using a rotary evaporator at room temperature to give a pale-yellow viscous liquid. When the viscous liquid was further dried using an oil pump, a pale-yellow (foamy) semi-solid product characterized as (LXXXV) was obtained (3.76 g., 96.91%); $^{31}P$ NMR (two stereoisomers): major $\delta P^1 = 48.90$, $\delta P^2 = 20.78$, $^2J_{P-P} = 35.4$ Hz; minor $\delta P^1 = 51.12$, $\delta P^2 = 20.66$, $^2J_{P-P} = 35.4$ Hz. A TLC analysis showed that the crude product was, in fact, quite pure. Further purification was not attempted because of the thermal instability of this compound and, for the same reason, reliable analytical data could not be obtained. The compound

has, however, been unambiguously characterized (see Results and Discussion).

3.3.5         3-Methyl-4-methylene-2-diphenylphosphoryl-1-phenyl-2-phospholene 1-oxide (LXXXVI)

The crude bromo product (LXXXV) (3.76 g., 0.0087 moles) was heated at 90 - 100°C in a rotary evaporator for about 45 minutes during which time the initial pale-yellow semi-solid compound turned to a dark-brown viscous liquid. This liquid was dissolved in $CH_2Cl_2$ (100 ml) and transferred to a separatory funnel where it was washed with 5% $NaHCO_3$ solution (3x50 ml) and then with water (3x50 ml). Drying of the organic layer was carried out over anhydrous $Na_2SO_4$. Another dark-brown viscous liquid was obtained after removing the solvent under reduced pressure. The crude product was purified by dry-column chromatography ($CHCl_3$ as eluent) on silica to give the pure product (LXXXVI) as a colourless, glassy solid (1.73 g., 58.05% based upon LXXXI); m.p. 58 - 60°C; $^{31}P$ NMR: $\delta P' = 48.22$, $\delta P^2 = 22.18$, $^2J_{P-P} = 33.5$ Hz.

Analysis (very freshly prepared sample)

Calcd. for $C_{24}H_{22}P_2O_2$:    C, 71.28; H, 5.45

Found:                     C, 71.11; H, 5.65

A reliable phosphorus analysis could not be obtained because of the sensitivity of this compound to molecular oxygen (see Results and Discussion).

3.3.6    Reduction of 3-methyl-4-methylene-2-diphenylphosphoryl-1-phenyl-2-phospholene 1-oxide (LXXXVI) by $HSiCl_3$

A 250 ml three-necked flask fitted with a condenser was flushed with dry $N_2$ for 10 minutes. Trichlorosilane (2.72 g., 0.02 moles) and pyridine (5.45 g., 0.06 moles) were mixed carefully in dry benzene (50 ml) in the flask under $N_2$ and the oxide (LXXXVI) (0.8 g., 0.002 moles) in dry benzene (25 ml) was added in one portion. The resulting suspension was heated under reflux for 2 hours during which time a light yellow suspension was produced. The mixture was cooled in an ice bath and quenched under $N_2$ with aqueous NaOH (20 ml) keeping the mixture ice-cold during quenching. Water (40 ml) was added to increase the volume of the aqueous layer. The sealed reaction flask was then transferred to a nitrogen filled glove box where the benzene layer was separated and the aqueous layer was again washed with benzene (40 ml). The two benzene extracts were combined and dried over $MgSO_4$. A yellow viscous material was obtained on concentrating the solution under reduced pressure with magnetic stirring to remove the solvent. The crude material was chromatographed on a dry silica column ($CHCl_3$ as eluent) to give a yellow viscous liquid (0.32 g.).

The $^{31}$P NMR spectrum indicated that the product was

a mixture (in which all of the components have the same $R_f$ value)

in which one of the components is 3-methyl-4-methylene-2-diphenyl-

phosphoryl-1-phenyl-2-phospholene (XCI), $^{31}$P NMR: $\delta P^1$ = -1.12,

$\delta P^2$ = 25.0, $^2J_{P-P}$ = 59.74 Hz. This compound was not further

characterized since on $H_2O_2$ oxidation, it formed the starting oxide

(LXXXVI) which was recovered in pure form.

