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S O M E V I N Y L -

A N D

C Y C L O P R O P Y L P H O S P H I N E S

BY

MAUREEN DAVIES

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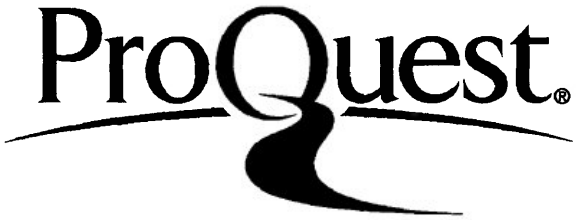

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ABSTRACT

Synthetic approaches to cyclic phosphonium ylides are reviewed and the syntheses are classified according to reaction type rather than ring size. Particular attention is paid to syntheses leading to isolable or easily characterizable cyclic ylides and a number of other reactions in which cyclic phosphonium ylides are postulated as transient intermediates are discussed. There is also a brief discussion regarding structure and bonding in certain of the more stable cyclic ylides such as the 1,1-disubstituted phosphorins and certain diphosph(V)orins.

Reactions of vinyl- and cyclopropylphosphines with electrophilic unsaturated compounds such as dimethyl acetylenedicarboxylate, benzyne and hexafluoro-2-butyne were investigated in an attempt to synthesize five-, six-, seven- and eight-membered cyclic ylides.

Diphenylvinylphosphine reacts with dimethyl acetylenedicarboxylate to give either an equilibrium mixture of two five-membered cyclic ylidic 1:1 adducts or a strained bicyclic ylidic 1:2 adduct depending upon the reaction conditions. These ylides have been characterized by trapping them as their hydrolysis or deuterolysis products or by their Wittig reactions.

Extensive spin decoupling and mass spectral studies were carried out to confirm the structures of the adducts.

Cyclopropyldiphenylphosphine reacts with dimethyl acetylenedicarboxylate to give an isolable 5-membered cyclic ylide in which the cyclopropyl-ring remains intact. Attempts, using high boiling solvents, to achieve ring opening of the cyclopropyl-ring during the cycloaddition proved unsuccessful.

The reactions of benzyne generated from various sources with diphenylvinylphosphine and *cis* and *trans* 1,2-bis(diphenylphosphino)ethylene provided evidence for the intermediacy of a cyclic ylide in only one instance although other interesting reactions including a self-addition of diphenylvinylphosphine were observed.

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

ACKNOWLEDGEMENTS

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INTRODUCTION

THE CHEMISTRY OF CYCLIC PHOSPHONIUM YLIDES

Interest in organophosphorus chemistry in general, and cyclic phosphonium ylides in particular, has grown steadily over the past decade and much of this interest was precipitated by Märkl (1,2,3) in 1963 when he synthesized and characterized the first-known cyclic phosphonium ylides I, II and III. The following account is a survey of the chemistry of cyclic phosphonium ylides to the end of 1971, a modified version of which has now been published as a review (4). These compounds are not well indexed in the literature since many of them occur as transient intermediates in various reactions leading to non-ylidic products. There is, therefore, the possibility that a few references have been overlooked.

This introduction might appear to be rather long. However, the literature has expanded at such a rapid rate that it was felt that an almost complete summary of the topic should be given in order

that the work described in the remainder of this thesis should be seen in its correct perspective.

The topic is treated mainly from a synthetic viewpoint and the discussion is organized according to the reaction type rather than the ring size. There is also a brief discussion regarding the electronic structure of certain cyclic phosphonium ylides of particular theoretical interest. For the sake of convenience, all ylides are represented as the ylene structure. Similarly, although their behaviour is in general not typical of phosphonium ylides, 1,1-disubstituted phosphorins are treated in this review as a special class of cyclic ylide.

Synthetic Approaches to Cyclic Phosphonium Ylides

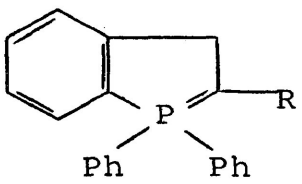
Many of the cyclic phosphonium ylides which have been isolated, characterized as intermediates or merely postulated as probable intermediates have not been synthesized by premeditated methods but have occurred as end-products or intermediates in reactions involving organophosphorus compounds. However, there appear to be three main reaction types into which the formation of these ylides normally fall. The first of these is proton abstraction from a phosphonium salt. This type may be subdivided into

α-proton abstraction from a cyclic salt, α-proton abstraction from an acyclic unsaturated salt followed by cyclization, and *o*-proton abstraction from an aryl phosphonium salt followed by cyclization. The second type is nucleophilic cycloaddition of a phosphine to an alkene, alkyne or aryne and the third type is radical or ionic attack at the phosphorus atom of a phosphorin derivative.

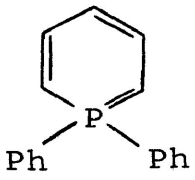
For the purposes of this discussion, a stable ylide is considered to be one which is isolable and which is stable in air for at least a short period of time.

(a) Proton Abstraction from a Phosphonium Salt.

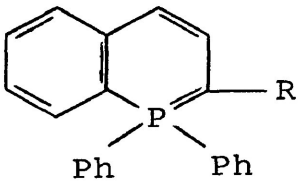
The first of these reaction types (proton abstraction) operates in the synthesis of many of the known relatively stable six-membered cyclic ylides and in the formation of some three- and five-membered cyclic ylides which have been postulated as intermediates in various reactions. α-Proton abstraction from a cyclic phosphonium salt, the mechanism which occurs most often in this reaction type, is also very effective in the synthesis of open chain ylides (5a).



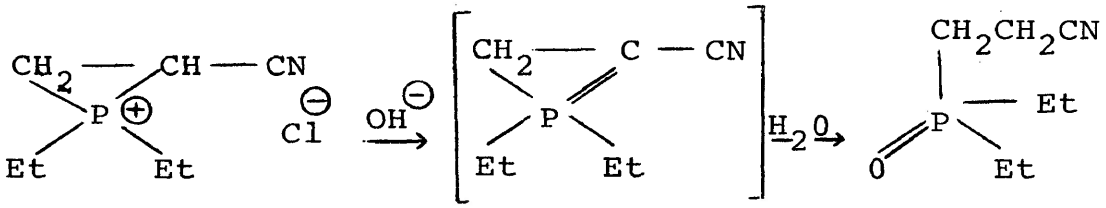
I (R=H, Ph or CO_2Me)



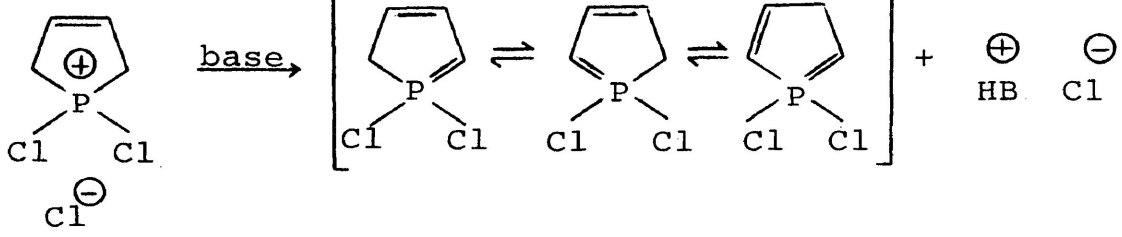
II



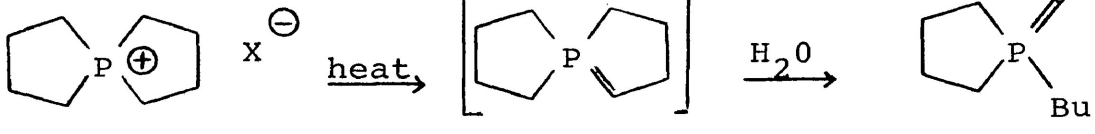
III (R=H or Ph)



IV V



VI VII



VIII IX

For example, Gundermann and Garming (6) have postulated that the cyclic ylide V occurs as an intermediate in the alkaline hydrolysis of the cyclic phosphonium salt IV. Similarly, Hunger and his co-workers (7) in a paper concerned with the position of the double bond in phospholene derivatives such as VI, considered the action of base on these compounds and suggested that ylides of type VII could occur as intermediates.

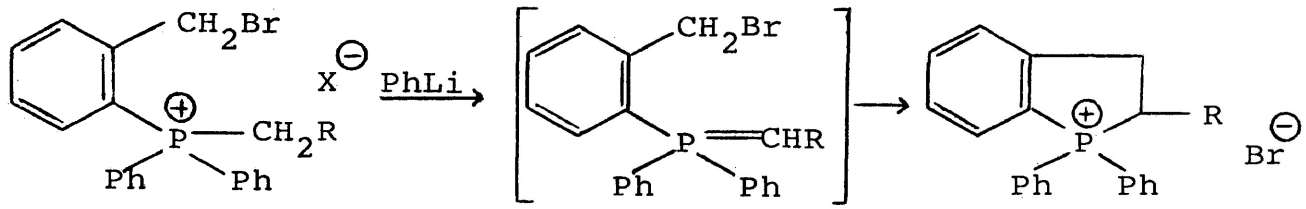
The cyclic ylide IX has also been suggested by Derkach and Kirsanov (8a) as a possible intermediate in the synthesis of 1-butylphospholane oxide from the spirophosphonium hydroxide VIII (X=OH). More recent studies by the same group (8b) have shown that the ylide IX can be generated by treatment of VIII (X=Br) with sodium hydride in dimethylsulphoxide or potassium *tert*-butoxide in *tert*-butanol. The ylide was trapped in Wittig reactions with suitable carbonyl compounds. In this connection, Walker (9) has very recently investigated several spirophosphonium salts including VIII (X=I) and has found that in NaOD/EtOD, the α-protons of VIII are readily exchangeable - presumably *via* the ylide IX. Furthermore, the ylide IX was found to be generated by treatment of VIII (X=I) with phenyllithium and

trapped by addition of methyl iodide.

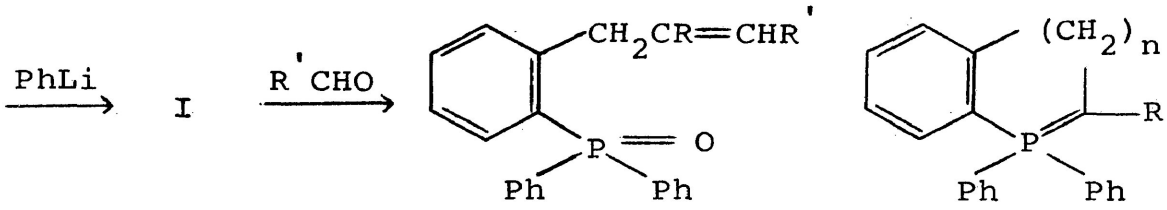
The first cyclic phosphonium ylide (I) to be fully characterized was prepared by Märkl (1) by basic abstraction of an α-proton from the bicyclic phosphonium salt XII which was in turn prepared by the sequence X→XII. However, at least one such ylide had been prepared earlier although its ylidic nature was not recognized at the time. This ylide will be discussed in a later section. The ylide I prepared by Märkl was studied only in solution and the highly substituted alkene XIII which was produced by reaction of the ylidic solution with a suitable aldehyde, was taken as additional proof for the existence of the ylide I. Märkl (1) used a similar method to synthesize the six- and seven-membered cyclic ylides XIV (n = 2 or 3).

Many of the known fully unsaturated six-membered cyclic phosphonium ylides have been prepared by this method of α-proton abstraction and are relatively stable. It has been suggested that this stability may be due to a certain amount of aromatic character in the ring. This will be discussed more fully later.

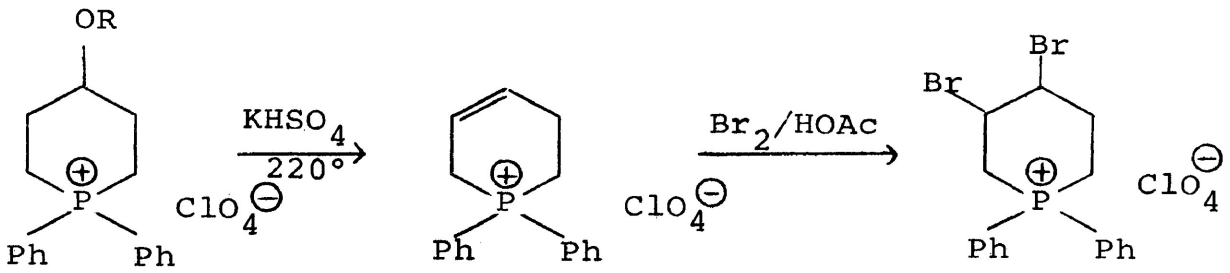
Thus, by a series of steps involving bromination, dehydrobromination and proton abstraction techniques, as shown in the sequence XV→II, Märkl (2)



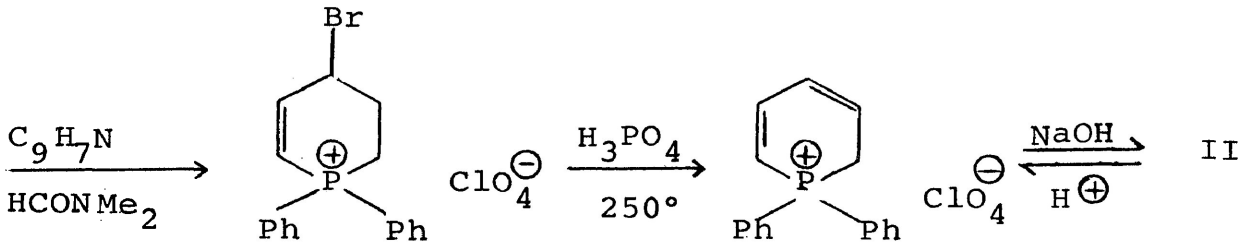
X XI XII



XIII XIV



XV XVI XVII

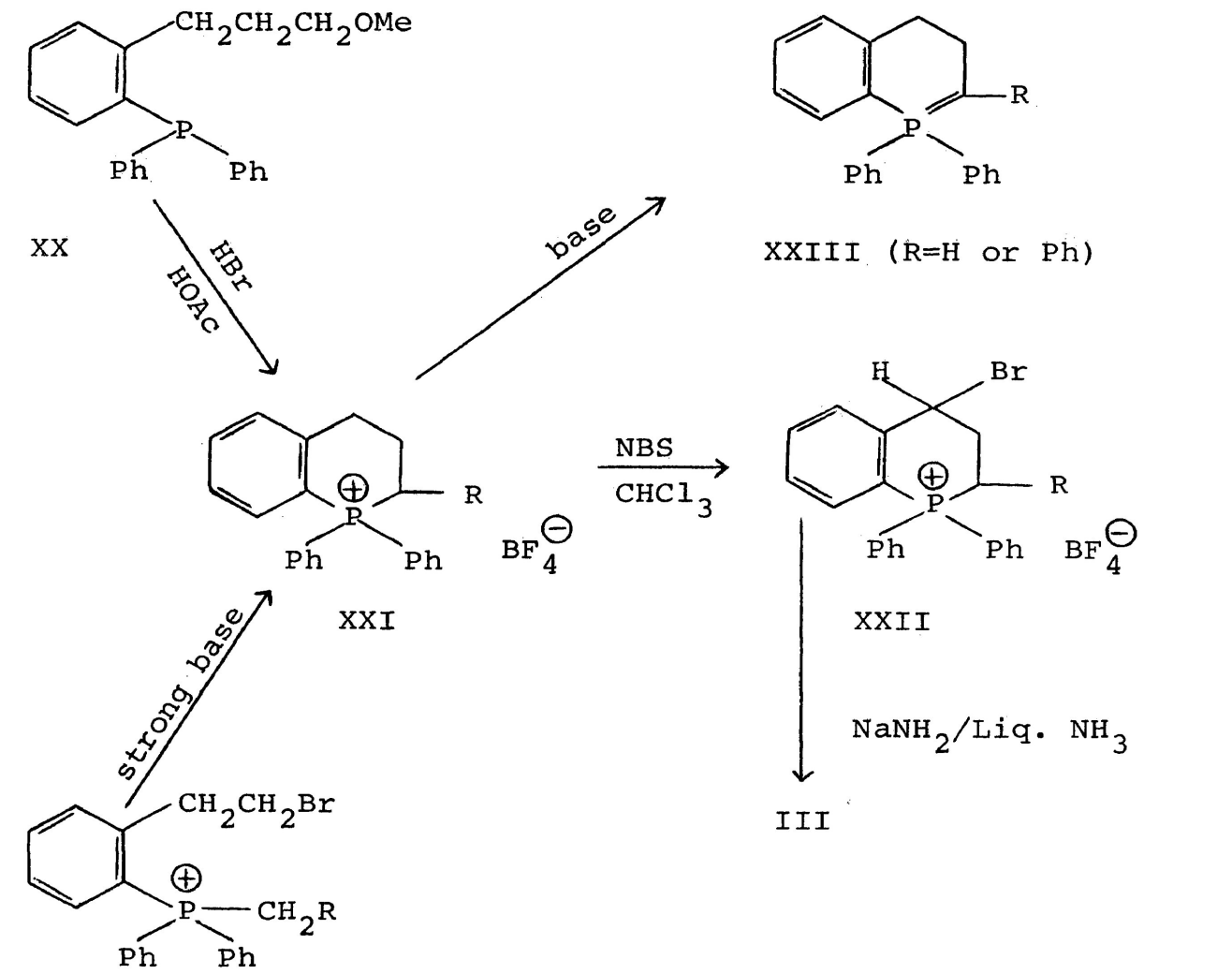


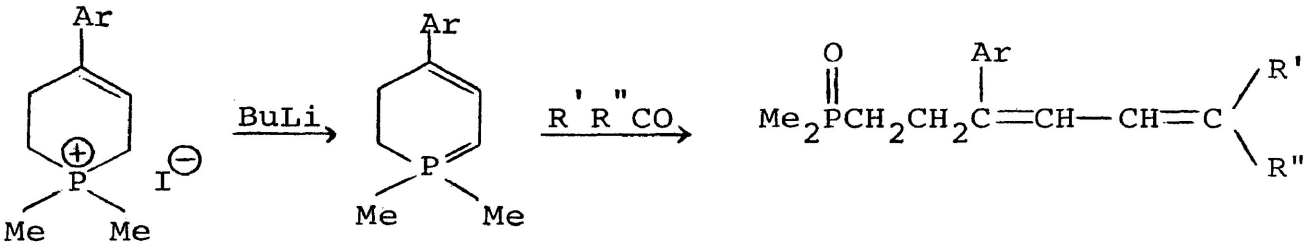
XVIII XIX II

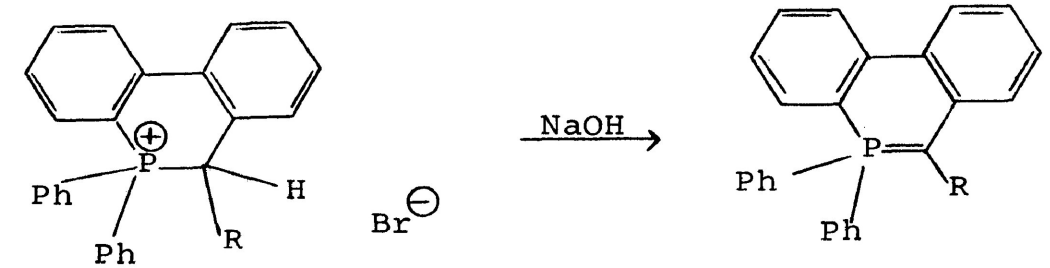
successfully synthesized 1,1-diphenyl-1-phospha-benzene (1,1-diphenylphosphorin) (II). No yield was reported for the ylide itself but all of the precursors were obtained in good yield. By similar methods (XX→III), Märkl (3) was able to prepare the 1,1-diphenyl-2-substituted-phosphanaph-thalenes III and, by a modification of the synthesis (XX→XXI→XXIII), the dihydrophosphanaphthalenes XXIII. Again no yields were reported.

Similarly, the related, partially unsaturated, monocyclic six-membered ylide XXV has been prepared by Lednicer (10) by treatment of the phosphonium salt XXIV with butyllithium. It was found that XXV reacts smoothly with carbonyl compounds to give open-chain unsaturated phosphine oxides, as shown, in good yield.

Another relatively stable six-membered cyclic ylide XXVII of the same general type was prepared by Cookson and Crofts (11) from the tricyclic phosphonium salt XXVI by treatment with base. It was not possible to obtain a pure sample because of its sensitivity to water and air and, therefore, no satisfactory analyti-cal data were obtained. However, the fact that the ylide was found to be relatively stable to hydrolysis (it was generated in an aqueous medium) was attributed to some aromatic character in the phosphorus-containing ring. Attempts to prepare the corresponding,


CH2CH2CH2OMe
P
Ph
Ph
XX
HBr
HOAc
base
R
XXIII (R=H or Ph)
BF4
XXI
NBS
CHCl3
H
Br
XXII
NaNH2/Liq. NH3
III
strong base
CH2CH2Br
CH2R


Ar
I
Me
BuLi
R'R"CO
O
Me2PCH2CH2C=CH—CH=C
R'
R"
XXIV
XXV


Ph
H
R
Br
NaOH
XXVI (R=H or Ph)
XXVII (R=H)

and probably more stable, compound with R=Ph were unsuccessful.

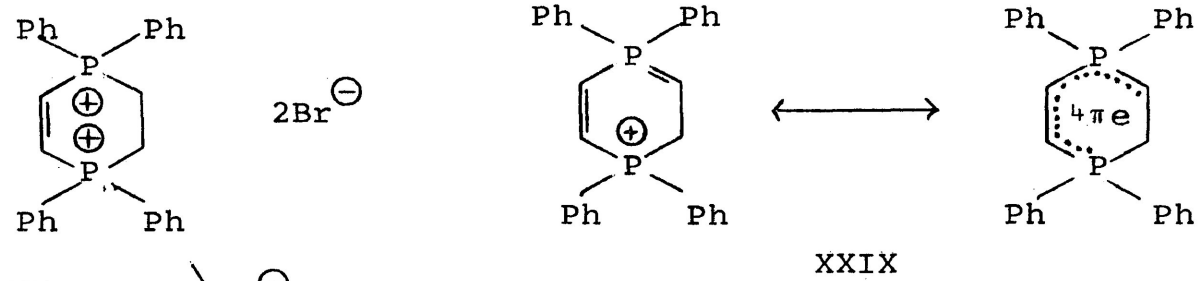
Several attempts have been made to prepare cyclic phosphonium bis-ylides from cyclic bisphosphonium salts by α-proton abstraction. For example, Aguiar and Aguiar (12) found during NMR studies that, when 1,1,4,4-tetraphenyl-1,4-diphosphoniacyclohex-2-ene (XXVIII) is dissolved in D_2O, proton exchange occurs between the methylene protons and the solvent. This was taken to indicate that the cyclic ylide XXIX is involved as an intermediate in the exchange equilibrium. In another experiment, Aguiar and Aguiar (12) attempted to synthesize the cyclic bis-ylide XXX by treatment of XXVIII with aqueous and other bases. However, the elimination of acetylene occurs to give the bisphosphine monoxide XXXII, probably *via* the intermediate XXXI. Similar eliminations have been observed in the treatment of the bisphosphonium salt XXXIII with aqueous base (13).

