

## Cyclic Phosphonium Ylides

*Maureen Davies and A. N. Hughes*

Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada

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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.

In connection with our studies on cycloaddition reactions of vinylphosphines (1) and bisphosphines (2) with dimethyl acetylenedicarboxylate, we have had occasion to survey the literature on cyclic phosphonium ylides. These are unsaturated phosphorus heterocycles in which one of the ring carbon atoms adjacent to the phosphorus atom often has appreciable carbanionic character and consequently, these systems are usually highly reactive. As a result of this survey, it became clear that although numerous cyclic phosphonium ylides are mentioned in the literature, many of them occur (or are postulated) as transient intermediates in various reactions leading to non-ylidic products. Thus, apart from the 1,1-disubstituted phosphorins, these compounds are not well indexed and detailed information is scattered through many papers published during the last ten years.

The following account is, therefore, a review of the chemistry of cyclic phosphonium ylides. 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.

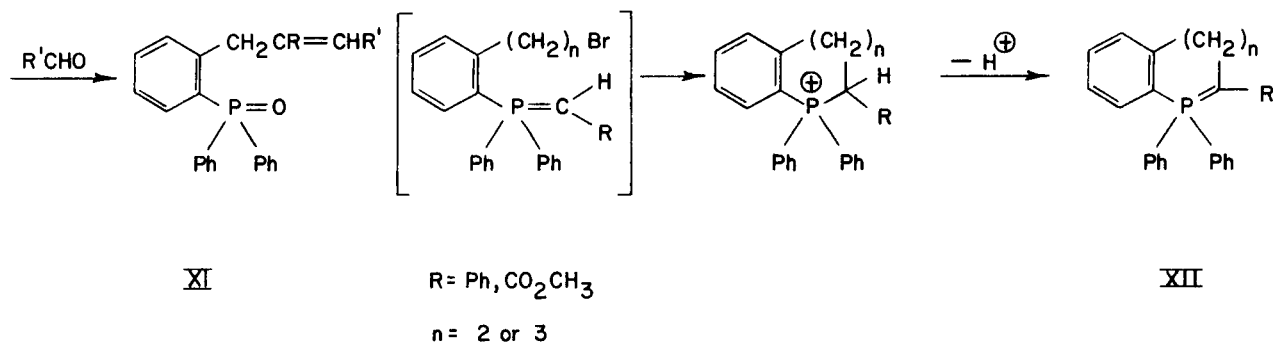
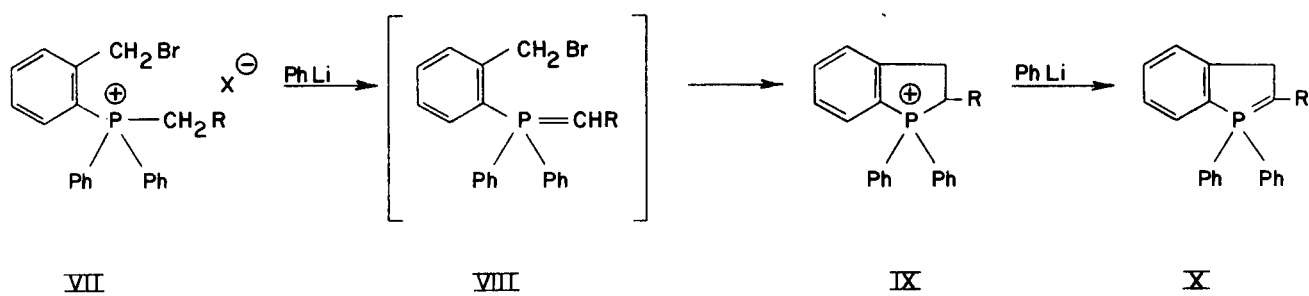
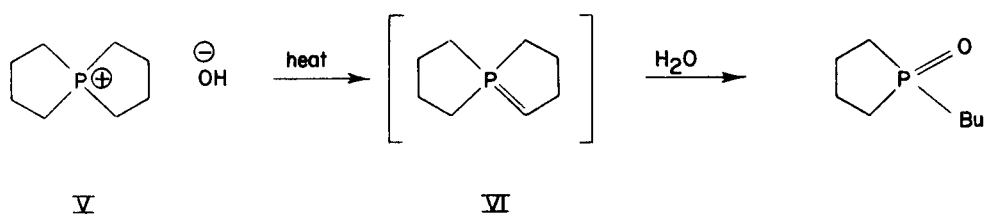
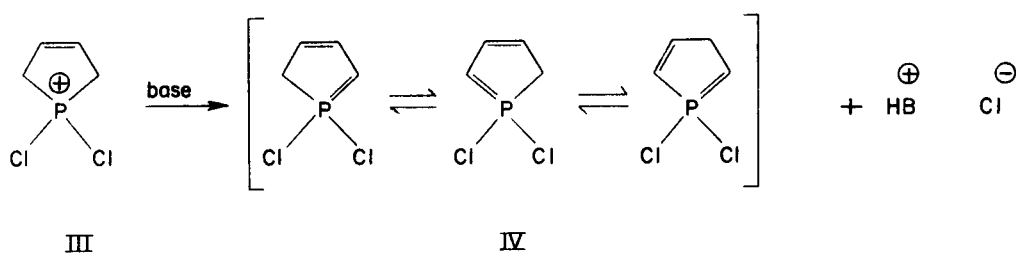
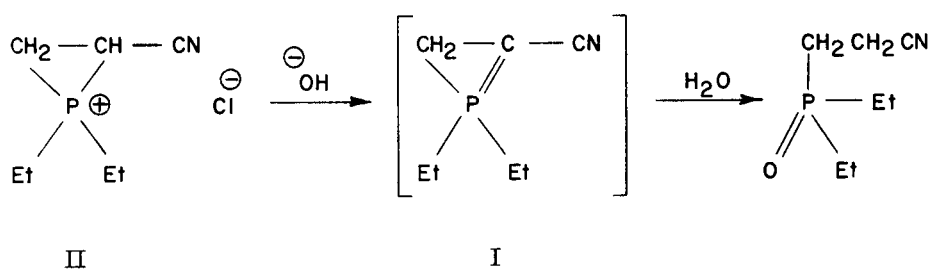
Many of the cyclic phosphonium ylides which have