The reduction was also carried out in the absence of

pyridine but similar results were obtained.

Characterization of the impure product was carried out

by an extensive spectroscopic analysis.

3.3.7    Formation of 3-methyl-4-oxo-2-diphenylphosphoryl-1-
         phenyl-2-phospholene 1-oxide (XCIII) by spontaneous
         oxidation of (LXXXVI)

3-Methyl-4-methylene-2-diphenylphosphoryl-1-phenyl-2-

phospholene 1-oxide (LXXXVI) (1.0 g., 0.0025 moles) was sealed

in a small flask and the flask was placed in the refrigerator. After

a few days, the $^{31}$P spectrum showed that the compound had commenced

oxidation and this oxidation was complete after ca. 2 months. On

purification by dry column chromatography on silica (CHCl$_3$ as eluent),

a colorless glassy solid characterized as (XCIII) was obtained

(o.75 g., 74.6%), m.p. 55 - 58°C; $^{31}$P NMR: $\delta P' = 32.50$, $\delta P^2 = 21.64$, $^2J_{P-P} = 24.7$ Hz; IR (Nujol) $\nu_{max}$: $\nu_{co}$ 1710 cm$^{-1}$.

## Analysis

Calcd. for $C_{23}H_{20}P_2O_3$:    C, 67.98; H, 4.92

Found:                 C, 67.88; H, 4.98

3.3.8       <u>Preparation of the ketone (XCIII) and the stereoisomeric</u>
<u>epoxides (XCVIIA) and (XCVIIB) by AIBN catalysed oxidation</u>
<u>of (LXXXVI)</u>

3-Methyl-4-methylene-2-diphenylphosphoryl-1-phenyl-2-phospholene 1-oxide (LXXXVI) (1.0 g., 0.0025 moles) in benzene (35 ml) was placed in a 100 ml flask fitted with a condenser, a thermometer and an air inlet, and AIBN (0.04 g., 0.00024 moles) in benzene (5 ml) was added. A slow stream of air was bubbled through the solution and the mixture was heated at 70°C with constant stirring. The solution gradually turned yellow. AIBN (0.04 g.) was added twice more at 12 hour intervals and heating was continued for 48 hours. The benzene was then removed under reduced pressure to give a yellow viscous liquid.

The $^{31}$P spectrum of the crude product showed that it was a mixture of three compounds. Separation was effected by dry silica column chromatography (CHCl$_3$ - C$_6$H$_6$ (4:1) as eluent

yielded the first fraction and $CHCl_3$ as eluent yielded the next

two fractions) which gave the ketone (XCIII) (0.253 g., 25.15%),

the minor stereoisomeric epoxide (XCVIIB) (o.106 g., 10.2%);

m.p. 180°C (decomp.); $^{31}P$ NMR: $\delta P' = 43.93$, $\delta P^2 = 21.61$,

$^2J_{P-P} = 31.34$ Hz; and, finally, the major stereoisomeric epoxide

(XCVIIA) (0.295 g., 28.42%); m.p. 65-66°C; $^{31}P$ NMR: $\delta P' = 46.5$,

$\delta P^2 = 20.27$, $^2J_{P-P} = 31.65$ Hz.