The only successful attempt to date to prepare a fully unsaturated six-membered cyclic bis-ylide by proton abstraction techniques was carried out by Märkl (14). The synthesis started from the bisphosphonium salt XXXIV and followed the sequence XXXIV→XXXVII. The two α-protons proved to be of different acidity,

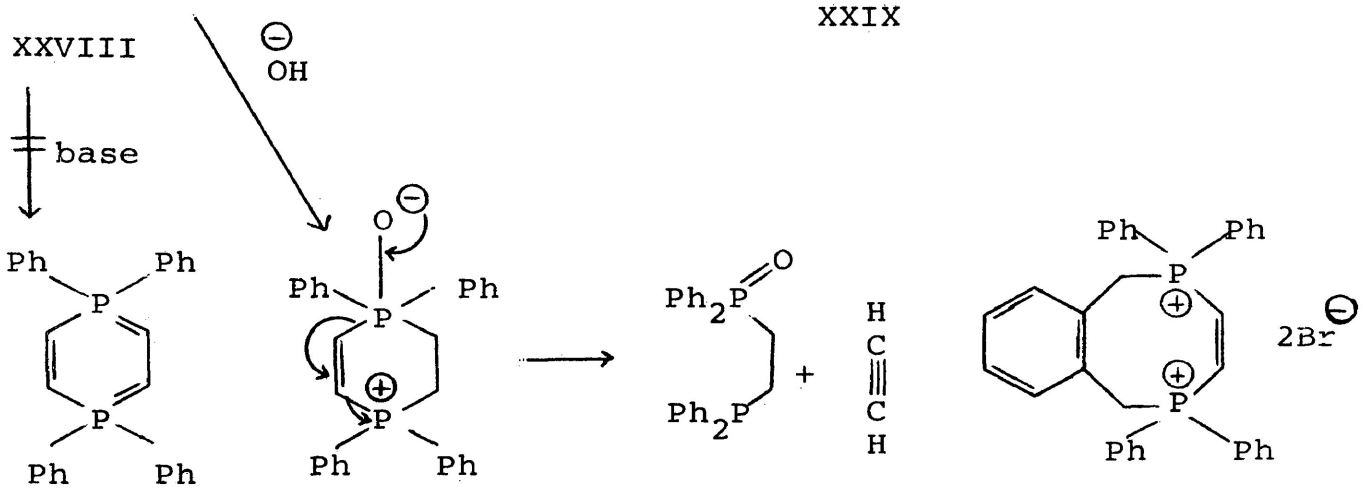
the first being removed by sodium carbonate and the second by sodium hydroxide. It might perhaps have been expected that one of the protons between the phosphorus atoms in XXXV would have been removed in the first deprotonation step to give the very stable $\gtrless P\cdots\overset{+}{C}H\cdots P\lessgtr$ link. Indeed, Märkl states (14) that this is the case for the analogous salt XXXIV in which the OH group is replaced by a hydrogen atom.

Märkl (15) has also prepared the fully unsaturated eight-membered cyclic bis-ylide XXXVIII by treatment of the corresponding bisphosphonium salt with aqueous base. This stability in water can be attributed to delocalization over an "internal cyanine" structure and Märkl (15) has suggested that the stability of such structures would be independent of ring size.

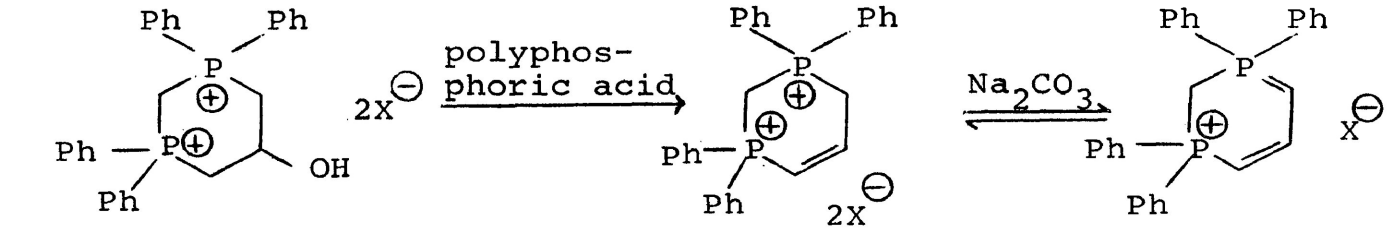
One recent and very interesting application of the α-proton abstraction technique is the formation (16) of the Si-Si stabilized cyclic ylide XXXIX. This was carried out by treatment of the open chain ylide $Me_3P{=}CHSiMe_3$ with dichlorotetramethyldisilane in the presence of butyllithium. In the opinion of the authors, the stability of this ylide can be attributed to delocalization of the carbanion negative charge into the d-orbitals of the Si-Si unit.



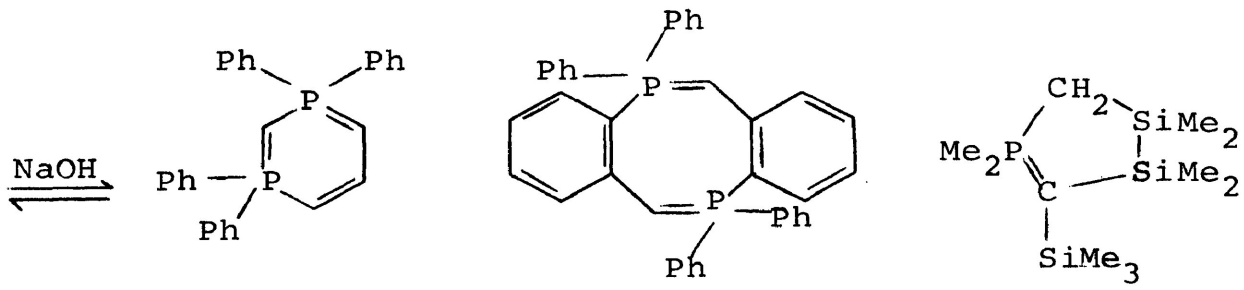
XXVIII XXIX



XXX XXXI XXXII XXXIII



XXXIV XXXV XXXVI



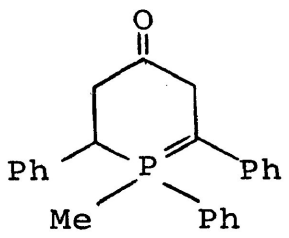
XXXVII XXXVIII XXXIX

Other unsuccessful attempts to prepare cyclic phosphonium ylides by α-proton abstraction have been made. For example, Welcher and Day (17) attempted to prepare the cyclic ylide XL from the phosphonium salt XLI by treatment with hydroxide ion but they obtained only the phosphine XLII by a competing elimination reaction. In this case, it is unlikely that the base used was sufficiently strong for ylide formation. Similarly, Katz and Turnblom (18) attempted to prepare the interesting ylide XLIII by treatment of the homocubylphosphonium salt XLIV with phenyllithium. In most phosphonium salts containing an α-hydrogen atom, this type of reaction readily yields a phosphonium ylide but in this case, the homocubyltriphenylphosphorane XLV is formed - *i.e.* the salt XLIV behaves more in the manner of a tetraarylphosphonium salt (19). These authors suggest that the reason is not that ylide formation is particularly inhibited compared with open-chain ylides but that phosphorane formation results in an increase in the bond angles around the phosphorus atom and hence releases some strain in the system. Ylide formation would leave the bond angles relatively unaffected.

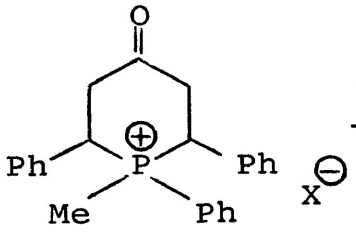
There appears to be only one example of a cyclic ylide being formed *via* α-proton abstraction from an

acyclic phosphonium unsaturated salt followed by cyclization. Savage and Trippett (20) have obtained evidence for the formation of a transient four-membered cyclic ylide XLVIII which arises from the abstraction of a proton from the methiodide XLVI followed by cyclization of the initially formed acyclic ylide XLVII. The products XLIX and L are both formed by a Wittig reaction of the ylidic solution with the appropriate aldehyde. This supports the intermediacy of the ylide XLVIII which, on this and other evidence, appears to be in equilibrium with the tautomers XLVII, LI and LII.

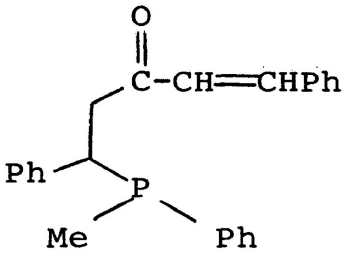
o-Proton abstraction from a tetraarylphosphonium salt followed by intramolecular cyclization *via* a cyclic phosphonium ylide intermediate operates in various syntheses of 9-phenyl-9-phosphafluorene (LIII) involving organometallic reagents as bases. Thus, 9-phenyl-9-phosphafluorene was first prepared in moderate yield by Wittig (19b) by treatment of tetraphenylphosphonium bromide with methyllithium over a period of several months. The reaction is thought to follow the sequence $Ph_4\overset{+}{P}\ Br^-$→LIV→LV→LIII and the intermediate LV is a cyclic ylide of the 3*H*-phosphole type. Similar results were obtained by Seyferth (21). The work has been extended by using other organometallic bases and greatly improved yields of



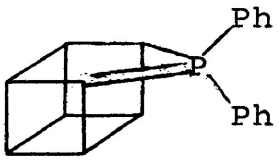
XL



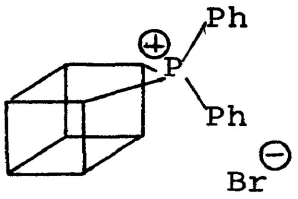
XLI



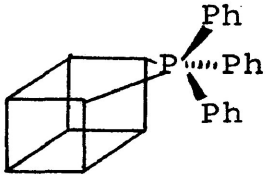
XLII



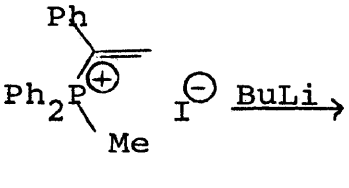
XLIII



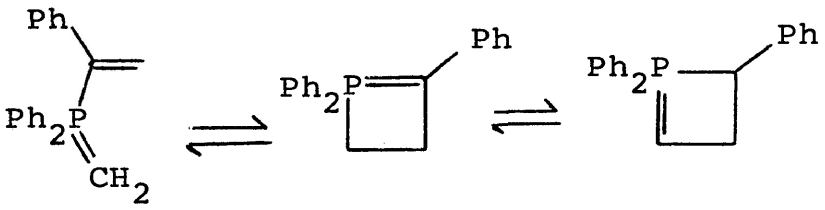
XLIV



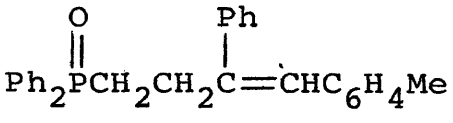
XLV



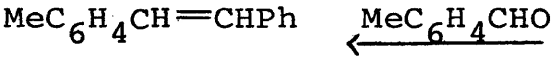
XLVI



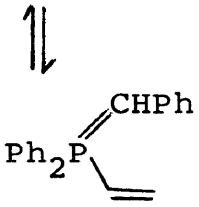
XLVII XLVIII LII



XLIX



L



LI

LIII (up to 60%) have been obtained using lithium piperidide (22) and lithium diethylamide (23, 24). Very recently, Tebby (25) found that the same type of cyclization occurs on treatment of tetraphenylphosphonium iodide with 2-thienyllithium. One interesting observation made by Seyferth (22) in this reaction is that *o*-proton abstraction (and therefore cyclic ylide formation) is a highly favoured process since treatment of the *tert*-butyltriphenylphosphonium ion (LVI) with lithium piperidide still gives LIII as the major product whereas proton abstraction from the *tert*-butyl group followed by elimination of triphenylphosphine might have been expected.

In a related reaction, Wittig (19b) found that treatment of triphenylphosphine itself with phenylsodium gives a low yield of LIII by *o*-proton abstraction. However, in this case, it is unlikely that a cyclic ylide is involved.

(b) Nucleophilic Addition to Activated Alkenes, Alkynes and Arynes

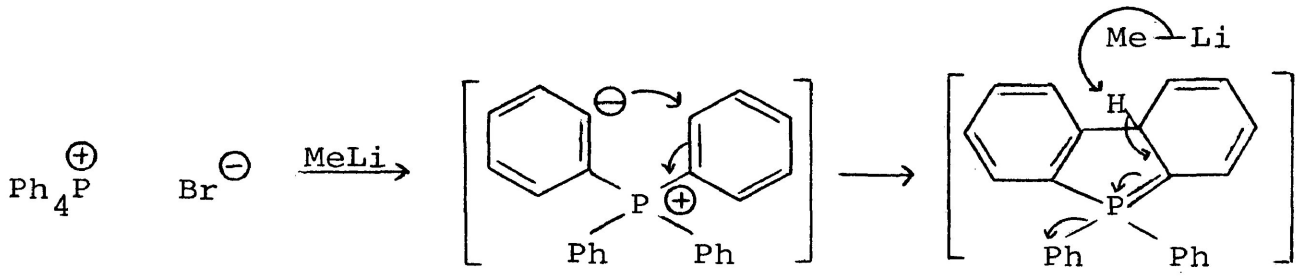
The second of these reaction types has resulted not only in the formation of probable five-membered cyclic ylidic intermediates and stable five and six-

membered cyclic ylides, but also in relatively stable five- and six-membered cyclic bis-ylides.

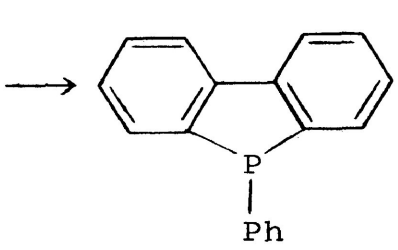
With respect to the reaction between phosphines and activated alkenes, there appears to be only one report by Savage and Trippett (20) which postulates the formation and reports the characterization of a cyclic ylidic intermediate. Trippett (26) had previously shown that the phosphines LVII where R' is an electron-withdrawing group, will react with activated alkenes to give acyclic ylides. With this in mind, and with the knowledge that vinylphosphonium salts will undergo Michael addition reactions (27), he suggested that it was likely that the zwitterion formed by the addition of a vinylphosphine to an activated alkene would cyclize to form a cyclic ylide. To test this idea, he treated diphenyl-1-phenylvinylphosphine LVIII with acrylonitrile in the presence of *p*-tolualdehyde (20) and obtained the phosphine oxide LX the structure of which (established by NMR and mass spectral data) indicated that it was formed *via* the five-membered cyclic ylide LIX. When benzaldehyde was used in place of *p*-tolualdehyde, an analogous oxide was obtained.

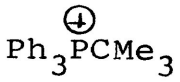
Reactions of tertiary phosphines with acetylenic esters in general have been a very fruitful source of cyclic phosphonium ylides. Thus, the

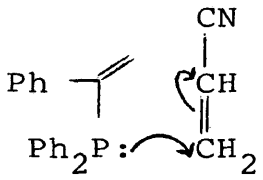
first cyclic ylide was prepared by Johnson and Tebby (28) in 1961 by treating triphenylphosphine with an excess of dimethyl acetylenedicarboxylate. However, the 1:2 adduct of the phosphine with the ester was not recognized as a cyclic ylide until 1969 when Tebby (29) revized the structure of the product. In 1961 Johnson and Tebby (28) had assigned the open-chain structure LXI to the methanol-insoluble product formed after the reaction mixture warmed from -50°C to room temperature. They also proposed that it is a rearrangement product of an intermediate formed initially at -50°C and to which they assigned the zwitterionic structure LXII. In 1969, Tebby and his co-workers (29) revized the structure of the methanol-insoluble adduct to that of the stable ylide LXIII on the basis of the IR spectrum and NMR studies on the adduct over a range of temperatures as well as obtaining chemical confirmation of the structure. Recently, Tebby (30, 31, 32) has elaborated on this work. He now believes that the adduct LXIII and another previously uncharacterized methanol-soluble 1:2 adduct formed in 20% yield and to which he has assigned the structure LXIV (32) may both be formed *via* the intermediate LXV (30, 31) and perhaps LXVI which are formed initially at -50°C.



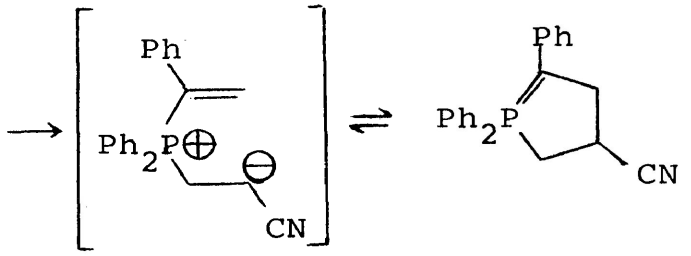
LIV LV

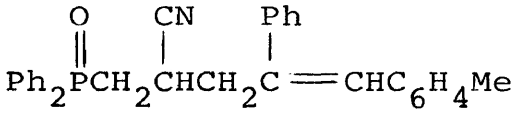




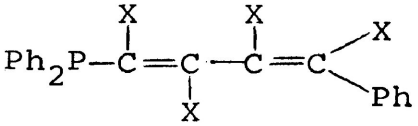


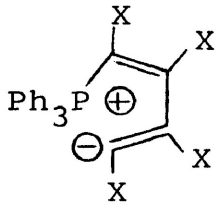
LIII LVI LVII LVIII

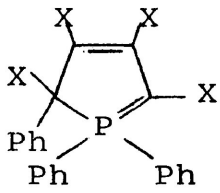


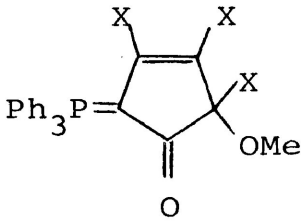


LIX LX









LXI LXII LXIII LXIV

X=CO_2Me

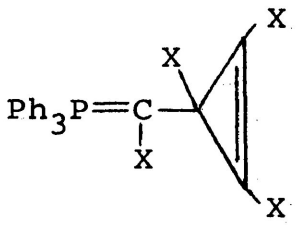
Similar reactions occur between tri-*p*-tolylphosphine and the ester (29, 32).

On the basis of the reported (33, 34, 35) mechanisms for ring opening and ring expansion reactions of phosphetans and the migrations noted in the reactions of tertiary phosphines with dimethyl acetylenedicarboxylate (29), Trippett and his co-workers (36) investigated the reaction of the phosphetan LXVII with the acetylenic ester. As with other phosphines, a stable cyclic ylide LXIX is formed in 44% yield and the reaction presumably proceeds *via* the trigonal bipyramidal spirophosphorane LXVIII in which the four-membered ring occupies the apical-equatorial arrangement. This arrangement would favour the migration of the CMe_2 group from the apical position to the carbon atom adjacent to the phosphorus atom in the five-membered ring.

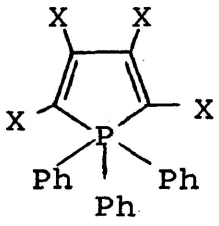
Another related stable ylide LXX has recently been reported by Waite and Tebby (37). It is a revized structure, which they assigned to a 1:2 adduct of 1,2,5-triphenylphosphole LXXI and dimethyl acetylenedicarboxylate originally isolated by Hughes and Uaboonkul (38) who proposed the spirobiphosphole structure LXXII for this adduct. However, on the basis of the ^{31}P NMR spectrum and the adduct's

behaviour in acid solution, Waite and Tebby (37) initially suggested that the spirobiphosphole is in fact the penultimate structure in the reaction and the isolated product is an ylidic structure derived from LXXII. Several rearrangement products of the spirobiphosphole leading to the ylides LXXIII, LXXIV and LXXV, the last one formed from LXXVI by a phenyl migration, were considered by Waite and Tebby but proton NMR data did not support any of these structures. Waite and Tebby then discarded the idea that the spirobiphosphole LXXII is formed as an intermediate and considered other methods by which the dipolar intermediate LXXVII, which is presumably formed, could cyclize. They finally decided on a mechanism (the sequence LXXVII→LXXVIII→LXX) very similar to the one proposed for the reaction of diphenylvinylphosphine with dimethyl acetylenedicarboxylate (see next chapter). Waite and Tebby confirmed the structure LXX mainly by spectroscopic measurements.