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  $\alpha$ -proton abstraction from a cyclic salt,  $\alpha$ -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.  $\alpha$ -Proton abstraction from a cyclic phosphonium salt is the mechanism which occurs most often in this reaction type and this method is also very effective in the synthesis of open chain ylides (3a).



For example, Gundermann and Garming (4) have postulated that the cyclic ylide I occurs as an intermediate in the alkaline hydrolysis of the cyclic phosphonium salt II. Similarly, Hunger and his co-workers (5) in a paper concerned with the position of the double bond in phospholene derivatives such as III, considered the action of base on these compounds and suggested that ylides of type IV could occur as intermediates.

A cyclic ylide VI has also been suggested by Derkach and Kirsanov (6) as a possible intermediate in the synthesis of 1-butylphospholane oxide from the spirophosphonium hydroxide V. In this connection, Walker (7) has very recently investigated several spirophosphonium salts including V (OH<sup>-</sup> replaced by I<sup>-</sup>) and has found that in NaOD/EtOD, the  $\alpha$ -protons of V are readily exchangeable - presumably *via* the ylide VI. Furthermore, the ylide VI was found to be generated by treatment of V (OH<sup>-</sup> replaced by I<sup>-</sup>) with phenyllithium and trapped by addition of methyl iodide.

The first cyclic phosphonium ylide (X) to be fully characterized was prepared by Märkl (8) by basic abstraction of an  $\alpha$ -proton from the bicyclic phosphonium salt IX which was in turn prepared by the sequence VII  $\rightarrow$  IX. 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 X prepared by Märkl was studied only in solution and the highly substituted alkene XI, which was produced by reaction of the ylidic solution with a suitable aldehyde, was taken as additional proof for the existence of the ylide X. Märkl (8) used a similar method to synthesize the six- and seven-membered cyclic ylides XII ( $n = 2$  or 3).

Many of the known fully unsaturated six-membered cyclic phosphonium ylides have been prepared by this method of  $\alpha$ -proton abstraction and are relatively stable and 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 XIII  $\rightarrow$  XVIII, Märkl (9) successfully synthesized 1,1-diphenyl-1-phosphabenzene (1,1-diphenylphosphorin) (XVIII). No yield was reported for the ylide itself but all of the precursors were obtained in good yield. By similar methods (XIX  $\rightarrow$  XXII), Märkl (10) was able to prepare the 1,1-diphenyl-2-substituted-phosphanaphthalenes XXII and, by a modification of the synthesis, the dihydrophosphanaphthalenes XXIII. Again no yields were reported.