Analyses (for epoxides)


Calcd. for $C_{24}H_{22}P_2O_3$:   C, 68.57; H, 5.24; P, 14.76

Found (major):   C, 68.53; H, 5.44; P, 14.39

(minor):   C, 68.47; H, 5.38; P, 14.35


3.3.9     Preparation of the stereoisomeric epoxides (XCVIIA) and (XCVIIB) by m-chloroperbenzoic acid oxidation of (LXXXVI)


3-Methyl-4-methylene-2-diphenylphosphoryl-1-phenyl-2-

phospholene 1-oxide (LXXXVI) (0.5g., 0.00125 moles) in $CH_2Cl_2$ (5 ml)

was placed in a 25 ml flask fitted with a condenser and m-chloroper-

benzoic acid (0.3 g., 0.00174 moles) was added in one portion. The

resulting mixture was heated under reflux for 24 hours with constant

stirring. At this stage an orange solution was obtained. The

solution was neutralized by 10% $NaHCO_3$ solution and the aqueous layer

was extracted with $CHCl_3$ (3x15 ml). The combined extracts were washed with water (3x20 ml) and dried over anhydrous $Na_2SO_4$. Removal of the solvent under reduced pressure gave a yellow viscous liquid. Purification of this crude product by dry column chromatography on silica ($CHCl_3$ as eluent) gave the minor isomeric epoxide (XCVIIB) (0.117 g., 22.5%) and the major isomeric epoxide (XCVIIA) (0.200 g., 38.3%) in pure form.

3.3.10        Preparation of 3-methyl-4-methylene-1-phenyl-2-phospholene 1-sulfide (LXXXVIII)

3,4-Dimethyl-1-phenylphosphole 1-sulfide (CI) (1.0 g., 0.0045 moles), obtained from a fellow student, was mixed with acetic acid (2.5 ml) and trifluoroacetic acid (2.5 ml) in a 25 ml flask fitted with a condenser. The mixture was gently heated under reflux for 3 hours with constant stirring. It was then cooled, neutralized with conc. NaOH solution and extracted with $CH_2Cl_2$ (3x25 ml). The solvent was removed under reduced pressure when a yellow semi-solid was otained. This was chromatographed using the usual dry silica technique ($C_6H_6$ as eluent) and then dried under reduced pressure. Slow crystallization occurred overnight to give yellow crystals of (LXXXVIII) (0.75 g., 75%) m.p. 68-70°C (lit. (134) m.p. 69-71°C); ^{31}P NMR: $\delta P$ = 48.94 (lit. $\delta P$ = 47.5).

Analysis
<u></u>

$$\text{Calcd. for } C_{12}H_{13}PS: \quad C, 65.45; \ H, 5.90$$

$$\text{Found:} \qquad\qquad\qquad C, 65.58; \ H, 6.07$$

A detailed spectroscopic analysis of this known compound is given in the Results and Discussion section.

3.3.11    Preparation of 3-methyl-4-oxo-1-phenyl-2-phospholene
1-sulfide (CII) and 3-methyl-4-oxo-1-phenyl-2-phospholene
1-oxide (CIII) by AIBN catalysed oxidation of (LXXXVIII)

The oxidation of the sulfide (LXXXVIII) (0.5 g., 0.0023 moles) in the presence of AIBN (0.05 g., 0.0003 moles) was carried out in a similar manner to that described in subsection (3.3.8). In this case, the reaction was complete in 36 hours and, as the reaction was proceeding, some insoluble material was formed. After completion of the reaction, the flask was cooled, and the benzene solution was decanted. The solvent was removed under reduced pressure when a yellow viscous liquid was obtained. The crude material was then chromatographed in the usual manner on dry silica ($C_6H_6$ as eluent) to give the yellow sulfide (CII) as a viscous liquid (0.151 g., 29.95%); $^{31}P$ NMR:  $\delta P = 31.98$; IR (Neat) $\nu_{max}$: $\nu_{co}$ 1710 cm$^{-1}$. Further elution of the column with $C_6H_6$ - CHCl$_3$ (1:1) gave the yellow oxide (CIII) as another viscous liquid

(0.047 g., 10%); $^{31}$P NMR: $\delta$P = 30.71; IR (Neat) $\nu_{max}$: $\nu_{co}$ = 1710 cm$^{-1}$, $\nu_{PO}$ = 1215 cm$^{-1}$.