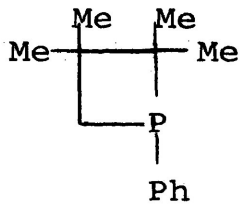
There have been several reports recently of the reaction of bisphosphines with dimethyl acetylenedicarboxylate to give cyclic phosphonium ylides. Hughes and Jafry (39) studied the reaction of the ester with bis(diphenylphosphino)ethane (LXXIX). On the basis of spectroscopic evidence, the product



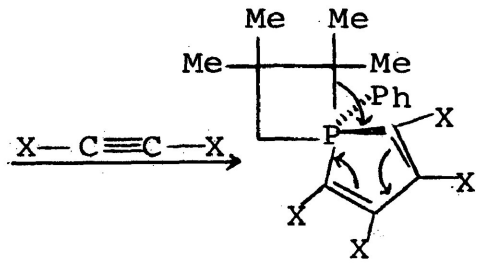
LXV



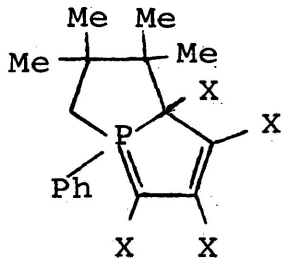
LXVI



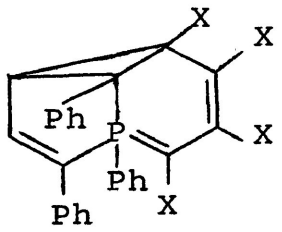
LXVII



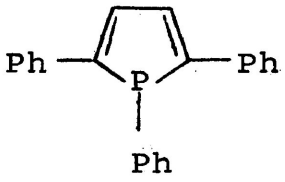
LXVIII



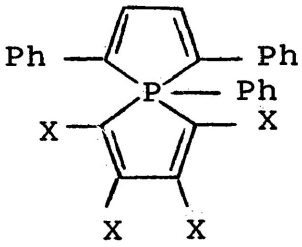
LXIX



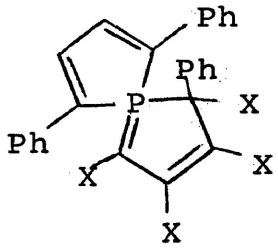
LXX



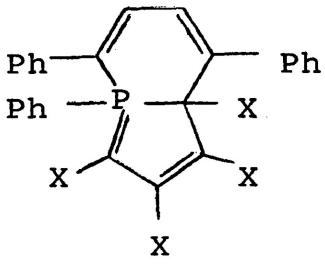
LXXI



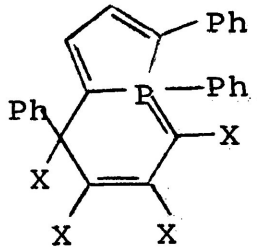
LXXII



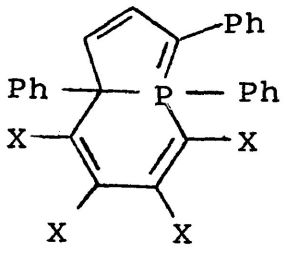
LXXIII



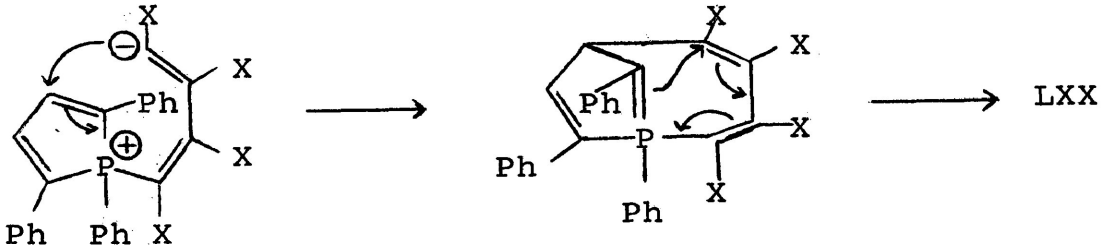
LXXIV



LXXV



LXXVI



LXXVII

LXXVIII

LXX

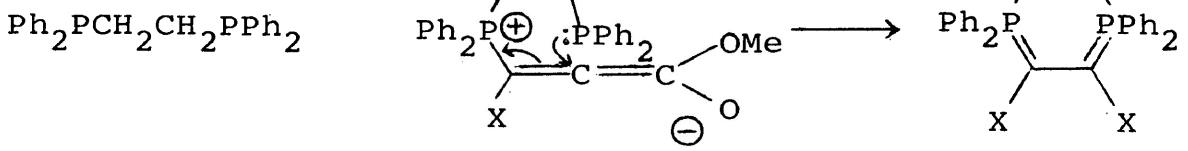
$X=CO_2Me$

was shown to have the structure LXXXI. This is supported by the fact that the ylidic product forms a bisperchlorate on treatment with perchloric acid and the dioxide of LXXIX on hydrolysis. The formation of LXXXI is thought to follow the sequence LXXIX→LXXX→LXXXI.

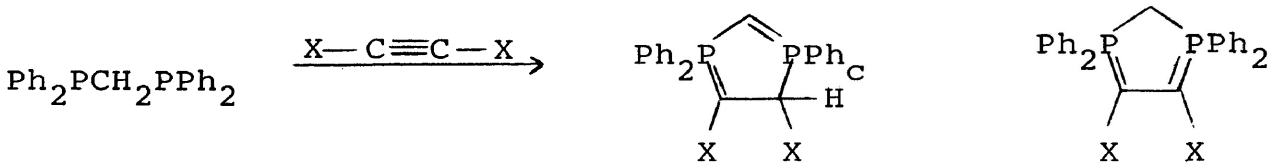
At about the same time, Tebby and his co-workers (40) reported the synthesis of the bis-ylide LXXXIII from the reaction between bis(diphenylphosphino)-methane LXXXII and dimethyl acetylenedicarboxylate. They proposed that the ylide LXXXIII is the preferred structure in a tautomeric equilibrium of LXXXIII and LXXXIV although LXXXIV is probably formed first in the reaction. They further proposed that the electronic structure of LXXXIII may best be represented by LXXXV and that LXXXV is an equilibrium mixture of the two conformers LXXXVI and LXXXVII. The proposed structure of the ylide was supported by IR, UV, NMR and mass spectral data together with elemental analyses. The preference for the delocalized ylidic structure LXXXV was based upon IR data and a consideration of the pK_a values (41) of the model alkylidenephosphoranes $Ph_3P{=}CHCO_2Et$ (pK_a=9.2) and $Ph_3P{=}CH{-}\overset{+}{P}Ph_3 \longleftrightarrow Ph_3P\cdots\overset{+}{C}H\cdots PPh_3$ (pK_a=5.4). Variable temperature NMR studies indicated the equilibrium LXXXVI $\rightleftharpoons$ LXXXVII.

In the same publication (40), Tebby and his co-workers presented some evidence for the successful synthesis of the 1,4-diphosph(V)orin LXXXIX from *cis* 1,2-bis(diphenylphosphino)ethylene (LXXXVIII). Although the solid product was reported to be too unstable for complete characterization, the IR and mass spectral data supported structure LXXXIX. In particular, the ester groups are clearly both attached to ylidic carbon atoms since the carbonyl stretching frequencies occur well below 1700 cm^{-1}. Moreover, hydrolysis of the adduct gives the dioxide of LXXXVIII.

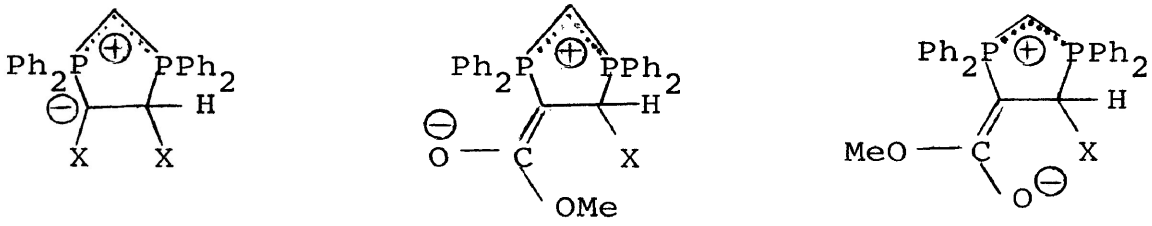
These and related reactions were being studied simultaneously by Hughes and Jafry (42). Their conclusions were the same for the structure of the ylide LXXXIII produced by the reaction of LXXXII with dimethyl acetylenedicarboxylate. However, they did manage to synthesize the monoperchlorate XC but, on hydrolysis of the original adduct, only bis(diphenylphosphino)methane monoxide was obtained whereas Tebby also obtained the dioxide. Hughes and Jafry (42) also studied the reaction between LXXXVIII and dimethyl acetylenedicarboxylate and came to the conclusion, on the basis of NMR studies, bisperchlorate formation and the nature of the hydrolysis product of the adduct, that LXXXIX is indeed formed and, although the adduct is readily hydrolyzed, it appears



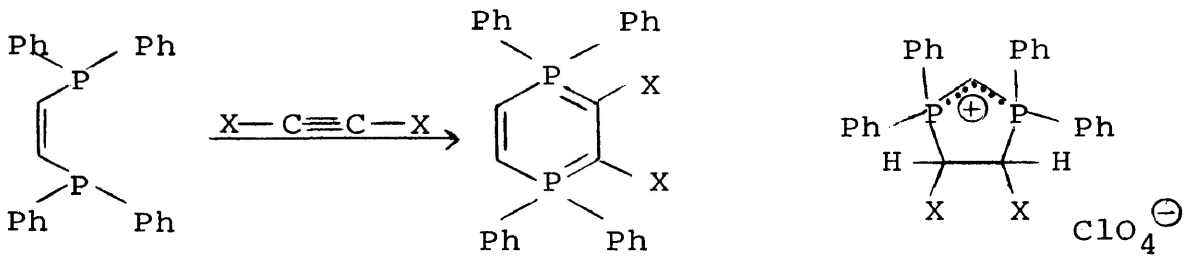
LXXIX LXXX LXXXI



LXXXII LXXXIII LXXXIV



LXXXV LXXXVI LXXXVII



LXXXVIII LXXXIX XC

$X=CO_2Me$

to have some aromatic character. This will be discussed in a later section.

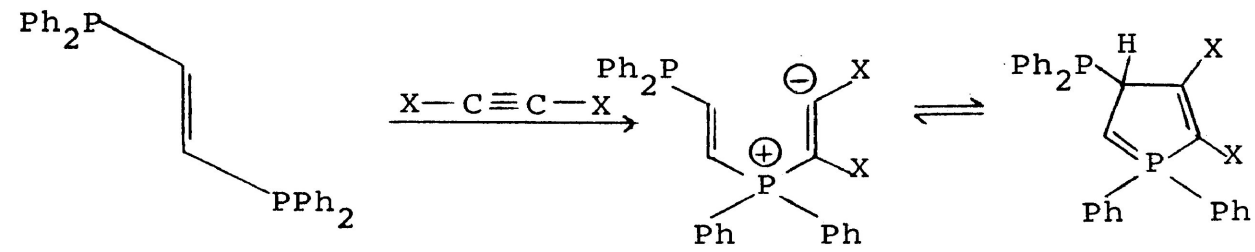
Hughes and Jafry (42) have also investigated the reaction of the bisphosphine *trans* 1,2-bis-(diphenylphosphino)ethylene (XCI) with dimethyl acetylenedicarboxylate and have obtained a highly water-sensitive adduct from the reaction. IR studies on the adduct indicate that it contains one normal ester group and one ester group adjacent to a carbon atom of strongly carbanionic character. The NMR spectrum in deuterochloroform indicates that the adduct exists largely in the form XCII which may be in tautomeric equilibrium with the ylidic structures XCIII, XCIV and possibly XCV. The NMR spectrum in trifluoroacetic acid shows that a mixture of protonated ylides is formed but, over a period of time, the protonated form XCVI of XCIV tends to predominate as a result of a series of equilibria until after several days, the spectrum of the adduct in trifluoroacetic acid is entirely due to XCVI.

The behaviour of the adduct XCII towards hydrolysis is very surprising. On treatment with water (42) the adduct rapidly hydrolyzes to give the phosphine XCIX - *i.e.* one of the diphenylphosphino groups has been eliminated. The mechanism

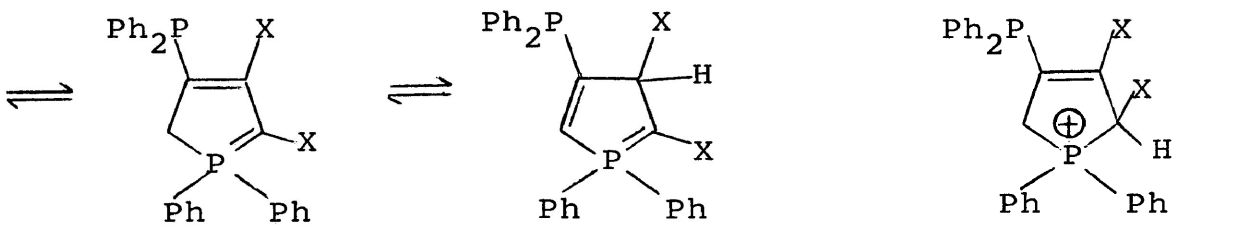
of this reaction is obscure but a possible (though unconfirmed) scheme is outlined in the sequence XCII $\rightleftharpoons$ XCIII→XCVII→XCVIII→XCIX. Deuterolysis experiments support this tentatively proposed mechanism (42).

Treatment of tetraphenylbiphosphine (Ph_2PPPh_2) with an excess of dimethyl acetylenedicarboxylate has given C - possibly by hydrolysis of the bis-ylide CI (42).

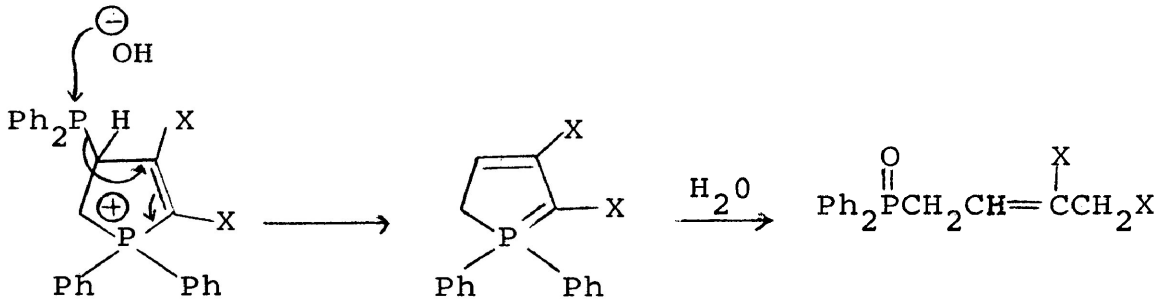
There are several references in the literature to reactions between phosphines and arynes but relatively few of these reactions lead to cyclic phosphonium ylides as intermediates or products. In one of the first of these studies, Wittig and Benz (43) investigated the reaction of triphenylphosphine with benzyne and obtained 9-phenyl-9-phosphafluorene (LIII) in low yield. Wittig (43) postulated the zwitterionic and cyclic ylidic structures LIV and LV as intermediates in the reaction and was able to trap the zwitterion LIV as the adduct CII by carrying out the reaction in the presence of triphenylboron. The reaction, therefore, proceeds by a mechanism closely related to that of *o*-proton abstraction from tetraarylphosphonium salts. More recently, Wittig and Matzura (44) have extensively investigated the properties of the zwitterion LIV at low tempera-



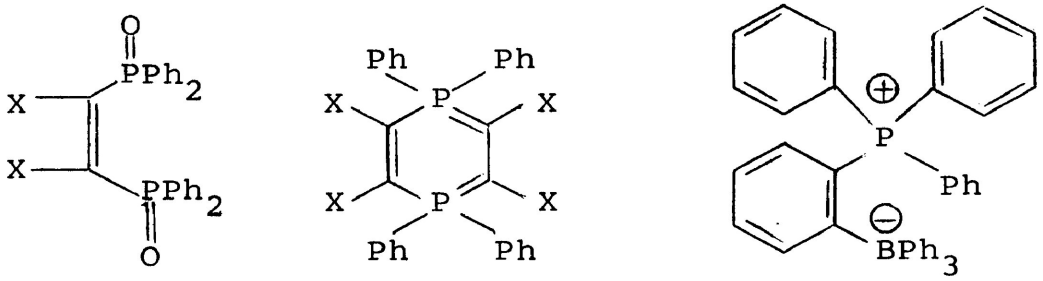
XCI XCII XCIII



XCIV XCV XCVI



XCVII XCVIII XCIX



C CI CII

X=CO_2Me

ture and similar zwitterions generated from triphenylphosphine and arynes derived from a variety of *o*-lithiofluoroaromatics.

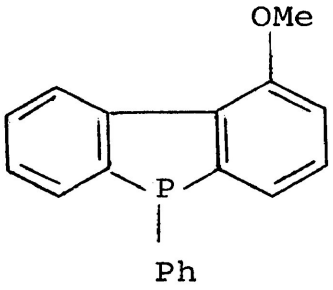
Zbiral (45) reinvestigated the reaction of triphenylphosphine with benzyne and was able to obtain up to 40% of LIII from this reaction. He also studied the reaction of 1-methoxy-9-phenyl-9-phosphafluorene (CIII) *via* a cyclic ylide mechanism. Similarly, 9-phenyl-9-phosphafluorene (LIII) was found to react with 1-methoxy-2-benzyne in a reaction involving a cyclic ylide intermediate. Two possible cyclizations of the zwitterion CIV were considered to give the ylides CV or CVI respectively followed by elimination of benzene to give CVII or CVIII. It was found that only the reaction path LIII→CIV→CV→CVII operates in this reaction.

Very recently, Märkl (46) has investigated the reactions of phosphorins of type CIX with arynes to give benzophosphabarrelenes such as CX. This is an extension of his earlier investigations of the reactions of phosphorins with alkynes to give phosphabarrelenes (47). Märkl found (46) that 2,4,6-triphenylphosphorin (CIX, R=Ph) is reluctant to react with benzyne generated from various sources and developed an alternative and ingenious benzyne type of addition. In this addition, the phosphorin

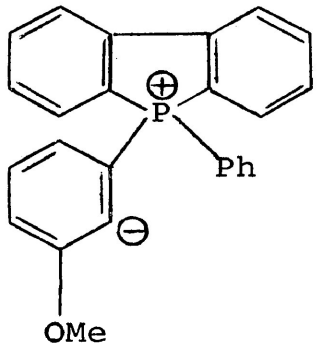
is treated with *o*-fluorophenylmagnesium bromide to give the anion CXI which subsequently cyclizes to give the benzophosphabarrelene CX. However, it was found that small quantities (10%) of a 2:1 adduct of benzyne with the phosphorin were also formed and this product proved to be a cyclic ylide. This ylide was found to be isomeric, though not identical, with the known ylide CXII (to be discussed in the next section) and on the basis of its UV spectrum, it was assigned structure CXIII.

(c) Radical and Ionic Addition to Phosphorin Derivatives.

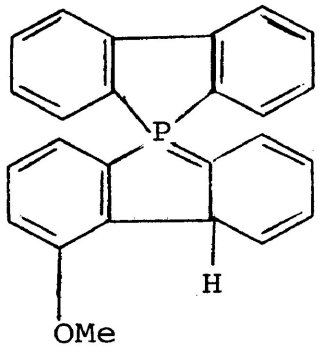
Although phosphorins of type CIX are poor nucleophilic donors, they will readily undergo radical addition to give stable and isolable cyclic phosphonium ylides. Thus, Dimroth and his co-workers (48) have found that oxidation of 2,4,6-triphenylphosphorin (CIX, R=Ph) with Hg(II) acetate in the presence of alcohols or phenols leads to the formation of the corresponding 1,1-dialkoxy- or 1,1-diaryloxy-2,4,6-triphenylphosphorin CXIV (R=alkyl or aryl). The reaction is thought to proceed *via* the cation radical CXV which has been detected by ESR spectroscopy. In closely related experiments, the same group of workers has shown (49) that CIX (R=Ph)



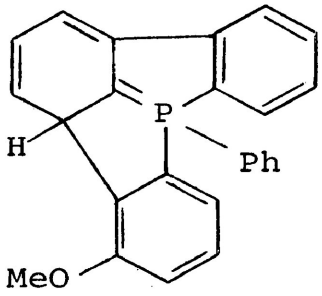
CIII



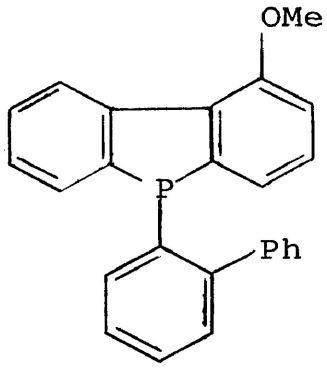
CIV



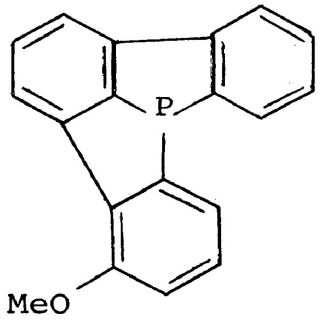
CV



CVI



CVII



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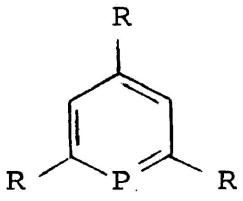

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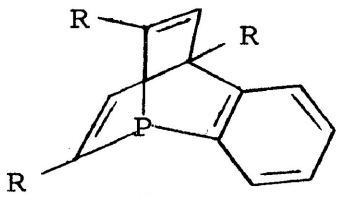

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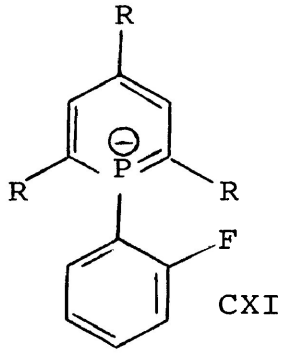

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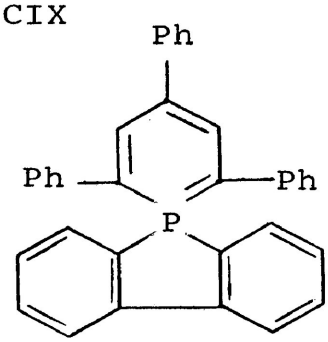

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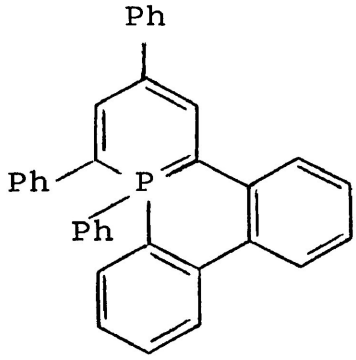

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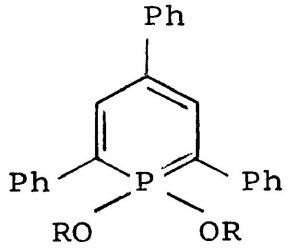


CXIV

undergoes radical addition with the 2,4,6-triphenylphenoxy radical and the diphenylamino radical to give CXIV (R=2,4,6-triphenylphenyl) and CXVI respectively. Cyclic ylides of this type have proved to be remarkably stable and are protonated only by strong acids.

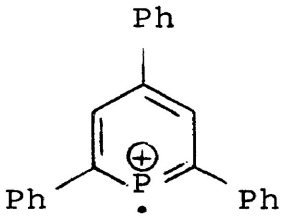
At about the same time, Märkl and his group were also investigating addition reactions of phosphorins and phosphorin derivatives. In particular, they investigated the generation of radical species in the presence of the phosphorin CIX (R=Ph) by the pyrolysis of organomercury compounds (50). By this method, they prepared 1,1,2,4,6-pentaphenylphosphorin (CXVII) from the phosphorin CIX (R=Ph) and diphenylmercury and the spiran CXII from the phosphorin CIX (R=Ph) and 2,2'-biphenylylenemercury (CXVIII). In this case, the addition was thought to go *via* radicals of type CXIX and this radical (and subsequently the phosphorin CXVII) could also be generated by treatment of CXX with diphenylmercury at 220° (50). Treatment of CXX with the 2,4,6-triphenylphenoxy radical leads to the formation of the phosphorin CXXI (Ar=2,4,6-triphenylphenyl) (50).