Another relatively stable six-membered cyclic ylide XXIV of the same general type was prepared by Cookson and Crofts (11) from the tricyclic phosphonium salt XXV

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

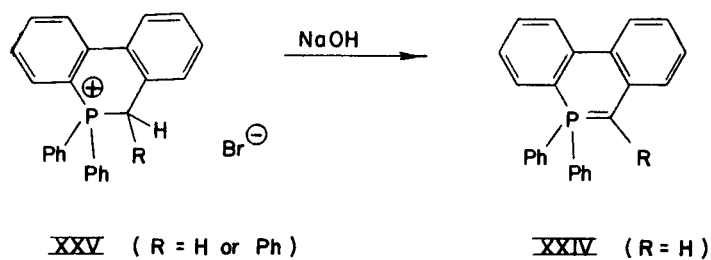
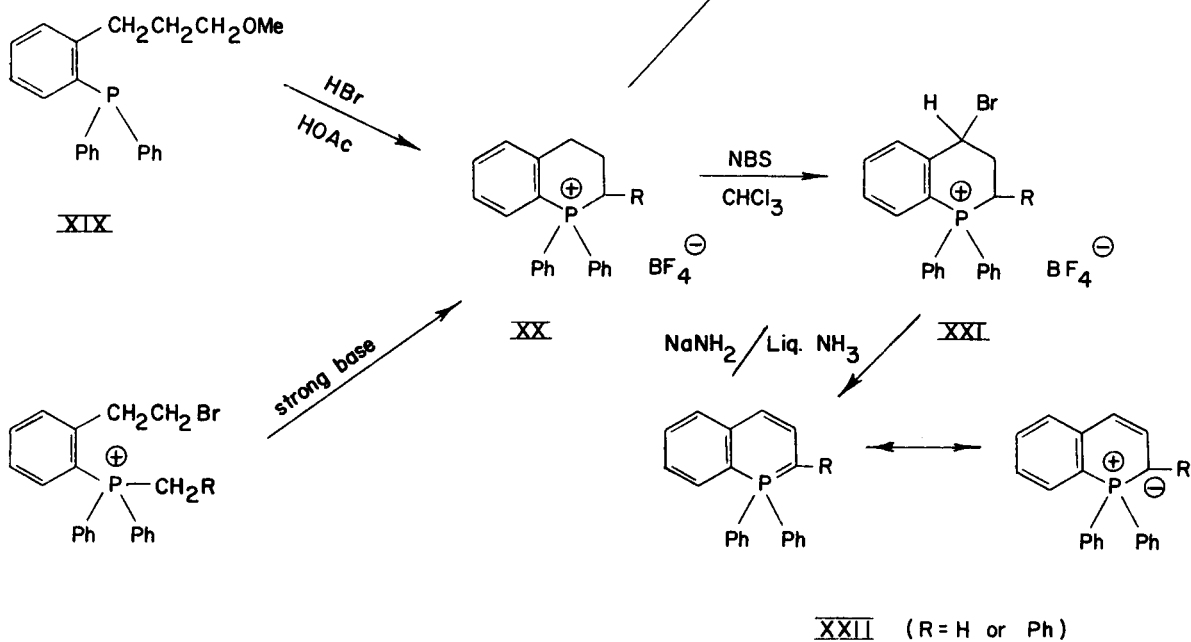
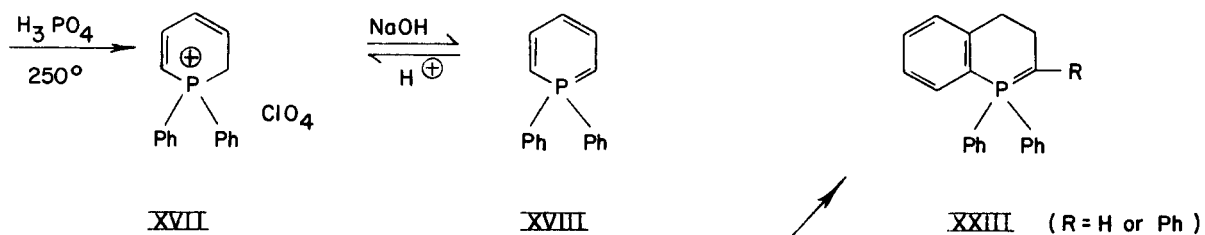
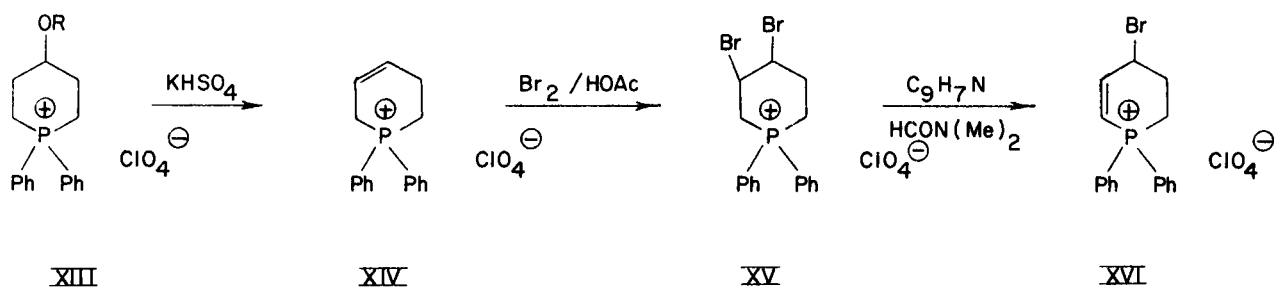
Several attempts have been made to prepare cyclic phosphonium bis-ylides from cyclic bisphosphonium salts by  $\alpha$ -proton abstraction. For example, Aguiar and Aguiar (12) found during nmr studies that, when 1,1,4,4-tetra-phenyl-1,4-diphosphonia cyclohex-2-ene (XXVI) is dissolved in deuterium oxide,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