<u>Analyses</u>

Calcd. for $C_{11}H_{11}PSO$ (CII): C, 59.46; H, 4.95

Found: C, 59.20; H, 5.01

Calcd. for $C_{11}H_{11}PO_2$ (CIII): C, 64.07; H, 5.34

Found: C, 63.96; H, 5.70

A further fraction was eluted from the column between the two main fractions. This was also found to be a viscous material (0.01 g.,), $^{31}$P NMR: $\delta$P = 49.79, but further characterization of this fraction was not successful because of the small quantity available.

3.3.12    <u>Preparation of 4-hydroxy-3-methyl-2-diphenylphosphoryl-</u>
<u>1-phenylphospholane 1-oxide (CVI) by NaBH$_4$ reduction</u>
<u>of the ketone (XCIII)</u>

Sodium borohydride (0.03 g., 0.0008 moles) was added to a cold solution of (XCIII) (0.2 g., 0.00049 moles) in 95% ethanol (10 ml). A yellow solution was immediately obtained. The mixture was stirred for 1.5 hours at 0-5°C and then acidfied with dil. HCl

while still cold. After removing the solvent under reduced pressure, water (10 ml) was added to increase the volume of the aqueous layer and the resulting slurry was extracted with $CHCl_3$ (3x20 ml). The chloroform extracts were combined and dried over anhydrous $Na_2SO_4$. On removing the solvent under reduced pressure, a solid was obtained. This was purified by dry column chromatography on silica in the usual manner. Some trace impurities were initially eluted from the column with $CHCl_3$ - $Me_2CO$ (9:1) as eluent and further elution with $CHCl_3$ - $Me_2CO$ (4:1) yielded 4-hydroxy-3-methyl-2-diphenylphosphoryl-1-phenylpholane 1-oxide (CVI) as a colourless solid (0.051 g., 25.2%); m.p. 242 - 244°C; $^{31}P$ NMR: $\delta P' = 60.05$, $\delta P^2 = 31.59$, $^2J_{P-P} = 2.2$ Hz.

## Analysis

Calcd. for $C_{23}H_{24}P_2O_3$:  C, 67.31; H, 5.85; P, 15.12

Found:                C, 67.16; H, 5.86; P, 15.03

Further elution of the column with methanol gave an impure solid (0.068 g.); m.p. 130 - 135°C (not sharp); $^{31}P$ NMR: $\delta P' = 47.04$; $\delta P^2 = 30.46$, $^2J_{P-P} = 6.05$ Hz with other minor peaks. Due to purification problems, the characterization of this compound was abandoned.

### 3.3.13 Reduction of 3-methyl-4-oxo-2-diphenylphosphoryl-1-phenyl-2-phospholene 1-oxide (XCIII) by HSiCl₃

Reduction of the ketone (XCIII) (0.812 g., 0.002 moles) was carried out in a similar manner to that described for (LXXXVI) in subsection (3.3.6) by trichlorosilane (2.72 g., 0.02 moles) in the presence of pyridine (5.46 g., 0.06 moles). In this case, however, a benzene-insoluble reddish-brown oil was obtained after quenching the reaction mixture with NaOH solution. The benzene layer was decanted, the oil was dissolved in $CHCl_3$ (50 ml), and the resulting solution was dried over anhydrous $Na_2SO_4$. The solvent was then removed under reduced pressure and the crude product was chromatographed on a dry silica column ($CHCl_3$ as eluent) to give a reddish-brown viscous oil characterized as 3-methyl-4-oxo-2-diphenylphosphoryl-2-phospholene (CVIII) (0.273 g., 35%) $^{31}P$ NMR: $\delta P' = -28.44$, $\delta P^2 = 23,70$, $^2J_{P-P} = 51.2$ Hz; IR (Neat) $\nu_{max}$: $\nu_{co} = 1710$ cm$^{-1}$. This compound was not further characterized apart from spectroscopic study (see Results and Discussion), since on $H_2O_2$ oxidation, it produced the starting ketone (XCIII).