In a series of papers dealing with various aspects of the electrophilic nature of 2,4,6-triphenylphosphorin (CIX, R=Ph), Märkl and his group (51-53) have found that CIX undergoes addition with

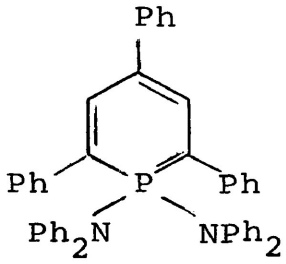
organolithium (51-53) or Grignard reagents (53) to give anions of type CXXII. Furthermore, treatment of this anion with alkyl or benzyl halides can lead to the formation of the 1,1-disubstituted phosphorins CXXIII (R=alkyl or benzyl). Märkl (52) established that the nature of the solvent is quite important in the reaction. For example, the phosphorins CXXIII are generally formed if ethereal solvents (such as tetrahydrofuran) are employed and the use of nonpolar solvents such as benzene leads to the formation of the isomeric cyclic phosphines CXXIV. One exception to this generalization is the reaction of the anion CXXII with methyl iodide where the product is always CXXIII (R=Me) regardless of the nature of the solvent. The isomeric compound CXXIV (R=Me) can be prepared from CXXII by treatment with trimethyloxonium fluoroborate (53). Märkl (53) has further generalized these observations by stating that the anion CXXII reacts with S_N1 reactive halides to give the cyclic phosphines CXXIV (*i.e.* reaction occurs at the site of highest electron density) whereas reaction with S_N2 reactive halides yields the 1,1-disubstituted phosphorins CXXIII. It is also interesting to note that the anion CXXII can also be generated from the phosphorin CXVII by treatment with Na/K alloy in tetrahydrofuran (50).

Thus, CIX (R=Ph) undergoes radical addition to give 1,1-disubstituted phosphorins of type CXII, CXIV and CXVI *via* radicals of type CXV and CXIX. It also undergoes anionic addition to give ions of type CXXII which react further with organic halides to give the corresponding 1,1-disubstituted phosphorins. In principle then, nucleophilic addition to cations of type CXXV should also lead to 1,1-disubstituted phosphorins. Unfortunately, the cation CXXV is not readily available directly from CIX (R=Ph) and indirect syntheses of CXXV) have had to be devised.

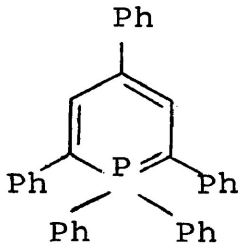
The first attempts to prepare CXXV (as an intermediate in the proposed synthesis of CXVII) were made by Price (54) who treated 2,4,6-triphenylpyrylium fluoroborate (CXXVI) with phenylphosphine in boiling pyridine. There is little doubt that the cation CXXV is formed in the reaction but it was found that under the conditions of the reaction, hydrolysis occurs and a mixture of two hydrolysis products is formed. Price (54) assigned the structures CXXVII and CXXVIII to these products, although CXXVII would be most unusual in that it would contain 5-coordinate hexacovalent phosphorus. More recently, Märkl (50, 51) has repeated this work and has also obtained two similar products (50) to which he



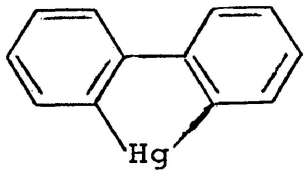
CXV



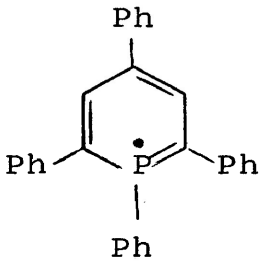
CXVI



CXVII



CXVIII



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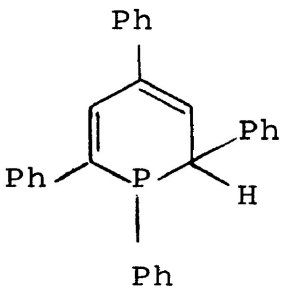

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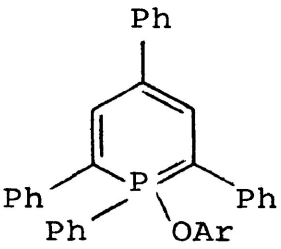
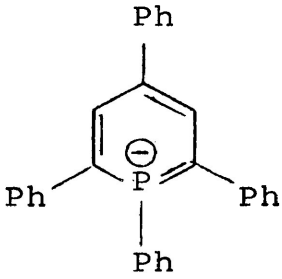


CXXI



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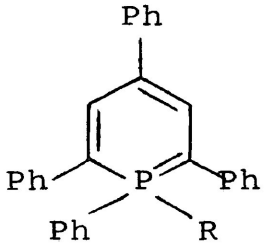

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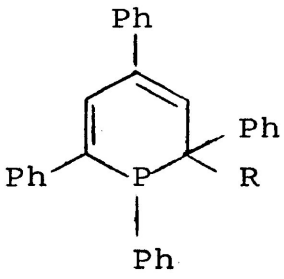
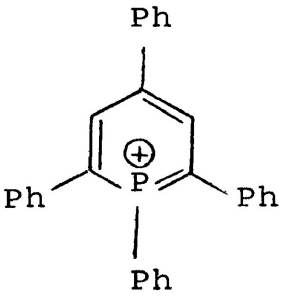
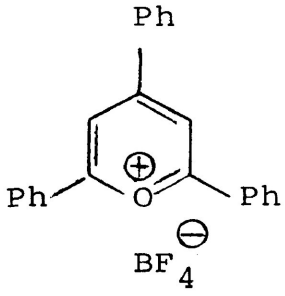


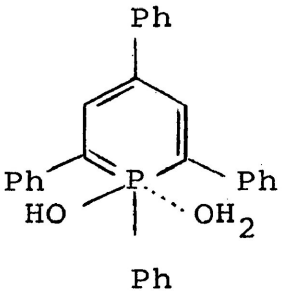
CXXIV



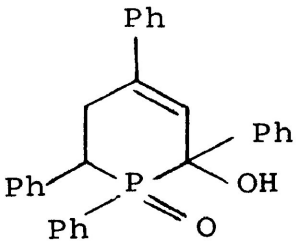
CXXV



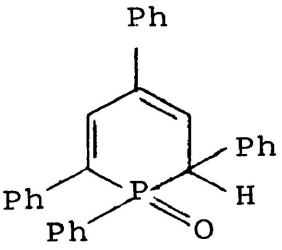
CXXVI



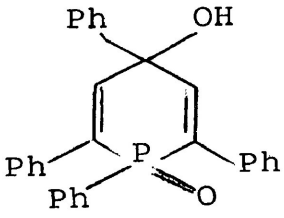
CXXVII



CXXVIII



CXXIX



CXXX

assigned the structures CXXIX and CXXX. Ultraviolet spectrophotometric studies indicate that in methanol solution, CXXIX is in equilibrium with its tautomer CXXXI (51). Although Märkl gives relatively few details, the fact that Price reported the formation of the hydrolysis products in nearly quantitative yield indicates that the two sets of products are the same and there can be little doubt that the structures proposed by Märkl are correct.

The cation CXXV has been prepared by an alternative route (50) which involves the treatment of CXX with trityl perchlorate and subsequent treatment of CXXV with phenyllithium does indeed give the 1,1-disubstituted phosphorin CXVII. The product is obtained in excellent yield.

In a very recent paper, Märkl (55) has reported the investigation of three routes to 1,1-disubstituted phosphorins *via* cations of type CXXXII. The first of these methods is direct treatment of pyrylium salts such as CXXVI with primary phosphines in the presence of alcohols, thioalcohols or phenols to give 1,1-disubstituted phosphorins such as CXXXIII (R=Ph or CH_2Ph, R'=alkyl or Ph), CXXXIV (R=Ph or CH_2Ph, R'=alkyl) and CXXXV (R=H, R'=Me; or R and R'=bridging saturated ring). In this reaction, the yields are poor to moderate.

The second method is a modification of the first in which the primary phosphine RPH_2 is replaced by the corresponding bis(hydroxymethyl)phosphine $RP(CH_2OH)_2$ and this greatly improves the yields.

The third method involves the oxidation of the cyclic phosphine CXX with mercuric acetate to give CXXV which is then treated with an alcohol or phenol to give CXXXIII (R=Ph, R'=Me or Ph). This reaction is reminiscent of Dimroth's experiments with phosphorins of type CIX in the presence of mercuric acetate and alcohols (48).

In connection with these studies, Märkl found (55) that treatment of 4-methyl substituted pyrylium salts with primary phosphines or bis(hydroxymethyl)phosphines gives compounds of type CXXXVI *via* an unexpected base catalyzed condensation.

The recent synthesis (56) of the completely unsubstituted phosphorin CIX (R=H) suggests that reactions of the type described in this section could be used to prepare a wide variety of simple 1,1-disubstituted phosphorins.

(d) Miscellaneous Reactions which Produce Cyclic Phosphonium Ylides.

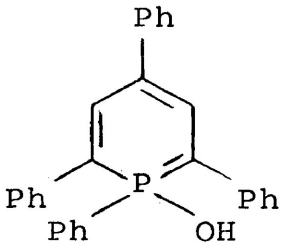
There appear in the literature several reports of the formation of cyclic phosphonium ylides by methods which do not fall into any of the three main categories already discussed and these are usually of limited scope.

One of these reactions which appears to have a good potential as a source of 1,1-disubstituted phosphorins is due to Märkl (53) and involves the controlled pyrolysis of 1,2-dihydrophosphorins of type CXXXVII. Thus, it has been found (53) that compounds of type CXXXVII are smoothly converted into the corresponding phosphorins CXXXVIII (R=Ph or CH_2Ph, $R'=CH_2Ph$ or $CH_2CH=CH_2$) in yields of 70-80% on heating to a temperature of 180-220°. As Märkl points out, this is apparently the first recorded instance of the isomerization of a phosphine into a phosphonium ylide and the reaction can only be rationalized on the assumption that the 1,1-disubstituted phosphorins possess a considerable resonance energy. Above 220° the 1,1-disubstituted phosphorin CXXXVIII ($R=R'=CH_2Ph$) decomposes to give the phosphorin CIX (R=Ph) and at elevated temperatures, a number of 1,2-dihydrophosphorins similar to CXXXVII decompose

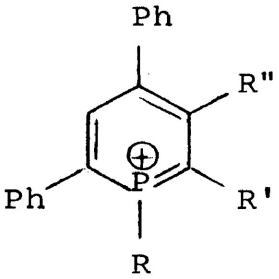
directly to give CIX (R=Ph) in high yield - presumably *via* the corresponding 1,1-disubstituted phosphorin CXXXVIII. Certain of these decompositions may involve 1*H*-1,1-disubstituted phosphorins such as CXXXIX.

Bergerhoff and his co-workers (57a) have recently elaborated on an earlier report (57b) concerning the reaction of arylphosphonous dichlorides ($ArPCl_2$) with malonate esters in the presence of tertiary amines. The resulting ylide CXL is of considerable interest since it is the only known cyclic ylide containing a P-P bond. The compound has been fully characterized (57a) and it has been suggested that CXL (R=Et, R'=Ph) is formed by a dimerization - rearrangement reaction of a hypothetical intermediate $PhP{=}C(CO_2Et)_2$.

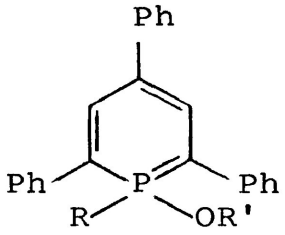
Cyclic phosphonium ylides have been postulated as transient intermediates in a variety of other reactions. For example, Märkl (58) has postulated a cyclic bis-ylide intermediate - presumably CXLI - in the proton catalyzed quantitative dimerization of diphenylvinylphosphine to give CXLII. Similarly Campbell (59) reported that, on one occasion, treatment of the quaternary salt CXLIII with concentrated aqueous alkali gave CXLIV and suggested that the intermediate in this reaction is the



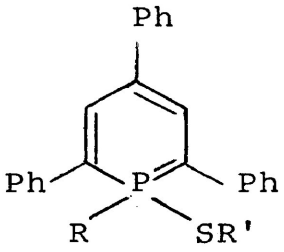
CXXXI



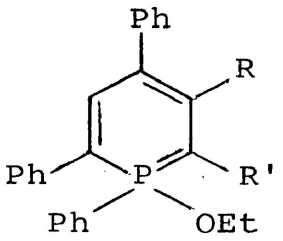
CXXXII



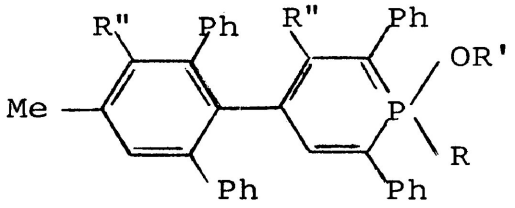
CXXXIII



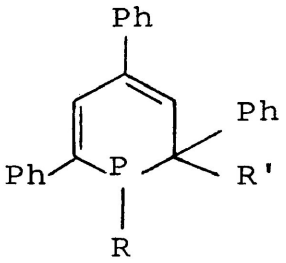
CXXXIV



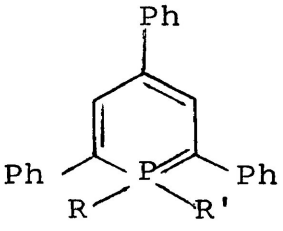
CXXXV



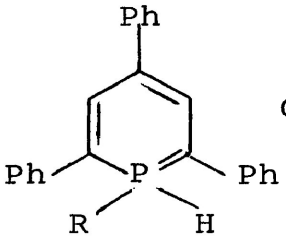
CXXXVI



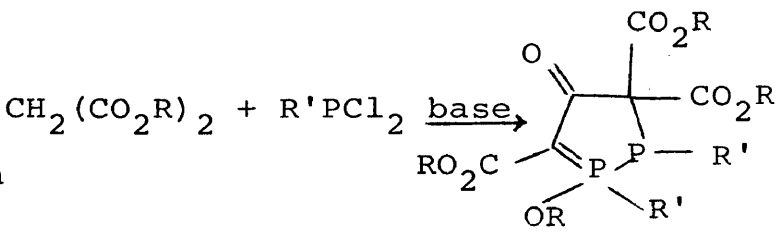
CXXXVII



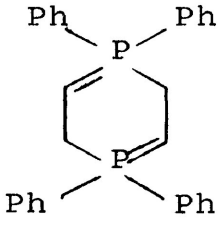
CXXXVIII



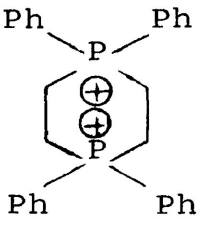
CXXXIX



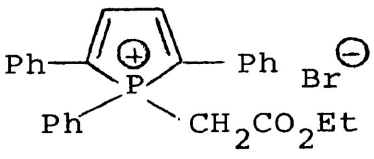
CXL



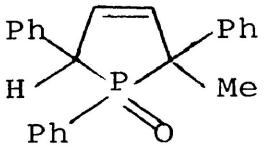
CXLI



CXLII



CXLIII



CXLIV

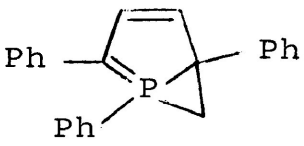
interesting bicyclic ylide CXLV. Hellwinkel (60) found that solutions of the spirophosphorane CXLVI in dry, oxygen-free benzene rapidly take on a deep violet colour due to the formation of the radical CXLVII. He also suggested that this radical is one contributor to a resonance hybrid to which the ylidic structure CXLVIII is also a significant contributor. Furthermore, when the phosphorane CXLVI is allowed to stand in benzene for several days followed by evaporation of the solution to dryness and treatment of the residue with ethanol, the phosphine CXLIX is obtained. In Hellwinkel's opinion, it is likely that addition of a hydrogen atom to CXLVIII occurs in this reaction to give the ylidic structure CL which rearranges to CXLIX as shown.

There have also been reports (61, 62) of the formation of cyclic phosphonium ylidic structures being induced by electron impact on various phosphorus containing molecules. For example, in a paper concerning the mass spectra of phosphinic acid derivatives, Haake (61) has postulated the formation of the ylidic radical cation CLI as a cyclized form of the molecular ion of diphenylphosphinic acid. Similarly, Williams (62) suggested that in the mass spectra of acylphosphoranes

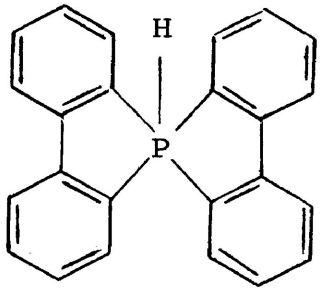
(Ph_3P=CHCOR), the $(M-1)^+$ ion could have the ylidic structure CLII or the alternative structure CLIII and presented arguments in favour of the latter. Very recently, these conclusions of Williams have been confirmed by Bowie and his group (63).

Structural Considerations.

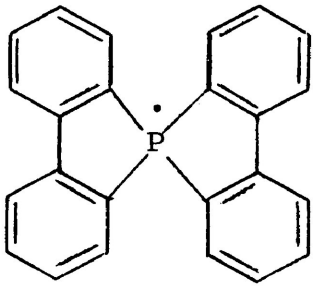
A detailed discussion of the bonding in phosphonium ylides would not be appropriate here since the topic has already been very well treated elsewhere (see for example ref. 5b and several later papers). Moreover, many of the three-, four- and five-membered cyclic phosphonium ylides discussed in this survey appear to behave in a fashion similar to the corresponding acyclic ylides. However, certain cyclic phosphonium ylides (notably the 1,1-disubstituted phosphorins) are of considerable theoretical interest since they may possess aromatic character or at least an extended delocalized character. Furthermore, if these compounds are aromatic, the aromaticity may be of a completely different type to that observed in benzenoid compounds and certain nitrogen heterocycles since it would involve the d-orbitals of the phosphorus atom. It is therefore in order to survey recent developments



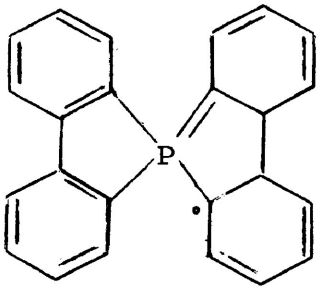
CXLV



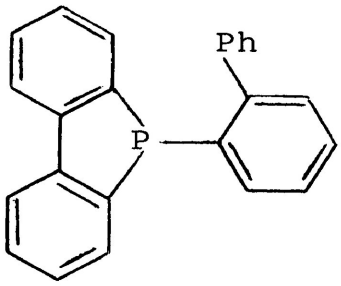
CXLVI



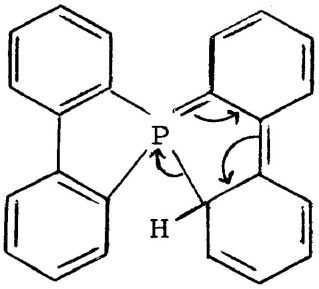
CXLVII



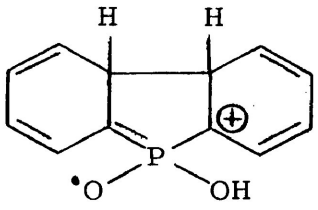
CXLVIII



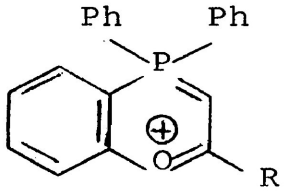
CXLIX



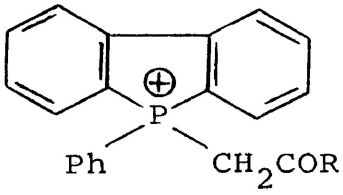
CL



CLI



CLII



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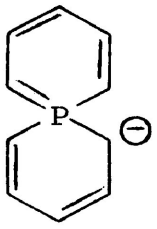
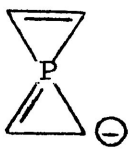
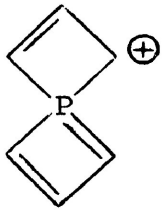


CLIV



CLV



CLVI

regarding bonding in the potentially aromatic cyclic phosphonium ylides.

The first suggestions regarding the electronic structure of the 1,1-disubstituted phosphorins came from Märkl (15, see also 58) and Price (64), Märkl's proposal being similar to that put forward by Dewar (65) for the structurally related cyclic phosphonitrilic trimers. In Märkl's scheme, the d_{xz} and d_{yz} orbitals of a tetrahedral phosphorus atom are combined to form two new d-orbitals, each of which is directed above and below the plane of the ring towards an adjacent carbon atom (and its $2p_z$ orbital) on either side of the phosphorus atom. These orbitals are so placed as to overlap with the $2p_z$ orbitals of the adjacent carbon atoms so as to form a p_π-d_π link. This would mean that the conjugation around the ring would not be complete since the phosphorus atom uses different d-orbitals to overlap with the orbitals of the adjacent carbon atoms.

Price's suggestion is a little different in that only one d-orbital (the d_{yz} orbital) is involved. This orbital is arranged such that its lobes are placed midway between the lobes of the $2p_z$ orbitals of the two carbon atoms adjacent to the phosphorus atom - *i.e.* one d-orbital overlaps

with two $2p_z$ orbitals and full conjugation is achieved.

Shortly after these suggestions, Mason (66) discussed four types of cyclic π-bonding and suggested that both 1,1-diphenylphosphorin (II) and the corresponding 1,3-diphosphorin XXXVII are anti-Hückel Möbius type conjugated systems. This approach also suggests that the corresponding phosphorus analogues of cyclobutadiene and cyclo-octatetraene would also have large resonance energies. However, Vilceanu (67) carried out HMO calculations on 1,1-diphenylphosphorin (II) using various models for heteroatoms possessing 3d-orbitals. Among the models used was that of Fukui (68) which assumes a normal d_π orbital and one π-electron for the phosphorus atom. A second model considered was that of Mason (66) and Craig and Paddock (69) which leads to an anti-Hückel system in which the β-integrals for the two ring P-C bonds are of opposite sign. A third model considered was that of Dewar (65) which has already been mentioned. Vilceanu also considered Fukui and anti-Hückel models involving weak interactions between the π-orbital of the phosphorus atom with those of the neighbouring atoms. As a result of these HMO calculations, Vilceanu concluded that

only the simple Fukui (68) and Dewar (65) models are consistent with the spectroscopic properties, the stability to water and the relatively weak basic character of II.

Very recently, Oehling and Schweig (70) have shown by CNDO/2 calculations that for the phosphorus atom in 1,1-disubstituted phosphorins, there is a significant d-orbital contribution to the P-C σ-bonds and a significant phosphorus $3p_z$ orbital contribution to the π-bonding.

These theoretical studies show therefore that 1,1-disubstituted phosphorins are extended delocalized and probably aromatic systems. However, as Märkl has pointed out in several papers, further experimentation is desirable.

The potentially aromatic character of the 1,1-disubstituted phosphorins has prompted three X-ray diffraction studies on these systems. Thus, Daly and Märkl (71) determined the crystal and molecular structure of 1,1-dimethyl-2,4,6-triphenylphosphorin (CXXXVIII, R=R'=Me) and found that the heterocyclic ring is almost planar and that the ring P-C bonds are almost identical in length and differ little from those in 2,6-dimethyl-4-phenylphosphorin (72). Furthermore, the C-C bond lengths in the molecule are essentially uniform and of very

similar length to those in benzene and pyridine. There is therefore every reason to assume that a delocalized aromatic system is present. Similar results were obtained by Thewalt in his X-ray studies of 1,1-dimethoxy-2,4,6-triphenylphosphorin (CXIV, R=Me) (73) and 1,1-bis(dimethylamino)-2,4,6-triphenylphosphorin (the *N*,*N*-dimethyl analogue of CXVI) (74) and similar conclusions were drawn regarding the aromatic character of these systems.

Other potentially aromatic cyclic phosphonium ylides have received little attention. For example, Mason (66) and Vilceanu (67) have made brief mention of theoretical treatments of 1,1,3,3-tetraphenyl-1,3-diphosphorin (XXXVII) and Vilceanu has predicted that XXXVII and 1,1-diphenylphosphorin (II) should have approximately the same λ_{max} values. 1,4-Diphosphorins such as XXX and LXXXIX have received no theoretical treatment or X-ray diffraction studies but some evidence for a delocalized π system in LXXXIX is provided by the infrared spectrum which shows (42) the main carbonyl stretching frequencies at 1640 and 1650 cm^{-1}. These frequencies are considerably higher than those of the analogous structure LXXXI (1600 cm^{-1}) and suggest that there is less delocalization of the ylidic carbon atom negative charges over the

ester groups and more participation in a delocalized π system in the ring. On the other hand, the system is highly sensitive to hydrolysis (42) unlike II and XXXVII which can be generated in aqueous media (2, 14).

Finally, Ashe (75) has discussed the stability of certain (n+1)-phosphonia[n,n]spirarenes such as the ylidic structures CLIV, CLV and CLVI. These are potentially novel aromatic systems in which the two rings are at right angles to one another but fully conjugated through p_{π}-d_{π} interactions.

Conclusion

It can be seen from the foregoing discussion that very rapid development has taken place during the last few years in the field of cyclic phosphonium ylide chemistry - particularly with regard to the chemistry of 1,1-disubstituted phosphorins.

This thesis is concerned with the exploration of one possible route to cyclic phosphonium ylides involving cycloaddition reactions of unsaturated phosphines. An account of this investigation is given in the next two sections of the thesis.

RESULTS AND DISCUSSION

Introduction

The work described in this section of the thesis was carried out on a part-time basis and was started in mid-1968.

As can be seen from the introduction to this thesis, most of the systematic work on cyclic phosphonium ylides has occurred since 1968. In particular, at the time this investigation was started, the only studies in the literature regarding cycloaddition reactions of phosphines leading to cyclic phosphonium ylides were those involving the reactions of benzyne with tertiary phosphines (43, 45). Furthermore, the ylides produced in these reactions occur only as transient intermediates and have not been isolated or trapped.

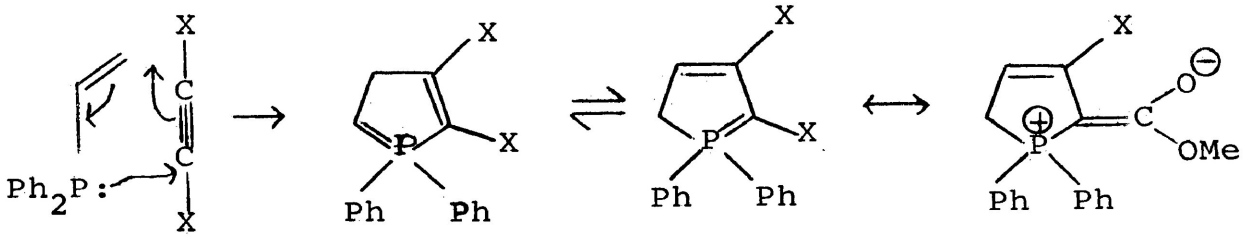
The object of the research described in this section was to devise a general synthesis of cyclic phosphonium ylides. A promising approach appeared to be the reaction of vinyl- and cyclopropylphosphines with electrophilic unsaturated compounds such as dimethyl acetylenedicarboxylate, benzyne and hexafluoro-2-butyne. These reactions could be expected to lead to five-, six-, seven- and eight-membered ring ylides in the manner outlined in the

following discussion.

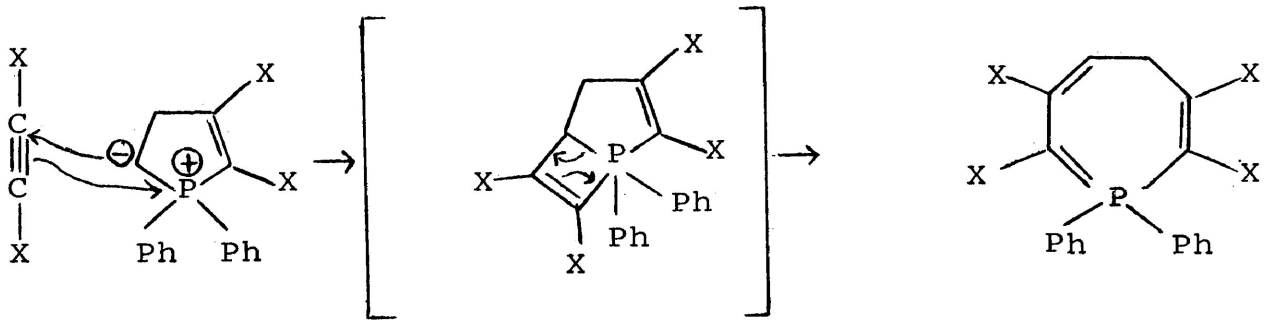
It was expected that by treating dimethyl acetylenedicarboxylate with diphenylvinylphosphine (CLVII), a five-membered ring phosphonium ylide CLVIII would first be formed. The resulting ylide CLVIII or its more stable tautomer XCVIII could then react with another molecule of dimethyl acetylenedicarboxylate in the manner of open-chain ylides (76) to insert a C=C unit into the P=C ylidic link by attack of the carbanionic carbon atom on the acetylenic system. This could give rise to a seven-membered cyclic ylide as shown in the sequences CLVIII→CLIX→CLX and XCVIII→CLXI→CLXII. Similar reactions could occur with hexafluoro-2-butyne ($F_3CC{\equiv}CCF_3$) as the electrophile.

The ylide XCVIII would be the more stable tautomer because of the delocalization of the ylidic carbon atom negative charge over the adjacent methoxy-carbonyl group.

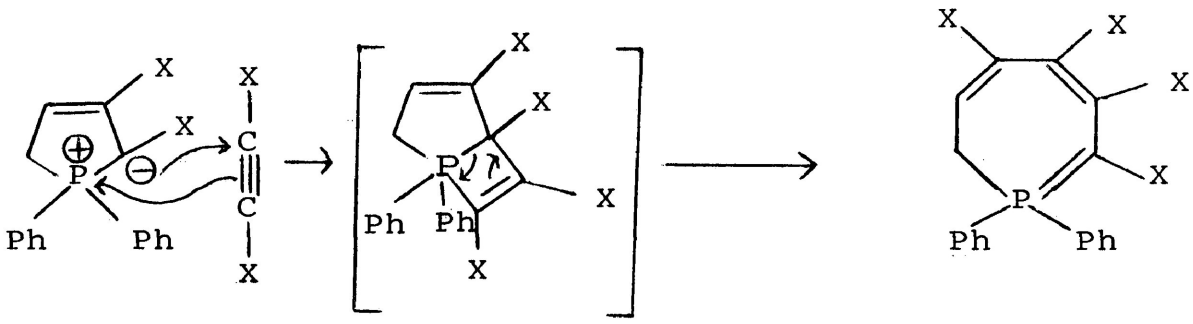
Since CLVIII would be the initially formed and more reactive tautomer, it would be expected to react preferentially with another molecule of dimethyl acetylenedicarboxylate if the ester were present in excess. Furthermore, it would be more difficult stereochemically for XCVIII to react with another molecule of the ester. Therefore, CLX would be the



CLVII CLVIII XCVIII



CLVIII CLIX CLX



XCVIII CLXI CLXII

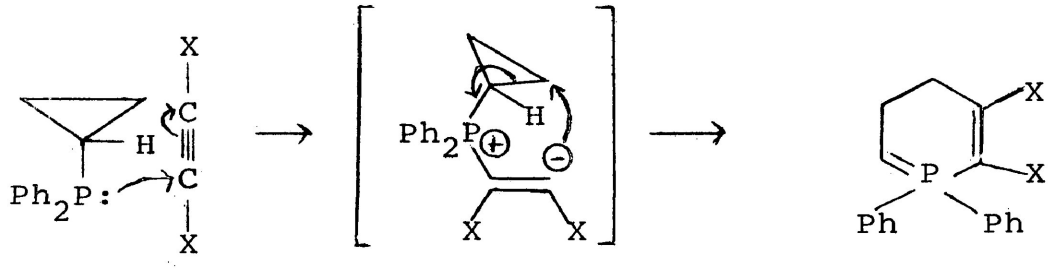
X=CO_2Me

expected seven-membered ring product.

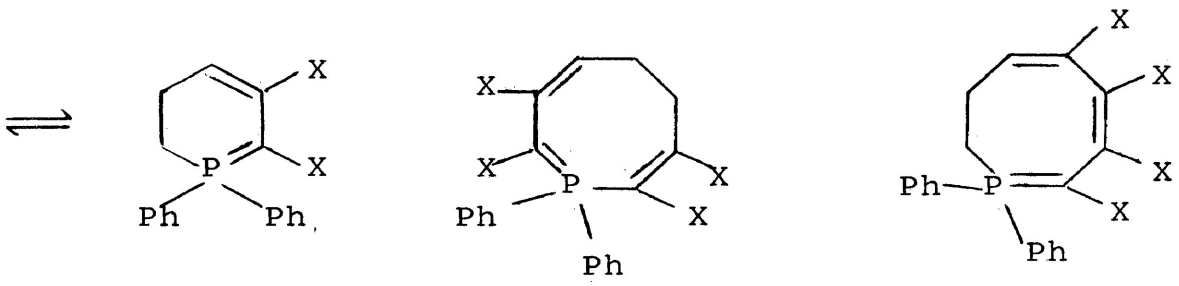
Similarly, the synthesis of six- and eight-membered cyclic ylides could be attempted using cyclopropyldiphenylphosphine. Because of the strained nature of the cyclopropyl ring, it is extremely reactive and cyclopropane derivatives react often *via* a ring-opening mechanism to give open-chain or ring expanded products in order to relieve this strain (77). Thus, cyclopropyldiphenylphosphine could be expected to react as outlined below.

One molecule of dimethyl acetylenedicarboxylate could possibly react with one molecule of cyclopropyldiphenylphosphine (CLXIII) to produce a highly reactive six-membered cyclic phosphonium ylide CLXV (or possibly a more stable tautomer CLXVI) which could then react with another molecule of dimethyl acetylenedicarboxylate to give an eight-membered cyclic phosphonium ylide CLXVII. For the same reasons as above, CLXV should react with another molecule of dimethyl acetylenedicarboxylate more readily than CLXVI which would give the isomeric eight-membered ring CLXVIII.

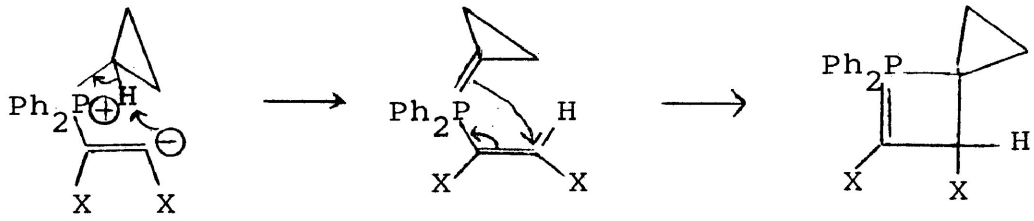
On the other hand, the proton α to the phosphonium grouping in the intermediate CLXIV would be quite acidic and the rearrangement CLXIV→CLXIX could occur. This in turn could lead to cyclization to the ylide CLXX although the strained and hindered nature of



CLXIII CLXIV CLXV



CLXVI CLXVII CLXVIII



CLXIV CLXIX CLXX

X=CO_2Me

CLXX would seem to make this unlikely.

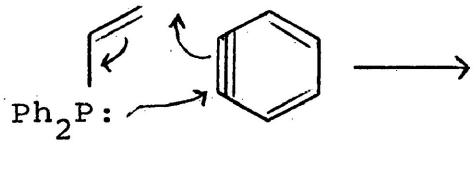
If the proposed reactions outlined above were successful, the method could be extended to the one-step synthesis of bicyclic, and perhaps polycyclic, phosphonium ylides by treating vinylphosphines such as CLVII with benzyne to give ylides of type I. These have been previously prepared by Märkl (1) by a somewhat longer route as outlined in the introduction to this thesis. The vinyl bisphosphines XCI and LXXXVIII could also serve as sources of bicyclic ylides in reactions with benzyne while reactions of cyclic vinylphosphines (such as the 2-phospholenes CLXXI and CLXXII) could produce bicyclic or polycyclic ylides in reactions with dimethyl acetylenedicarboxylate, hexafluoro-2-butyne or benzyne.

In view of the potentially general and one-step nature of reactions of this type, an investigation along the lines discussed in this introduction was carried out and the results are summarized in the remainder of this thesis. It should be noted that the reactions of the bisphosphines XCI and LXXXVIII with the acetylenic ester were omitted from the investigation since they have been the subject of a separate detailed study by Jafry (42).

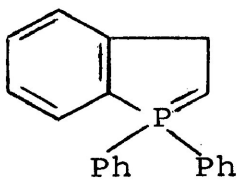
Reactions of Diphenylvinylphosphine with Dimethyl Acetylenedicarboxylate

As expected, diphenylvinylphosphine (CLVII) reacts readily with dimethyl acetylenedicarboxylate in ether or benzene although the nature of the product depends upon the mode of addition and the proportions of the reactants. Thus, dropwise addition of an ethereal solution of the ester to an equimolar amount of the phosphine in ether at room temperature under nitrogen leads immediately to the formation of a very dark solution. Evaporation of the solution yields a tarry material in which the principal product appears to be a dark blue polymeric material. Repeated extraction and crystallization of the crude product leads to the isolation* (in about 7% yield) of colourless crystals, m.p. 130-132°, which analyze well for a molecular formula of $C_{20}H_{21}O_5P$ - *i.e.* a 1:1:1 adduct of the phosphine, the ester and water. The mass spectrum shows a molecular ion at *m/e* 372 which is consistent with the proposed molecular formula. The same product is formed regardless of

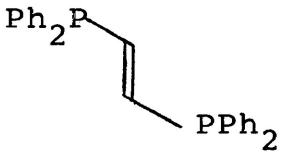
*By a modification of the procedure, Hughes (78) has very recently obtained up to 25% yield of this product.



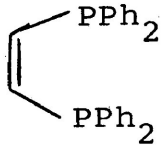
CLVII



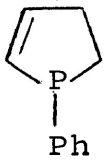
I



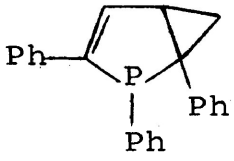
XCI



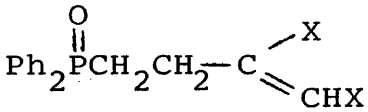
LXXXVIII



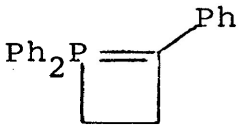
CLXXI



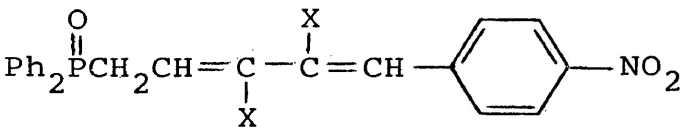
CLXXII



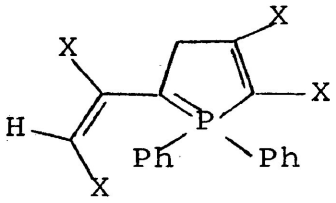
CLXXIII



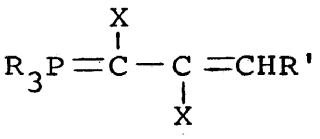
XLVIII



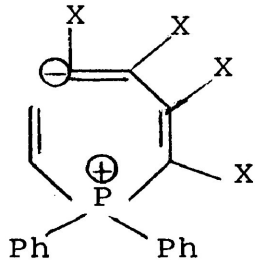
CLXXVII



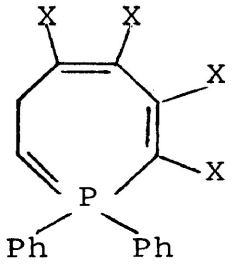
CLXXIX



CLXXX



CLXXXI



CLXXXII

$X=CO_2Me$

whether dried or undried solvents are used (although ether containing appreciable amounts of ethanol should be avoided) and this indicates that during the reaction (or during work-up if anhydrous solvents are used), hydrolysis of an initially formed 1:1 adduct of the ester with the phosphine occurs.

The expected initial product of the reaction is the cyclic ylide CLVIII (a 3*H*-phosphole derivative) and, since most phosphonium ylides are very sensitive to water, this might be expected to hydrolyze to give the phosphine oxide CLXXIII by protonation followed by ring cleavage of the resulting cyclic phosphonium hydroxide by elimination of the most stable carbanion (5). In support of this, the base peak in the mass spectrum of the 1:1:1 adduct occurs at *m/e* 201 which is typical of compounds containing the $Ph_2\overset{O}{\overset{\|}{P}}-$ grouping (20). Furthermore, the infrared spectrum also shows a typical (79) P=O stretching frequency at 1193 cm^{-1} and a weak substituted C=C vibration at 1664 cm^{-1}. However, the ^1H NMR spectrum is inconsistent with structure CLXXIII since, although it shows the presence of two methylene groups, the coupling pattern clearly shows that these two groups are not adjacent. The spectrum shows a ten proton aromatic/olefinic complex multiplet at τ 2.0 - 2.6, an olefinic one proton quartet (with the peaks

somewhat broadened) at τ 2.6-3.3, two ester methyl groups at τ 6.30 and τ 6.37, one methylene group as a doublet of doublets centered on τ 6.69 (with the indication that J_{HH} = 8 Hz and $^{2}J_{PH}$ = 16 Hz) and one methylene group as a very closely spaced doublet (J = *ca.* 1.5 hz) at τ 6.65 superimposed upon the other methylene signal. One interesting feature of this spectrum is that to some extent it is concentration dependent. For example, at concentrations approaching 50%, the ester peaks are shifted a few cycles upfield while the two methylene signals are shifted very slightly downfield.

This spectrum fits the isomeric structure CLXXIV (see Scheme 1) extremely well and this structure is also consistent with the infrared and mass spectral data. Thus, the tentatively assigned values of J_{HH} and $^{2}J_{PH}$ for the methylene group (τ 6.69) adjacent to the phosphorus atom are in excellent agreement with those observed for related structures in the literature (see for example, values for $^{2}J_{PH}$ for compounds containing the $Ph_2\overset{O}{\overset{\|}{P}}CH_2$ - grouping quoted in ref. 20). Furthermore, the locations of the two methylene groups in the spectrum are as expected for CLXXIV. The methylene group adjacent to the terminal ester group (τ 6.65) presumably occurs as a poorly defined doublet (J = *ca.* 1.5 Hz) because of long range coupling with the phosphorus atom. Such

long range couplings are known to give rise to values of $^{5}J_{PH}$ of the order of 1 Hz (80). On the other hand, it is possible that this methylene group is coupled to the olefinic proton which could account for the broadening of the peaks in the olefinic quartet. The fact that the olefinic signal occurs as a quartet (in the approximate ratio 1:3:3:1) implies that J_{HH} and $^{3}J_{PH}$ have approximately the same value (7 Hz).

These tentative NMR assignments have been confirmed by ^{1}H - ^{1}H spin decoupling (field sweep) experiments. In this case, since the couplings in some instances are relatively large and the signal width is therefore considerable, selective decoupling techniques (81) were found to give the best results. Irradiation of the low field doublet of the doublet of doublets of the methylene signal centred on τ 6.69 while scanning the olefinic signal causes the two high field peaks of the olefinic signal to collapse to a singlet centred on the more intense (peak C) of the original peaks (see Fig. 1).

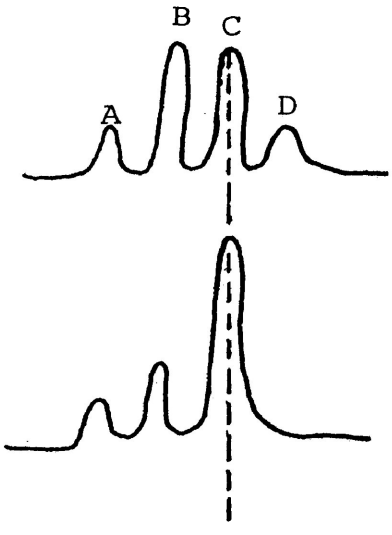
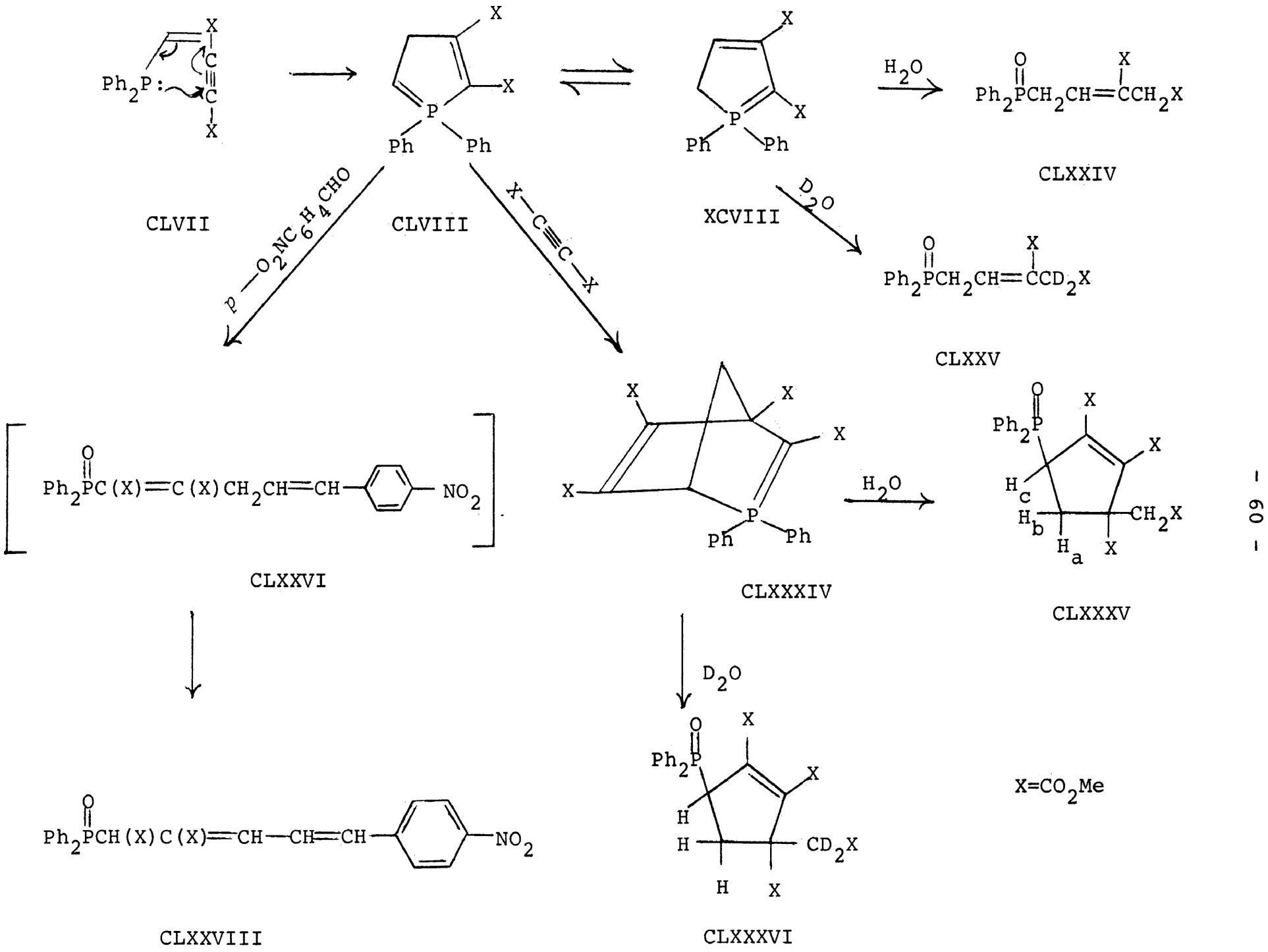


Fig. 1

(a) *Normal scan of olefinic signal*

(b) *Olefinic signal observed upon irradiation of low field doublet of methylene signal at τ 6.69.*


CLVII
CLVIII
XCVIII
CLXXIV
CLXXV
CLXXVI
CLXXXIV
CLXXXV
CLXXVIII
CLXXXVI
X=CO2Me

SCHEME I

Likewise, irradiation of the high field doublet of the methylene doublet of doublets causes the low field pair of peaks of the olefinic signal to collapse in a similar fashion. Conversely, irradiating peak B (Fig. 1) of the olefinic signal while scanning the methylene signal at τ 6.69 causes the high field doublet of this signal to collapse to a singlet. Irradiation of peak C leads to a similar collapse of the low field doublet of the methylene signal.