The reduction was also carried out in the absence of pyridine and similar results were obtained.

3.3.14     Preparation of 1-ethoxy-3,4-dimethyl-3-phospholene
           1-oxide (CXIII)

A 500 ml wide-mouth bottle was flushed with dry $N_2$ for

30 minutes. 2,3-Dimethyl-1,3-butadiene (20.5 g., 0.25 moles) and

phosphorus tribromide (67.67 g., 0.25 moles) were then mixed to-

gether in n-hexane in the bottle. The bottle was immediately stoppered

and stored in the refrigerator for 24 hours. The bottle was then

transferred into a $N_2$-filled glove box and the solid adduct was

filtered, washed several times with n-hexane and dried under reduced

pressure.

A mixture of absolute ethanol (5.12 g., 0.113 moles)

and triethylamine (11.4 g., 0.113 moles) was added dropwise to a

suspension of the adduct (20.0 g., 0.056 moles) in dry $CH_2Cl_2$ (150 ml)

at 0°C under nitrogen with constant stirring. During the addition,

the solution gradually became clear until two-thirds of the

reagent had been added but it later became cloudy again when more

reagent was added. The resulting suspension was washed with

water (3x100 ml) and dried over anhydrous $Na_2SO_4$. Evaporation of

the solvent under reduced pressure yielded a yellow oil. Purifica-

tion by dry column chromatography (silica) ($CHCl_3$ as eluent) gave,

initially, a colourless oil, b.p. 93-94°C at 2.5 Torr, which after

24 hours in the refrigerator, became a glassy solid (CXIII) (6.65 g.,

67.75%); m.p. 35 - 36°C; ^{31}P NMR: δP = 68.83. Further characteriza-

tion of this known compound was not considered to be necessary.

3.3.15    Preparation of 1-ethoxy-4-hydroxy-3,4-dimethyl-
         2-phospholene 1-oxide (CXI)


1-Ethoxy-3,4-dimethyl-3-phospholene 1-oxide (5.0 g.,
0.028 moles) was placed in a three-necked flask and dry THF (∿25 ml)
was directly distilled into the flask.  Tetramethylethylenediamine
(TMEDA) (10 ml) was added in one portion and 1.6 M n-BuLi (20 ml,
0.032 moles) was added slowly over a period of 30 minutes at -75°C
under $N_2$ with constant stirring.  The resulting dark-red solution
was stirred at -75°C for six hours under a slow stream of dry air
(ordinary air passed through conc. $H_2SO_4$ and KOH).  At this
stage, a deep yellow solution was obtained.  The solution was
hydrolysed by a mixture of MeOH (12 ml) and water (6 ml).  The
temperature was then raised to 20°C and the solution was neutralized
by dil. HCl.  At this stage, the solution became colorless.  The
THF was removed under reduced pressure, the aqueous layer was
extracted with $CH_2Cl_2$ (3x50 ml) and the combined extracts were dried
over anhydrous $Na_2SO_4$.  Evaporation of the solvent under reduced
pressure yielded an oily liquid.  The crude material was chromato-
graphed on a dry silica column (CHCl$_3$ as eluent) to give a stereo-
isomeric mixture of the two possible 1-ethoxy-4-hydroxy-3,4-dimethyl-
2-phospholene 1-oxides; $^{31}$P NMR:  $\delta$P = 61.59 and 60.99.  The stereo-
isomeric mixture was rechromatographed and careful collection of
the fractions yielded one of the isomers (CXI) as a solid in pure
form; m.p. 64 - 65°C; $^{31}$P NMR:  $\delta$P = 61.4.

Analysis

Calcd. for $C_8H_{15}PO_3$:  C, 50.52; H, 7.89, P, 16.31

Found:                        C, 50.59; H, 7.88; P, 16.32

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