These results clearly show that the olefinic proton is coupled to the methylene protons at τ 6.69 (J = 8 Hz) and that the olefinic $^{3}J_{PH}$ coupling is 7 Hz (the small difference in these couplings accounts for the broadened peaks in the olefinic quartet). Furthermore, the $^{2}J_{PH}$ coupling of the methylene group adjacent to the phosphorus atom is 16 Hz and these selective decoupling experiments show (81) that $^{2}J_{PH}$ and $^{3}J_{PH}$ are of opposite sign.

Very careful scanning of the spectrum in the decoupling mode shows that there is no coupling between the olefinic proton and the methylene group centered on τ 6.65 (assigned to the methylene group adjacent to the terminal ester group) and the narrow splitting of

this signal (1.5 Hz) is therefore confirmed as being due to long range P-H coupling.

Very strong support for structure CLXXIV is also provided by the mass spectrum which shows weak peaks at *m/e* 299 (possibly $M^+ - CH_2CO_2Me$), 215 (possibly $Ph_2\overset{O}{\overset{\|}{P}}CH_2^+$) and 157 (possibly $M^+ - Ph_2\overset{O}{\overset{\|}{P}}CH_2$). These tentative assignments are confirmed by precise mass measurements (*m/e* 299: calculated 299.0837; found, 299.0839. *m/e* 215: calculated, 215.0626; found, 215.0623. *m/e* 157: calculated, 157.0501; found, 157.0509). These peaks are very weak because cleavage would be preferred in a position allylic to the C=C link - *i.e.* adjacent to the phosphorus atom or the terminal ester group. These expected peaks are very strong in the mass spectrum. Finally, the spectrum shows a peak of medium intensity at *m/e* 340 corresponding to loss of methanol from the $-CH_2CO_2Me$ grouping. The fragmentation is confirmed by a weak metastable peak at *m** 310.7. Such eliminations are common in esters of this type (82).

The infrared spectrum also shows two ester carbonyl stretching frequencies at 1722 (α,β-unsaturated ester) and 1749 cm^{-1} (saturated ester) and this is in agreement with structure CLXXIV.

Structure CLXXIV could be derived either from CLXXIII by proton migration (a process which seems

unlikely) or from hydrolysis of the cyclic ylide XCVIII (a 2*H*-phosphole derivative) which is a tautomer of CLVIII. Moreover, in such a tautomeric equilibrium, XCVIII should be preferred over CLVIII since in XCVIII there is more delocalization of the ylidic carbon atom negative charge over the adjacent ester group. Deuterolysis experiments support the suggestion that CLXXIV is derived from XCVIII by hydrolysis. Thus, when cycloaddition of the vinylphosphine CLVII and the acetylenic ester was carried out in rigorously dried ether followed by addition of a little deuterium oxide (hereafter abbreviated to D_2O) to the reaction mixture, it was found that mainly double deuteration (to give CLXXV) and some triple deuteration occurs. For example, the mass spectrum shows that the strongest molecular ion peaks occur at *m/e* 374 (double deuteration) and *m/e* 375 (triple deuteration). The NMR spectrum shows that the narrow doublet due to the methylene group adjacent to the terminal ester group has almost disappeared from the spectrum although there is also a reduction (from 2 to about 1.4 protons) in the intensity of the other methylene signal. The ^1H NMR spectrum therefore shows that deuteration occurs mainly at the site adjacent to the terminal ester group (although some deuteration occurs at the other methylene group) and this is consistent with the behaviour expected of XCVIII on hydrolysis.

These observations then are fairly good evidence that the ylide XCVIII is formed from the initially formed ylide CLVIII by tautomerization. Furthermore, similar tautomeric equilibria have been observed in the case of the four-membered ylide XLVIII (20). Several attempts to trap CLVIII before tautomerization could occur were therefore made. Attempts to trap CLVIII in a Wittig reaction with acetone and with benzaldehyde were unsuccessful. The use of acetone gave only uncrystallizable materials and use of benzaldehyde gave the adduct CLXXIV as the only isolable product. However, cycloaddition of the ester and phosphine in the presence of *p*-nitrobenzaldehyde leads to the formation of a 1:1:1 adduct of the ester, the phosphine and the aldehyde for which elemental analyses are in excellent agreement with the formula $C_{27}H_{24}O_7NP$. The mass spectrum confirms the molecular weight as 505 and the base peak is again at *m/e* 201 indicating the presence of the $Ph_2\overset{O}{\overset{\|}{P}}-$ grouping. Thus, a Wittig reaction has occurred and the intermediacy of a cyclic ylide is established.

The adduct expected from CLVIII would be CLXXVI while that from XCVIII would be CLXXVII but the ^1H NMR spectrum shows that the adduct is neither of these since there are no signals due to methylene groups in the spectrum. The spectrum shows 17 aromatic/olefinic protons as a broad complex multiplet at τ 1.6-3.4,

one methine proton as a doublet (J = 15 Hz) centered on τ 4.38 and two ester methyl group signals at τ 6.33 and τ 6.38. Of the various possible isomers obtainable by addition of *p*-nitrobenzaldehyde to CLVIII or XCVIII, only CLXXVIII agrees with all the physical data since it contains no methylene groups and the low field location and the splitting of the methine proton (J = 15 Hz) are consistent with its position adjacent to a phosphoryl grouping and two other electron withdrawing groups. Clearly CLXXVIII cannot be derived directly from CLVIII or XCVIII and is presumably derived from CLXXVI by a prototropic shift. Such a shift is not surprising since it increases the conjugation in the system and the conditions of the reaction (the ylide CLVIII would be a strong base) would favour migration of the mildly acidic protons of the methylene group in CLXXVI. A similar prototropic shift in CLXXVII could produce a methine proton adjacent to an ester group (though far removed from the phosphorus atom) but this would decrease the conjugation. Some further, though not conclusive evidence for structure CLXXVIII is given by the mass spectrum which shows a peak at *m/e* 273 probably corresponding to the fragment $[Ph_2\overset{O}{\overset{\|}{P}}CHCO_2Me]^+$ (precise mass calculated: 273.0681, found: 273.0673). This could only be derived from CLXXVIII unless major rearrangements occur on electron impact. This peak is

comparable in intensity with the molecular ion peak though much weaker than the base peak. In addition, the infrared spectrum shows both saturated (1745 cm^{-1}) and α,β -unsaturated (1692 cm^{-1}) ester carbonyl stretching frequencies.

As already mentioned, the mode of reaction and proportions of the reactants in the reaction of the phosphine CLVII with the acetylenic ester can influence the nature of the product. If the phosphine (1 mole) in ether is added to an ethereal solution of the ester (2 moles) under the same reaction conditions as the 1:1 addition, a 1:2:1 adduct of the phosphine, the ester and water is obtained in about 10% yield. Analyses are in excellent agreement with a molecular formula of $C_{26}H_{27}O_9P$ and the mass spectrum shows a molecular ion at *m/e* 514 together with the base peak at *m/e* 201 ($Ph_2\overset{O}{\overset{\|}{P}}$——). On the basis of the arguments used in the case of the 1:1:1 adduct of diphenylvinylphosphine with the ester and water, it is virtually certain that the 1:2:1 adduct is derived from hydrolysis of an ylidic 1:2 adduct of the phosphine and the ester.

There are several possible modes of reaction. For example, Michael addition of the ylide CLVIII to a second mole of the ester could occur to give the ylide CLXXIX although this type of addition is not possible for the ylide XCVIII. This type of mechanism was

suggested by Trippett (83) for the addition of cyanomethylenetriphenylphosphorane ($Ph_3P=CHCN$) to dimethyl acetylenedicarboxylate and would presumably be due to the highly acidic nature of the methine proton in the initially formed zwitterion. On the other hand, Bestmann (76) has found that addition of alkylidenephosphoranes to the ester leads (in every case studied by his group), to insertion of the ester into the $R_3P=CHR'$ link to give compounds of type CLXXX. This would suggest that CLVIII or XCVIII could react further with the ester to give the seven-membered ylides CLX or CLXII respectively (or, possibly, tautomers of these) as already outlined. Another possible mode of reaction is the generation of the zwitterion CLXXXI followed by cyclization to give CLXXXII. A similar reaction path occurs in the reaction of 1,2,5-triphenylphosphole with an excess of the ester (37,38). Finally, the initially formed ylide CLVIII could react further with the ester to give CLXXXIII which could cyclize by attack at the β-position of a vinylphosphonium grouping to give the strained bicyclic ylide CLXXXIV in much the same way as CLVIII itself is formed.

Examination of the ^1H NMR spectrum of the 1:2:1 adduct shows that it is CLXXXV which is derived from hydrolysis of the bicyclic ylide CLXXXIV. Thus, hydrolysis of the other possible intermediates CLX, CLXII, CLXXIX or

CLXXXII (or possible tautomers) would lead to a product containing olefinic protons whereas careful integration of the ^{1}H NMR spectrum of the 1:2:1 adduct shows clearly that the adduct contains no olefinic protons.

The spectrum of the 1:2:1 adduct shows ten aromatic protons as a complex multiplet at τ 1.9-2.7, one methine proton as eight unevenly spaced, poorly defined and partly overlapping peaks of similar intensity centered on τ 5.72, four ester methyl groups at τ 6.29, 6.32 6.38 and 6.82, two methylene protons as an *apparent* doublet at τ 6.72 and 6.81 and two other methylene protons as a poorly defined multiplet of at least twelve maxima at τ 6.80 - 7.70. Since the two ring methylene protons in CLXXXV would be non-equivalent, they would have somewhat different chemical shifts and may couple with each other, the neighbouring methine proton and the phosphorus atom to give up to sixteen peaks of which at least twelve are observed (τ 6.80 - 7.70). Similarly, the methine proton should appear at a much lower field location as two doublets of doublets through coupling with the phosphorus atom and the non-equivalent ring methylene protons. The side chain methylene group presumably occurs as an apparent doublet (the inner peaks of a closely spaced AB signal of which the outer peaks are buried under the ester signals and the other methylene signals) in the spectrum because its proximity to an

asymmetric centre renders the two protons non-equivalent as is the case with the diastereotopic protons of 1,2-dichloropropane (84). The signal separation of the two inner peaks in such cases normally falls in the range 2-15 Hz (85). It is unlikely that the splitting of this signal is due to long range coupling with the phosphorus atom since the value of J = 5.5 Hz is rather high compared with other measured values of $^{5}J_{PH}$ (80).

Again, double resonance and mass spectral studies confirm the proposed structure CLXXXV for the 1:2:1 adduct. Careful scanning of the NMR spectrum in the decoupling mode shows that fairly strong irradiation (*i.e.* full decoupling) at τ 7.00 while scanning the region of the eight-peak one-proton signal centred on τ 5.72 causes the latter signal to collapse to a doublet of doublets with one coupling constant of 7 Hz and the other of 12 Hz. Similarly, irradiation at τ 7.32 again causes the one-proton eight-peak signal to collapse to a doublet of doublets in which one coupling constant is 4.5 Hz while the other is 12.5 Hz. Designating the proton at τ 7.32 as H_a, the proton at τ 7.00 as H_b and the proton at τ 5.72 as H_c, it is clear that $J_{H_aH_c}$ = 4.5 Hz, $J_{H_bH_c}$ = 7 Hz and J_{PH_c} = 12.5 Hz. Thus, the P-H coupling constant is of the right order of magnitude for $^{2}J_{PH}$ while the couplings of H_c with H_a and H_b are consistent with the proposed structure CLXXXV.

Irradiation of the proton at τ 5.72 (H_c) while scanning the proton signals at τ 7.00 (H_b) and τ 7.32 (H_a) causes considerable changes in these regions but no clear pattern emerges because of overlap of the H_a and H_b signals. Decoupling of H_a from H_b was not feasible since instrumental limitations did not allow decoupling of two such closely spaced signals.

One fact which did emerge from these decoupling experiments is that the weak outer peaks of the closely spaced methylene AB signal centred on τ 6.77 appear to be at τ 6.50 and τ 7.02 since irradiations of H_c while scanning H_a or H_b show that these peaks remain unchanged while considerable changes occur in the remaining peaks. Further support for this assignment comes from the fact that the intensity ratio (5.5:1) of the two fairly clearly seen low field peaks of the AB pattern (τ 6.50 and τ 6.72) is as predicted by theory (86).

Mass spectral studies offer further confirmation for the structure CLXXXV. For example, the loss of methanol characteristic of the $-CH_2CO_2Me$ grouping (82) is shown by a peak at *m/e* 482 and the one-step fragmentation is confirmed by a metastable peak at *m** 452. Furthermore, the expected loss of the allylic $-CH_2CO_2Me$ group is shown by a weak peak (25% of the molecular ion peak and 3% of the base peak) at *m/e* 441.

Again, this fragmentation is confirmed by a weak metastable peak at *m** 378.3. Unfortunately, precise mass measurements for these peaks were not possible because suitable reference peaks were not available. Similarly, a weak peak at *m/e* 240 suggests the loss of both of the allylic $Ph_2\overset{O}{\overset{\|}{P}}-$ and $-CH_2CO_2Me$ groups and this is confirmed by precise mass studies (calculated, 240.0634; found, 240.0636). Presumably this peak is weak because the charge would tend to stay with the $Ph_2\overset{O}{\overset{\|}{P}}-$ grouping and the fact that the base peak in the spectrum at *m/e* 201 is due to this grouping offers some support for this suggestion.

As with the 1:1:1 adduct, deuterolysis experiments on the 1:2 adduct offer further confirmation of these assignments since generation of this adduct in rigorously dried solvents followed by treatment of the solution with a little D_2O leads to the formation of CLXXXVI. The ^1H NMR spectrum is virtually identical with that of CLXXXV except that the AB pattern due to the side chain methylene group has vanished from the spectrum. The only other change is a very small reduction in the signal strength of the other methylene multiplet. The heavy deuteration in the side chain of CLXXXVI is strong evidence for the intermediacy of CLXXXIV. Reactions of CLVII with the ester are summarized in Scheme I.

Attempts to trap the ylide CLXXXIV in a Wittig reaction with acetone, benzaldehyde and *p*-nitrobenzaldehyde were unsuccessful. However, this is not surprising since the ylidic link in CLXXXIV would be highly hindered. Attempts to prepare perchlorate salts of CLVIII, XCVIII and CLXXXIV were also unsuccessful but this too is not unexpected since recent work on related cyclic ylides (42) has shown that these salts are highly soluble in water and ethanol and are extremely difficult to crystallize even when the ylides themselves are available in considerable quantity.

Before leaving this topic, it should be noted that the oxide CLXXIV has also been isolated from the hydrolysis of the 1:1 adduct XCII obtained by reaction of XCI with the acetylenic ester (42). The reaction is thought to involve XCVIII as an intermediate and the reaction is discussed more fully in the introduction to this thesis.

Two extensions of the work so far described in this section were considered. In the first of these, the readily available (87) analogue CLXXII of the 2-phospholene CLXXI was treated with dimethyl acetylenedicarboxylate in an attempt to achieve cycloadditions of the type observed for CLVII. The highly strained and hindered ylides which would be produced by such cyclizations would be of considerable interest. However, attempts to carry out the cycloaddition under a wide

variety of conditions using rigorously dried ethereal and non-ethereal solvents and even no solvent other than excess of the ester, gave only the oxide of CLXXII. The change in appearance of the various reaction mixtures clearly indicates that a reaction occurs rapidly but it seems that the probable initially formed zwitterion CLXXXVII is too hindered to cyclize or react further and hydrolyzes on work-up in the manner observed for similar zwitterions (88) to give the corresponding phosphine oxide.

The second attempted extension involved reactions of diphenylvinylphosphine (CLVII) with hexafluoro-2-butyne ($F_3C-C\equiv C-CF_3$) in place of the acetylenic ester. These reactions would be of interest because carbanion (ylidic or zwitterionic) stabilization by resonance delocalization over an ester group would not be possible and the resulting ylides or zwitterions should be very reactive. Both 1:1 and 1:2 additions were tried in ether and in both cases brownish, granular, high-melting and probably polymeric materials were obtained. These proved impossible to characterize except that mass spectral investigation of the 1:1 adduct showed that it contained traces of the unexpected product bis(diphenylphosphino)ethane ($Ph_2PCH_2CH_2PPh_2$) since the spectrum obtained using a direct inlet at 175°C was identical to that of pure $Ph_2PCH_2CH_2PPh_2$. Discussion of this will be deferred

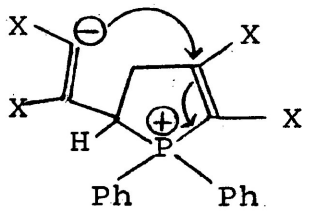
to the section on attempted benzyne additions since the same product was obtained in much larger quantities in these reactions.

A preliminary communication regarding some of the reactions of diphenylvinylphosphine (CLVII) has been published (89) and a full paper on this and some related work has been accepted for publication.

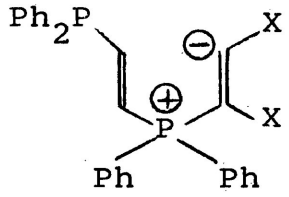
Reactions of Cyclopropyldiphenylphosphine with Dimethyl Acetylenedicarboxylate

As already explained, it was thought that in this reaction the cyclopropyl ring would open giving, with 1:1 molar ratios, a six-membered cyclic ylide (CLXV or CLXVI) and, with 1:2 molar ratios, an eight-membered cyclic ylide (CLXVII or CLXVIII). The possibility was not overlooked, however, that after the addition of one molecule of dimethyl acetylenedicarboxylate to the phosphine, the initially formed zwitterion CLXIV would abstract a proton internally giving the open-chain ylide CLXIX. Hydrolysis of this open-chain ylide, or of the intermediate zwitterion, should lead to cyclopropyldiphenylphosphine oxide plus dimethyl fumarate or maleate depending upon the stereochemistry of attack on the intermediate zwitterion.

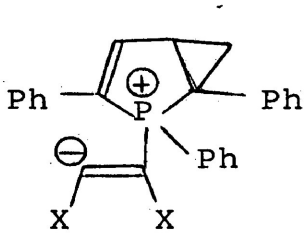
Several experiments regarding the reaction of the phosphine with the ester were carried out involving the reactants in a 1:1 or 1:2 ratio. In addition, a number of solvents were tried, the effects of the temperature at which the reaction was carried out and the mode of



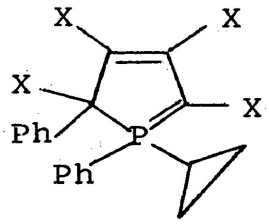
CLXXXIII



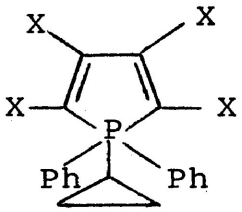
XCII



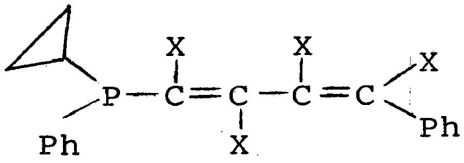
CLXXXVII



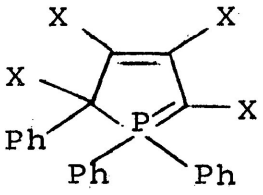
CLXXXVIII



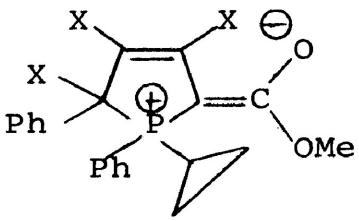
CLXXXIX



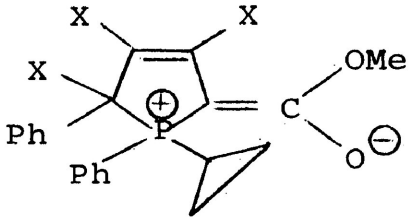
CXC



LXIII



CXCI



CXCII

$X=CO_2Me$

addition were thoroughly explored. In tetrahydrofuran, for example, 1:1 addition of the ester to the phosphine gave dimethyl fumarate as the only identifiable product (presumably though hydrolysis of the intermediate CLXIV) whereas addition of the phosphine to the ester gave dimethyl fumarate and an almost colourless compound (m.p. 235°) which analyzed very well for a 1:2 adduct. This proved to be the cyclic ylide CLXXXVIII although the structures CLXVII, CLXVIII, CLXXXIX and CXC were briefly considered bearing in mind the predicted ring opening and also Johnson's and Tebby's original experiments with triphenylphosphine and the ester (28) as discussed in the introduction to this thesis.

Clearly, the expected opening of the cyclopropyl ring did not occur. Attempts were made using higher boiling solvents such as benzene, toluene and *p*-xylene to force ring-opening by carrying out the addition at the boiling point of the solvent. However, no such reaction occurred.

It appears as though irrespective of the molar ratio of the two reactants or the order of addition in dry solvents such as benzene, that the ylide CLXXXVIII is obtained, together with varying amounts of dimethyl fumarate depending upon the mode of addition and the dryness of the solvent. The crude product was washed with ethanol to remove the fumarate.

The structure of this 1:2 adduct was proved in the following manner.

The infrared spectrum (Nujol mull) of the adduct shows a complex carbonyl absorption pattern. Thus, there is an intense ester carbonyl doublet at 1752 cm^{-1} and 1742 cm^{-1}, an even more intense and somewhat broader carbonyl absorption at 1660 cm^{-1} and a peak at 1550 cm^{-1} which is of comparable intensity and is also probably due to a carbonyl function. The carbonyl absorptions at 1660 cm^{-1} and 1550 cm^{-1} are at unusually low locations in the spectrum and this pattern has been observed in the infrared spectra of ester carbonyl stabilized phosphonium ylides (90).

The mass spectrum of the 1:2 adduct shows a molecular ion peak at *m/e* 510. A strong peak at *m/e* 451 is presumably due to loss of one methoxycarbonyl group from the molecular ion. The remainder of the spectrum is relatively featureless except for a strong peak at *m/e* 439 (M^+ - 71) to which it is difficult to assign a structure. In particular, the strong peak at *m/e* 201 noticed in the other mass spectra described in this section is absent and this, together with the molecular weight, confirms that no hydrolysis of an intermediate ylide containing the $Ph_2\overset{|}{P}=CHR$ group had occurred as has been observed in the other cycloadditions so far discussed. Furthermore, there is no peak at *m/e*

226 corresponding to an intact cyclopropyldiphenylphosphine residue and the strong peaks at *m/e* 185 and *m/e* 183 normally (91) associated with the Ph_2P- grouping are also absent. This indicates that in the 1:2 adduct, at least one phenyl group has migrated and, therefore, the structure CLXXXIX can tentatively be ruled out.

The NMR spectrum shows a complex multiplet of five protons centered at τ 8.90 indicating an intact cyclopropyl ring. The four ester methyl groups occur at τ 5.98, 6.50, 6.52 and 6.92, while the ten aromatic protons occur as another complex multiplet at τ 1.85 - 2.90.

At this point in the investigation, Tebby (29) published his structure revision of the stable, methanol-insoluble 1:2 adduct of triphenylphosphine and dimethyl acetylenedicarboxylate and assigned to it the cyclic ylide structure LXIII. This has been fully discussed in the introduction to this thesis. It therefore seemed likely that, since the infrared spectrum of the adduct showed probable ylidic character, the 1:2 adduct obtained from cyclopropyldiphenylphosphine and the ester would have structural characteristics similar to those of LXIII. In this connection, the structure CLXXXVIII was the most probable since cyclopropyl migration seems an unlikely event to occur and the mass spectrum suggests a phenyl migration.

In fact, the infrared spectrum in the carbonyl region and the NMR spectrum in the ester methyl region of the 1:2 adduct are very similar to those of LXIII as reported by Tebby (29). The remainder of this discussion presents additional evidence that CLXXXVIII is indeed the structure of the 1:2 adduct of cyclopropyldiphenylphosphine with dimethyl acetylenedicarboxylate.

Variable temperature NMR studies help to confirm the basic structure of the adduct. Thus the signal at τ 6.52 in the spectrum at 42°C probably corresponds to the methyl group of the methoxycarbonyl group attached to the ylidic carbon atom since recording the NMR spectrum at 0°C causes this peak to broaden and merge into a singlet with the peak at τ 6.50. Cooling the solution to -30°C causes broadening of all methoxy-group resonances and the broad resonance at τ 6.50 in the spectrum at 0°C is replaced at -30°C by three resonances of unequal intensity at τ 6.53, τ 6.46 and τ 6.33. The resonance at τ 6.46 integrates for approximately three protons and presumably corresponds to the signal at τ 6.50 in the spectrum at 42°C. This would mean that the signal at τ 6.52 is split into two unequal resonances at τ 6.33 and τ 6.53 at -30°C. This behaviour is identical to that described by Tebby and co-workers (29) for the cyclic ylide LXIII.

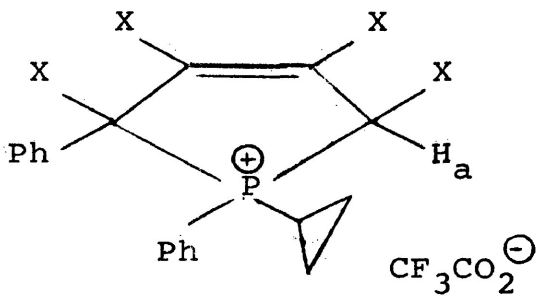
This behaviour at varying temperatures, as explained by Tebby (29), is consistent with the existence of two conformers caused by delocalization of the ylidic carbon atom negative charge over the neighbouring ester group. These conformers would have different populations and the energy barrier between them would be such that at high temperature (42°C) the NMR signals would be time-averaged. However, as the temperature is lowered the interconversion between the conformers becomes slower and the resonances observed then correspond to the different conformers. The two most likely conformers for CLXXXVIII would be CXCI and CXCII and the unequal resonances at τ 6.33 and τ 6.53 in the spectrum at -30°C are therefore probably due to the ester group adjacent to the ylidic carbon atom.

Studies of NMR spectra of the adduct in trifluoroacetic acid solution confirm the proposed structure CLXXXVIII. If a little trifluoroacetic acid is added to a solution of the adduct in $CDCl_3$, the spectrum at 42°C shows ten aromatic protons at τ 1.8-2.8, two peaks in the methine region of the spectrum at τ 4.70 and τ 5.02 integrating for less than one proton, twelve methoxy protons as *five* unequal resonances in the range τ 5.80 - 6.60, and five cyclopropyl protons as a broad hump at τ 8.40 - 9.70. The fact that the peaks in the methine region (H_a) integrate for less than one

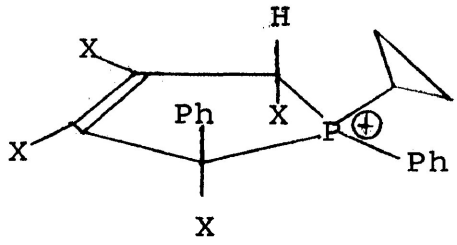
proton and the four methoxy groups appear as five peaks indicate that, because of incomplete protonation, the spectrum is due to a mixture of the ylide CLXXXVIII and a protonated form — probably CXCIII (no stereochemistry implied). UV measurements (to be discussed later) support this suggestion.

If the spectrum is recorded at 42°C in undiluted trifluoroacetic acid (TMS added), several poorly defined peaks appear in the methine region at τ 4.1 - 5.0 although the integration still indicates much less than one proton. The methoxy region is more complex showing five main resonances but with most of these showing further splitting. The cyclopropyl region is little changed. At 0°C, the spectrum in undiluted trifluoroacetic acid shows seven peaks (slightly less than one proton) in the methine region at τ 3.9 - 5.1 and seven unequal but distinct methoxy signals together with signs of further splitting at τ 5.60 - 6.60.

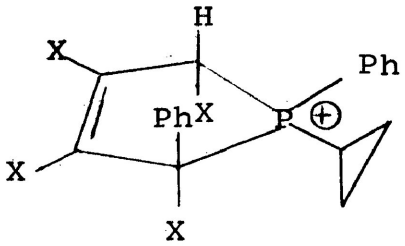
This behaviour is precisely what would be expected of CLXXXVIII in trifluoroacetic acid. Thus, if one considers the most probable protonated form CXCIII, there are three asymmetric centres and therefore 2^3=8 possible stereoisomers (four pairs of enantiomers). Two of these possible stereoisomers are shown in CXCIV and CXCV. Because there are four pairs of enantiomers,



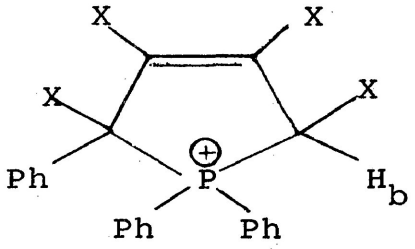
CXCIII



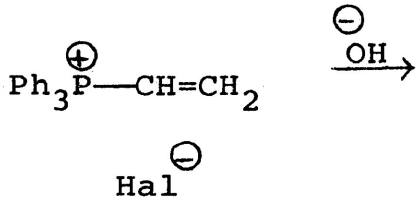
CXCIV



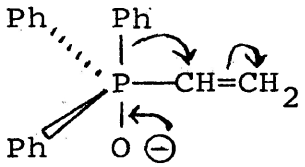
CXCV



CXCVI

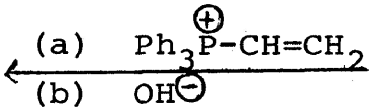


CXCVII

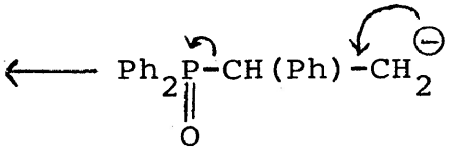


CXCVIII

CCI



CC



CXCIX

X=CO_2Me

there are four different chemical (and therefore magnetic) environments possible for H_a. Furthermore, since H_a is adjacent to a phosphorus atom, its signal in the NMR spectrum should be split by ^{31}P coupling. Therefore, if all possible protonated forms are present in the solution of CLXXXVIII in trifluoroacetic acid, the proton H_a should appear as a multiplet of up to eight peaks of which seven are observed. If, on the other hand, the cyclopropyl group had migrated (an unlikely event), the resulting cyclic ylide would contain only two asymmetric centres and would show a maximum of four H_a peaks. This is clear evidence that the structure of the 1:2 adduct is CLXXXVIII.

The spectrum of the protonated form CXCVI in CF_3CO_2H of the ylide LXIII as recorded by Tebby (29) is rather simpler than that of CXCIII since it shows at 0°C H_b as a doublet at τ4.06 and only four methoxy signals. Since CXCVI contains two asymmetric centres, one would expect H_b to appear as two doublets by analogy with the arguments outlined for CXCIII. Furthermore, more than four resonances would be expected for the methoxy signals. It therefore appears that one stereoisomer of CXCVI is preferred. Tebby (29) does, however, briefly mention that there is some evidence in the NMR spectrum for another protonated form of LXIII (~5%) which shows a very weak doublet at τ 4.54 and some

weak methoxy resonances. Tebby did not discuss stereochemical considerations.

Finally, the UV spectrum of CLXXXVIII in chloroform (λ_{max} 342 mμ, ε 23,120) is almost identical with that (29) of LXIII in 95% ethanol (λ_{max} 344, ε 19,000). In the UV spectra of both compounds in concentrated HCl, the long wavelength peak at 344 mμ is absent indicating that complete protonation occurs in strong acid. The spectrum of CLXXXVIII in chloroform containing a few drops of CF_3CO_2H, shows a peak at 351 mμ but this peak is much reduced in intensity. This shows that in chloroform acidified with CF_3CO_2H, protonation of CLXXXVIII is incomplete and this agrees with the tentative conclusions already presented regarding the interpretation of NMR spectra of $CDCl_3$ solutions of the adduct acidified with CF_3CO_2H.

Attempted Cycloadditions Using Benzyne

As described in the foregoing account, vinyl- and cyclopropylphosphines undergo cycloaddition reactions with acetylenic systems to give a variety of cyclic ylides although, in some cases, the ylides are not necessarily those originally predicted. In an attempt to extend this type of reaction to the synthesis of bicyclic ylides (as outlined in the introduction to this section) the reactions of diphenylvinylphosphine (CLVII), *trans* 1,2-bis(diphenylphosphino)ethylene

(XCI) and *cis* 1,2-bis(diphenylphosphino)ethylene (LXXXVIII) were treated with benzyne. Several sources of benzyne were considered and it was decided that the three most convenient methods for smooth but rapid generation of the aryne for the purpose described above are controlled pyrolysis of *o*-benzenediazonium carboxylate (92), thermal decomposition of *N*-nitrosoacetanilide (93) as described by Cadogan (94) and modified by Rüchardt (95), and direct formation of benzyne from aniline by treatment with amyl nitrite and acetic anhydride (96).

The results of these trial experiments are difficult to fit into any mechanistic pattern. Some experiments gave no identifiable product, others led to self-addition reactions of the vinylphosphine while in only one reaction was there any evidence for the formation of a cyclic ylide. Those experiments which yielded some kind of positive results are briefly described in the following discussion.

Treatment of diphenylvinylphosphine with *o*-benzenediazonium carboxylate in boiling dry tetrahydrofuran gave a tarry mass from which only 1,2-bis(diphenylphosphino)ethane ($Ph_2PCH_2CH_2PPh_2$) could be isolated. This product was obtained (7% yield of pure material) regardless of the dilution of the reaction mixture and its identity was confirmed from its m.p., and its NMR

and mass spectra which were found to be identical with those of an authentic sample.

The mechanism of this reaction is obscure. This reaction could initially involve attack of the phosphine directly upon the *o*-benzenediazonium carboxylate (in the normal manner of phosphines with diazonium compounds (97)) or upon benzyne derived from the diazonium compound. In this connection, the fact that the same product is obtained from the 1:1 reaction of diphenylvinylphosphine with hexafluoro-2-butyne (as mentioned earlier in this section of the thesis) suggests that a triply bonded species such as benzyne is the cause of the reaction. Furthermore, there are several reports in the literature regarding the formation of derivatives of the 1,2-bis(diphenylphosphino)ethane system from a diphenylvinylphosphine derivative. For example, the diphenylphosphide ion ($Ph_2P^{\ominus}$) is known (98) to add smoothly to diphenylvinylphosphine to give $Ph_2PCH_2CH_2PPh_2$ in good yield. Similarly, triphenylvinylphosphonium salts (CXCVII) on alkaline hydrolysis give 1,2-bis(diphenylphosphinyl)ethane (CCI) as one of the products (99). The postulated reaction scheme for the formation of this product is shown in the sequence CXCVII→CCI and probably involves a diphenylphosphide derivative as the key intermediate.

It therefore seems possible that the reaction is initiated by benzyne and that at some stage in the reaction, the diphenylphosphide ion ($Ph_2P^{\ominus}$) is generated in the presence of an excess of diphenylvinylphosphine. However, because of the unpromising nature of the reaction, it was not investigated any further.

In contrast, treatment of diphenylvinylphosphine in benzene with *N*-nitrosoacetanilide in the presence of potassium acetate gave mainly tarry materials from which trace quantities of pale yellow crystals were obtained by chromatography in benzene on silica gel. Insufficient was available for analysis but the melting point (74 - 75°) was very close to that of triphenylphosphine (78 - 80°). This tentative structure assignment was confirmed by a mass spectrum which proved to be identical to that of an authentic sample of triphenylphosphine.

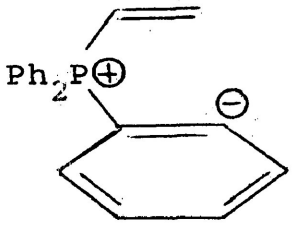
Again, the mechanism of the reaction is not clear but it seems possible that initial attack of the phosphine upon benzyne occurs to give the expected zwitterion CCII but that protonation, perhaps by trace amounts of water, converts this into the triphenylvinylphosphonium system. Clearly this does not hydrolyze by the normal mechanism which leads , among other products, to CCI as already described. However, since the hydroxide ion concentration would be very low, it

is possible that hydrolysis occurs under these conditions by attack at a site other than the phosphorus atom in such a manner as to eliminate triphenylphosphine. Numerous reactions involving the displacement of phosphines from phosphonium salts by base are known (100).

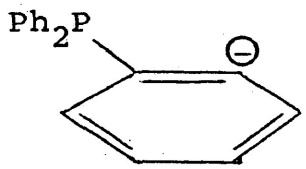
Alternatively, if the $Ph_2P^{\ominus}$ ion is generated in this reaction as suggested for the case where *o*-benzenediazonium carboxylate is the benzyne source, this ion could attack benzyne in the expected manner to give the ion CCIII which could then abstract a proton from water. The reaction was, however, so unpromising that attempts to confirm these suggestions were considered to be not worth while.

Reactions of *cis* and *trans* 1,2-bis(diphenylphosphino)ethylene (LXXXVIII and XCI) with various sources of benzyne again gave very mixed results. For example, treatment of LXXXVIII with *o*-benzenediazonium carboxylate gave only the *P,P*-dioxide of LXXXVIII regardless of the reaction conditions. On the other hand, treatment of LXXXVIII in benzene with aniline, amyl nitrite and acetic anhydride (96) caused *cis-trans* isomerization such that the *P,P*-dioxide of XCI was the only product obtained. It is not clear whether the reaction is caused by benzyne or some precursor.

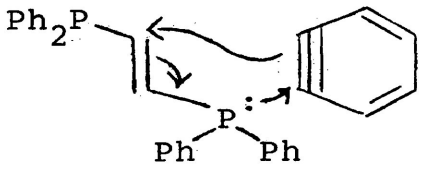
Finally, treatment of the *trans* bisphosphine XCI with *N*-nitrosoacetanilide in benzene with prolonged



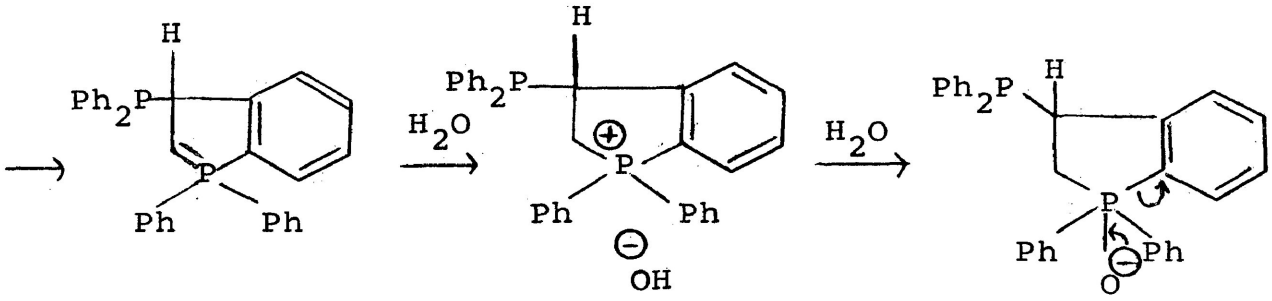
CCII



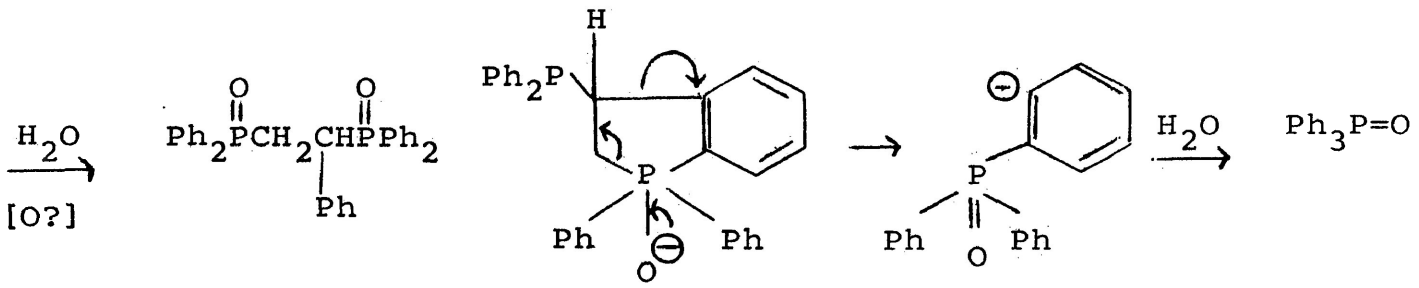
CCIII



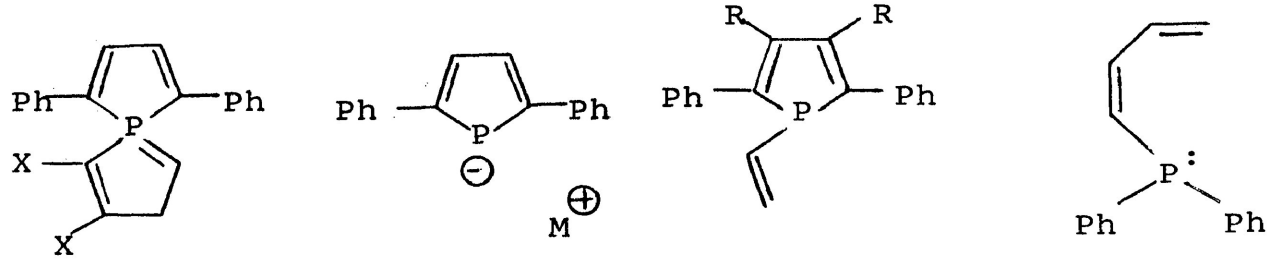
XCI



CCIV CCV CCVI



CCVII CCVI CCVIII



CCIX CCX CCXI CCXII

X=CO_2Me

reflux gave a tarry mass which was washed with acetone and then ether to give a small amount (*ca.* 1 mg) of colourless fluffy crystals (m.p. 266°) as a residue. Analysis (C,H only) of these crystals suggested a molecular formula of $C_{32}H_{28}OP_2$ or $C_{32}H_{28}O_2P_2$ - *i.e.* a 1:1:1 adduct of the phosphine, benzyne and water possibly with one additional oxygen atom. Confirmation of the molecular formula $C_{32}H_{28}O_2P_2$ came from the mass spectrum which showed a molecular ion at *m/e* 506. This suggested that the expected cycloaddition and hydrolysis had occurred and that the second phosphorus atom had become oxidized either during the reaction or upon work-up. A possible reaction scheme is illustrated in the sequence XCI→CCVII.

Since such small quantities (less than 400 μg after analysis) were available, reliable NMR measurements were not possible.

The best evidence for structure CCVII comes from the mass spectrum in which the fragmentation pattern is entirely consistent with the proposed structure. The spectrum shows strong ions at *m/e* 429 (probably $Ph_2\overset{\overset{O}{\|}}{P}CHCH_2\overset{\overset{O}{\|}}{P}Ph_2^{\oplus}$), 428 (probably $Ph_2\overset{\overset{O}{\|}}{P}\text{-}CH{=}CH\overset{\overset{O}{\|}}{P}Ph_2^{\oplus}$), 402 ($Ph_2\overset{\overset{O}{\|}}{P}\text{-}\overset{\overset{O}{\|}}{P}Ph_2^{\oplus}$), 325 ($Ph_2\overset{\overset{O}{\|}}{P}\text{-}\overset{\overset{O}{\|}}{P}Ph^{\oplus}$), 305 ($Ph_2\overset{\overset{O}{\|}}{P}CH_2CHPh^{\oplus}$), 262 ($Ph_3P^{\oplus}$) and 228 ($Ph_2P\text{-}CH{=}CH_2^{\oplus}$). This spectrum is similar in many respects to those of other bisphosphines (101).

In a repeat of the reaction of XCI with *N*-nitrosoacetanilide, the colourless residue (a few mg.) appeared to be a mixture melting over a range at around 170°C. At 165°C, the mass spectrum was identical to that of triphenylphosphine oxide while at 270°C (after prolonged pumping at 165°C) the spectrum was identical to that of the adduct assigned structure CCVII. Clearly, the product is a mixture of both of these compounds. Consideration of the hydrolysis of the postulated intermediates CCV and CCVI shows that triphenylphosphine oxide could also be obtained from CCVI by the route CCVI→CCVIII→$Ph_3P{=}O$ as shown.

Because of the very poor synthetic potential of these reactions of vinylphosphines and bisphosphines with benzyne, the investigation was terminated.

Conclusion

As expected, the phosphines mentioned in the introduction to this section of the thesis react readily with dimethyl acetylenedicarboxylate, hexfluoro-2-butyne or benzyne to form, in many cases, cyclic phosphonium ylides. These ylides are usually not isolable but most of them have been fully characterized by trapping them as their hydrolysis, deuterolysis or Wittig reaction products. The structures of these products have been confirmed by extensive NMR studies.

There were two main problems encountered during the course of this research. The first was that in almost every reaction, extensive polymerization of starting materials occurred and tarry materials were obtained as the principal product. The second main problem was that from the work-up of the complex mixture of tarry products, only small amounts of characterizable materials could be obtained making the reactions a poor proposition from a purely synthetic point of view. One other disadvantage from a synthetic viewpoint is that some of the reactions follow mechanistically unexpected reaction paths and it is therefore difficult to predict the outcome of any extension of the work described. However, in the opinion of this author, much valuable chemical information was obtained.

Suggestions for Further Work

Although the work is not mentioned in the foregoing discussion, a brief attempt was made to prepare the spiran CCIX by reaction of the ion CCX (102) with vinyl bromide to give CCXI (R=H) which was expected to react with dimethyl acetylenedicarboxylate to give CCIX. The work was abandoned because CCXI (R=H) could not be prepared by this method.

However, compounds of type CCIX would be interesting because of their similarity to the (n+1)-phosphonia-[n,n]spirarenes which have received a theoretical treatment by Ashe (75). Recently, CCXI (R=Ph) has been prepared (103) by dehydrobromination of 1-(2-bromoethyl)-2,3,4,5-tetraphenylphosphole and this would seem to offer a feasible route to compounds of type CCIX.

Because the cyclopropyl ring in cyclopropyldiphenylphosphine failed to open in reactions with dimethyl acetylenedicarboxylate, no seven-membered cyclic ylides were obtained in this investigation. Perhaps the reaction of the phosphine CCXII with the acetylenic ester could lead to such ylides although formation of five-membered rings is also possible.

EXPERIMENTAL

Introduction

The experimental work described in this section was carried out by the author between May 1968 and May 1972 in the Department of Chemistry at Lakehead University, Thunder Bay, Ontario, Canada.

Instrumental Techniques

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

IR spectra were recorded on a Beckman IR12 spectrophotometer, the calibration of which was checked against a standard polystyrene film. The spectra were recorded for samples mulled in Nujol using sodium chloride demountable cells.

UV spectra were recorded on a Unicam SP 800A recording spectrophotometer, using 1 cm. fused silica cells. Spectroscopic grade chloroform or concentrated hydrochloric acid was used as solvent. The calibration of the spectrophotometer was checked against a holmium filter.

NMR spectra were obtained with a Varian model A60-A spectrometer and the samples were dissolved in deuterated chloroform ($CDCl_3$) or trifluoroactic acid

(CF_3CO_2H) with tetramethylsilane (TMS) as the internal standard. The spin decoupling studies were carried out using a V-6058A field sweep decoupling unit and the signal averaging using a VarianData Systems model 620i unit.

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

Elemental analyses were carried out by Dr. Franz Pascher of Bonn, by Dr. W.J. Buis of Utrecht and with a Perkin-Elmer Model 240 Elemental Analyzer in these laboratories.

Column chromatography was carried out using silica or alumina (Woelm) as the adsorbent with benzene as eluent.

Starting Materials

Diphenylvinylphosphine (CLVII) was prepared by a modification of the method described in the literature (104) in which vinylmagnesium chloride is treated with chlorodiphenylphosphine. In the modification, vinyl bromide was used in place of vinyl chloride since it was found that this led to a smoother, faster reaction with magnesium to form the required Grignard reagent. Cyclopropyldiphenylphosphine (CLXIII) (first prepared by Bestmann (105)) was prepared for this project by a similar method to that described above in which magnesium was

treated with cyclopropyl bromide followed by addition of chlorodiphenylphosphine to the resulting cyclopropylmagnesium bromide. Yields of over 70% were obtained.

3,4,5-Triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene was prepared by the method described by Hughes and Srivanavit (87), while the other phosphines used in this work (LXXXVIII and XCI) were available commercially.

N-Nitrosoacetanilide was prepared by the method of Grieve and Hey (93) and was used immediately after preparation.

Where necessary, ether and tetrahydrofuran were dried over sodium or by distillation from lithium aluminium hydride while benzene and toluene were dried by distillation from calcium hydride. Dimethyl acetylenedicarboxylate (Aldrich Chemical Co.), diphenylvinylphosphine and cyclopropyldiphenylphosphine were freshly distilled before use. Commercial (Pressure Chemical Co.) *cis* and *trans* 1,2-bis(diphenylphosphino)ethylene (LXXXVIII and XCI) were used without further purification.

Nitrogen (certified pure) was dried by passage through concentrated sulphuric acid followed by passage through sodium hydroxide pellets.

Addition of Dimethyl Acetylenedicarboxylate to Diphenylvinylphosphine (CLVII)

A solution of diphenylvinylphosphine (2.206 g, 10.41 mmole) in vigorously stirred dry ether (80 ml) was

treated slowly with a slight excess of dimethyl acetylene-dicarboxylate (1.543 g, 10.87 mmole) in dry ether (20 ml) and the mixture was heated under reflux in a slow stream of nitrogen for 20 min. After cooling, the dark mixture was filtered and colourless crystals were collected. This crude solid was recrystallized from hot benzene to give colourless, long, fine needles (248 mg, 6.4% yield) of the 1:1:1 hydrolysis adduct CLXXIV, m.p. 130-132°. (Found: C, 64.74; H, 5.81; P, 8.78. $C_{20}H_{21}O_5P$ requires: C, 64.51; H, 5.64; P, 8.33%)

The IR spectrum shows υ_{max} at 1749, 1722, 1664, 1450, 1444, 1342, 1310, 1223, 1193, 1130, 1105, 751, 732, 708 cm^{-1}.

The NMR spectrum in deuterated chloroform shows a ten proton aromatic complex multiplet at τ 2.0 - 2.6, an olefinic one-proton quartet at τ 2.6 - 3.3, two ester methyl groups at τ 6.30 and τ 6.37, one methylene group as a doublet of doublets centred on τ 6.69 and one methylene group as a very closely spaced doublet at τ 6.65 (J=*ca.* 1.5 Hz) superimposed upon the other methylene signal.

The mass spectrum shows a molecular ion peak at *m/e* 372.

Repetition of this experiment using a 2:1 ester-phosphine ratio but still adding the ester to the phosphine again gives the 1:1:1 adduct CLXXIV as the only isolable product.

Addition of Dimethyl Acetylenedicarboxylate to Diphenylvinylphosphine (CLVII) in the Presence of D_2O

A solution of diphenylvinylphosphine (2.05 g, 9.7 mmole) in rigorously dried ether (200 ml) wetted with D_2O was treated slowly as described in the previous experiment with a solution of dimethyl acetylenedicarboxylate (1.34 g, 9.4 mmole) in dry ether (50 ml) again wetted with D_2O. After the addition was complete, more D_2O was added (5 ml). The mixture was heated under reflux in a slow stream of nitrogen for 20 min. After cooling, the mixture was filtered and a blackish solid collected. This crude solid was recrystallized twice from hot benzene to give colourless crystals (70 mg, 2% yield) of the deuterated adduct CLXXV, m.p. 132 - 133°.

The NMR spectrum is virtually identical to that of the 1:1:1 adduct CLXXIV except that the narrow doublet due to the methylene group adjacent to the terminal ester group has almost vanished from the spectrum.

The mass spectrum shows the strongest molecular ion peak at *m/e* 374 with a lesser peak (corresponding to triple deuteration) at *m/e* 375.

Addition of Dimethyl Acetylenedicarboxylate to Diphenylvinylphosphine (CLVII) in the Presence of *p*-Nitrobenzaldehyde.

A vigorously stirred solution of diphenylvinylphosphine (5.00 g, 23.6 mmole) and *p*-nitrobenzaldehyde (3.21 g, 21.3 mmole) in dry ether (600 ml) was

treated slowly (dropwise addition) with dimethyl acetylenedicarboxylate (3.53 g, 24.9 mmole) in dry ether (80 ml) and the mixture was heated under reflux in a slow stream of nitrogen for 20 min. After cooling, the dark green mixture was filtered and the filtrate evaporated to low bulk. This concentrated solution was chromatographed on a neutral alumina column using benzene as eluent. Evaporation of the benzene fraction gave a yellow solid (1.145 g, 10.6% crude yield). This crude solid was purified by dissolving it in chloroform and precipitating with ether. The m.p. of the pure adduct CLXXVIII was found to be 195 - 197° (decomp.). (Found: C, 63.69; H, 4.98; N, 2.98; P, 6.14. $C_{27}H_{24}O_7NP$ requires: C, 64.16; H, 4.79; N, 2.77; P, 6.13%)

The IR spectrum shows υ_{max} at 1745, 1692, 1630, 1600, 1515, 1440, 1345, 1275, 1249, 1159, 1110, 1020, 991, 731, and 700 cm^{-1}.

The NMR spectrum shows 17 aromatic/olefinic protons as a complex multiplet at τ 1.6 - 3.4, one methine proton as a doublet (J=15 Hz) centred on τ 4.38 and two ester methyl group signals at τ 6.33 and τ 6.38.

The mass spectrum shows a molecular ion peak at *m/e* 505.

Addition of Diphenylvinylphosphine to Dimethyl Acetylenedicarboxylate

Diphenylvinylphosphine (8.8 g, 41.5 mmole) in ether (50 ml) was added dropwise with stirring to freshly distilled dimethyl acetylenedicarboxylate (12.4 g, 87.2 mmole) in ether (1500 ml) at room temperature under nitrogen. After the addition was complete, the dark coloured mixture was filtered and the crude 1:2:1 adduct CLXXXV was obtained as a greenish precipitate (2.3 g, 11%). This product was recrystallized from hot benzene to give the pure adduct CLXXXV as colourless granular crystals, m.p. 198 - 201°. (Found: C, 60.59; H, 5.22; P, 6.77. $C_{26}H_{27}O_9P$ requires: C, 60.70; H, 5.29; P, 6.02%).

The IR spectrum (in $CHCl_3$) shows υ_{max} at 1738 (very broad), 1649, 1605, 1439, 1277, 1220 (very broad) and 1180 (shoulder) cm^{-1}.

The NMR spectrum shows ten aromatic protons as a complex multiplet at τ 1.90 - 2.70, one methine proton as eight unevenly spaced, poorly defined and partly overlapping peaks of similar intensity centred on τ 5.72, four ester methyl signals at τ 6.29, 6.32, 6.38 and 6.82, two methylene protons as an AB signal centred on τ 6.77 and two other methylene protons as a poorly defined multiplet of at least twelve maxima

at τ 6.80 - 7.70 partly obscuring the outer peaks of the AB signal.

The mass spectrum shows a molecular ion at *m/e* 514.

Addition of Diphenylvinylphosphine to Dimethyl Acetylenedicarboxylate in the Presence of D_2O

A solution of dimethyl acetylenedicarboxylate (2.79 g, 19.6 mmole) in dry ether (200 ml) wetted with a little D_2O was treated dropwise with a solution of diphenylvinylphosphine (2.13 g, 10.0 mmole) in dry ether (50 ml). After the addition was complete, more D_2O (5 ml) was added. The mixture was heated under reflux in a slow stream of nitrogen for 20 min. and then filtered. The crude solid was recrystallized from hot benzene to give colourless crystals of the adduct CLXXXVI, m.p. 206 - 213°.

The NMR spectrum is identical to that of the 1:2:1 adduct CLXXXV except that the methylene AB signals have vanished from the spectrum.

Addition of Diphenylvinylphosphine to Dimethyl Acetylenedicarboxylate in the Presence of *p*-Nitrobenzaldehyde

A solution of dimethyl acetylenedicarboxylate (5.28 g, 37.2 mmole) and *p*-nitrobenzaldehyde (2.86 g,

18.9 mmole) in dry ether (200 ml) was treated dropwise with stirring with a solution of diphenylvinylphosphine (3.74 g, 17.6 mmole) in dry ether (50 ml) and the mixture heated under reflux in a slow stream of nitrogen for 20 min. The mixture was evaporated and the resulting tar treated with a little ethanol and ether. The yellow solid residue produced by this method was filtered off and dissolved in chloroform. On the addition of ether, yellow crystals of the 1:1:1 adduct CLXXVIII precipitated out (182 mg, 2% yield), m.p. 201.5 - 204.5° (decomp.).

No trace of a 1:2:1 adduct of the phosphine with the ester and the aldehyde could be detected.

Reaction of 3,4,5-Triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene (CLXXII) with Dimethyl Acetylenedicarboxylate

3,4,5-Triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene (0.218 g, 0.669 mmole) and dimethyl acetylenedicarboxylate (0.166 g, 1.17 mmole) were added together with no solvent. In the early stages of the reaction, heat was evolved but the reaction mixture cooled rapidly. After standing for two weeks ether was added to the mixture and the ether-insoluble fraction recrystallized from benzene to give a colourless solid, m.p. 221°C. This product subsequently proved (IR and mass spectra) to be a slightly impure sample of the *P*-oxide of the

starting material CLXXII (lit. m.p. 234° (59)).

The experiment was repeated several times as above and also in dry benzene under reflux but each time only the oxide of CLXXII was produced.

Reaction of Diphenylvinylphosphine with Hexafluoro-2-butyne

A solution of diphenylvinylphosphine (2.89 g, 13.6 mmole) in ether (200 ml) was treated slowly with hexafluoro-2-butyne (2.19 g, 13.5 mmole) introduced to the reaction mixture as a gas. After the addition was complete, the mixture was evaporated. The resulting tar was dissolved in benzene and this solution was then poured into ether giving a light brown precipitate which was washed with acetone to give a light brown powder (1.12 g), m.p. ∿ 180° (decomp.). This material appeared to be mainly polymeric but the mass spectrum shows (at 175°) a molecular ion at *m/e* 398 and a fragmentation pattern identical to that of 1,2-bis-(diphenylphosphino)ethane ($Ph_2PCH_2CH_2PPh_2$). The crude solid therefore contains appreciable quantities of this compound.

Repetition of this reaction with the phosphine and the hexafluoro-2-butyne in a 1:2 ratio produced a similar solid which appeared to be entirely polymeric.

Reaction of Cyclopropyldiphenylphosphine (CLXIII) with Dimethyl Acetylenedicarboxylate

A solution of cyclopropyldiphenylphosphine (9.93 g, 43.9 mmole) in dry benzene (75 ml) was added slowly with stirring to a solution of dimethyl acetylenedicarboxylate (12.47 g, 87.1 mmole) in dry benzene (500 ml). The mixture was heated under reflux in a slow stream of nitrogen for two hours. The reaction mixture was then evaporated and a little ethanol added to the residual tar. The resulting solid residue which was a mixture of dimethyl fumarate and the adduct CLXXXVIII was washed with ethanol to remove the dimethyl fumarate. The remaining solid (1.51 g, 6.7 % yield) was dissolved in chloroform and, on addition of ether, a pink solid (CLXXXVIII) was obtained, m.p. 231.5 - 233.5° (decomp.). Found: C, 63.33; H, 5.36; P, 6.04. $C_{27}H_{27}PO_8$ requires: C, 63.53; H, 5.33; P, 6.07%)

The IR spectrum shows υ_{max} at 1752, 1742, 1683, 1658, 1548, 1431, 1330, 1269, 1208, 1180, 1101, 1080, 1020, 1009, 888, 773, 750, 729 and 693 cm^{-1}.

The NMR spectrum shows ten aromatic protons as a complex multiplet at τ 1.85 - 2.90, four ester methyl signals at τ 5.98, 6.50, 6.52 and 6.92 and five cyclopropyl protons as a broad, complex multiplet centred on τ 8.90.

The UV spectrum in chloroform shows a peak at λ_{max} 342mμ (ε 23120) but in concentrated hydrochloric acid, this band is absent.

The mass spectrum shows a strong molecular ion peak at *m/e* = 510.

Reaction of Diphenylvinylphosphine with Benzyne Generated from *o*-Benzenediazonium Carboxylate

o-Benzenediazonium carboxylate was prepared according to the method described by Friedman (92) using anthranilic acid (4.03 g, 29.4 mmole), amyl nitrite (5.29 g, 45.2 mmole) and trifluoroacetic acid (0.04 g, 0.24 mmole). The resulting solid diazonium salt (kept wet with tetrahydrofuran) was added to a solution of diphenylvinylphosphine (6.01 g, 28.3 mmole) in dry tetrahydrofuran (800 ml). The mixture was heated under reflux in a slow stream of nitrogen for five hours. The mixture was evaporated and a little hot ethanol added to the resulting tar. The crude solid residue produced was recrystallized from hot ethanol to give colourless needles (379 mg, 6.6% yield) of 1,2-bis-(diphenylphosphino)ethane, m.p. 144.5 - 146°.

The product proved to have an m.p. and NMR and mass spectra identical to those of an authentic sample purchased from the Pressure Chemical Co.

Reaction of Diphenylvinylphosphine with Benzyne Generated from *N*-Nitrosoacetanilide

N-Nitrosoacetanilide was prepared according to the method described by Grieve and Hey (93) using As_2O_3 (50 g, 252.5 mmole), concentrated nitric acid (40 g, 634.0 mmole) and acetanilide (20 g, 148.1 mmole). An ice-cold solution of *N*-nitrosoacetanilide (4.70 g, 28.7 mmole) in benzene (30 ml) was added slowly with stirring to a solution of diphenylvinylphosphine (3.10 g, 14.6 mmole) in benzene (20 ml) with anhydrous potassium acetate (4.71 g, 48.1 mmole) present. The mixture was heated under reflux in a slow stream of nitrogen for twenty four hours. The excess of undissolved potassium acetate was filtered off and the filtrate evaporated. The resulting tarry residue was chromatographed on a silica column with benzene as eluent. A very small amount (a few mg) of yellowish crystals of triphenylphosphine were obtained, m.p. 74 - 75°. Commercial (Aldrich) triphenylphosphine melts at 78 - 80°.

The mass spectrum shows a molecular ion peak at *m/e* = 262 and a fragmentation pattern identical to that of authentic triphenylphosphine.

Reaction of *Cis* 1,2-Bis(diphenylphosphino)ethylene (LXXXVIII) with Benzyne Generated from *o*-Benzenediazonium Carboxylate

o-Benzenediazonium carboxylate was prepared by the method described by Friedman (92) using anthranilic acid (1.04 g, 7.6 mmole), trifluoroacetic acid (0.015 g, 0.13 mmole) and amyl nitrite (1.77 g, 15.1 mmole). The diazonium salt produced was added while still wet with tetrahydrofuran to a solution of LXXXVIII (1.97 g, 5.0 mmole) in dry tetrahydrofuran (350 ml). The mixture was then heated under reflux in a slow stream of nitrogen for 3 1/2 hours. Water was added to destroy any excess of diazonium salt which might still be present (unlikely) and the mixture was dried over anhydrous potassium carbonate overnight. During this time, the mixture changed colour from red to yellow. The mixture was then evaporated giving a tar to which a little ethanol was added. The resulting solid residue was recrystallized from an acetone/chloroform mixture to give colourless crystals of the *P,P*-dioxide of LXXXVIII similar in all respects to a authentic sample. Several repetitions of this experiment gave yields of about 30%. No other compound could be isolated from the tarry product.

Reaction of *Cis* 1,2-Bis(diphenylphosphino)ethylene (LXXXVIII) with Benzyne Generated Directly from Aniline

A solution of *cis* 1,2-bis(diphenylphosphino)-ethylene (2.1 g, 5.3 mmole), aniline (0.47 g, 5.1 mmole), amyl nitrite (0.95 g, 8.2 mmole) and acetic anhydride (1.53 g, 15.0 mmole) in dry benzene (15 ml) was heated under reflux in a slow stream of nitrogen for 7 hours. The mixture was cooled and then filtered. A small quantity of colourless crystals (m.p. 303 - 307°) was collected and these proved to be similar in all respects (IR, NMR and mass spectra) to an authentic sample of the *P,P*-dioxide of the *trans* bisphosphine XCI. Several repetitions of this experiment gave this compound as the only isolable product.

Reaction of *Trans* 1,2-Bis(diphenylphosphino)ethylene (XCI) with Benzyne Generated from *N*-Nitrosoacetanilide

In a trial experiment, *N*-nitrosoacetanilide (93) (1.06 g, 6.4 mmole) in ice-cold benzene (40 ml) was added dropwise to a solution of XCI (1.31 g, 3.3 mmole) in benzene (15 ml) in the presence of anhydrous potassium acetate (1.07 g, 10.9 mmole). After the addition was complete, the mixture was heated under reflux in a nitrogen atmosphere overnight. The mixture was then evaporated to dryness and the residue was

washed in turn with small quantities of methanol, acetone and ether. The residue (*ca.* 1 mg) consisted of fine, colourless crystals, m.p. 266°, of the adduct CCVII. (Found: C, 74.57; H, 5.48. $C_{32}H_{28}P_2O_2$ requires: C, 75.89; H, 5.53%. This analysis was performed on *ca.* 0.5 mg material).

The mass spectrum shows a molecular ion peak at *m/e* 506 and the fragmentation pattern is consistent with the proposed structure CCVII as described in the Results and Discussion section of this thesis.

In a repeat of this experiment on a larger scale, an ice-cold solution of *N*-nitrosoacetanilide (3.64 g, 22.2 mmole) in benzene (40 ml) was added slowly to a solution of XCI (4.48 g, 11.3 mmole) in benzene (15 ml) with potassium acetate (3.37 g, 34.4 mmole) present. The mixture was heated under reflux in a slow stream of nitrogen overnight. The mixture was filtered and the filtrate upon evaporation, yielded three solid fractions. These fractions appeared to be the starting material XCI, impure triphenylphosphine oxide and a colourless solid, m.p. ∿ 176°, which appeared from mass spectral investigation to be a mixture of triphenylphosphine oxide and CCVII. Thus, at 165°, the mass spectrum of the residue was identical to that of pure triphenylphosphine oxide while at 270° it was identical to that of the adduct assigned structure CCVII.

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