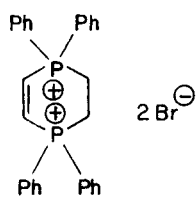
The only successful attempt to date to prepare a fully unsaturated six-membered cyclic bis-ylyde by proton abstraction techniques was carried out by Märkl (14). The synthesis started from the bisphosphonium salt XXXII and followed the sequence XXXII  $\rightarrow$  XXXV. The two  $\alpha$ -protons proved 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 XXXIII would have been removed in the first deprotonation step to give

the very stable  $\text{>P}^{\text{+}}\text{-}\overset{\text{+}}{\text{C}}\text{-P}^{\text{-}}\text{<link}$ . Indeed, Märkl states (14) that this is the case for the analogous salt XXXII in which the OH group is replaced by a hydrogen atom.

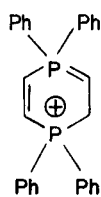
One recent and very interesting application of the  $\alpha$ -proton abstraction technique is the formation (15) of the Si-Si stabilized cyclic ylide XXXVI. This was carried out by treatment of the open chain ylide Me<sub>3</sub>P=CHSi(Me)<sub>3</sub> with dichlorotetramethyldisilane in the presence 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.

Although little information is available, there is one other cyclic ylide synthesis which possibly falls into the mechanistic category of  $\alpha$ -proton abstraction. The interesting ylide XXXVII was prepared by Bergerhoff and co-workers (16) by treatment of PhPCl<sub>2</sub> with malonic

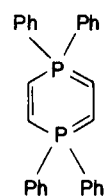
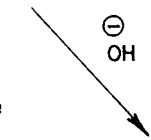
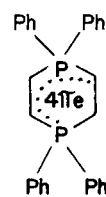




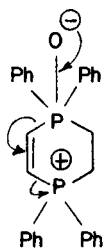
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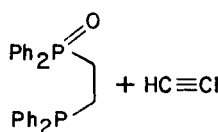
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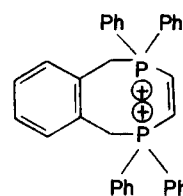
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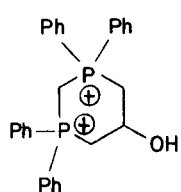
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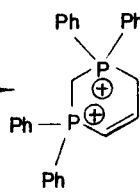
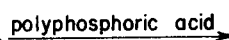
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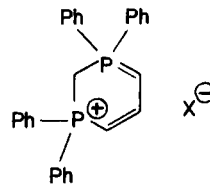
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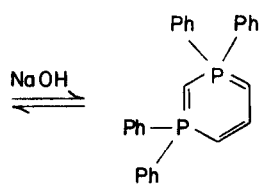
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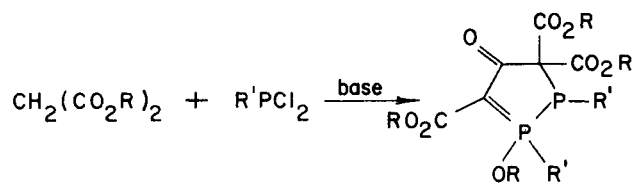
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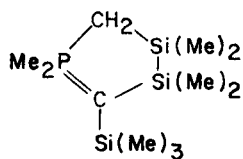
XXXIV



XXXV



XXXVII



XXXVI

esters and base and, although no mechanism was given, it could be that the reaction involves basic abstraction of a proton from a cyclic phosphonium salt. This ylide is of considerable interest since it is the only known cyclic ylide containing a P-P bond.

Other unsuccessful attempts to prepare cyclic phosphonium ylides by  $\alpha$ -proton abstraction have been made. For example, Welcher and Day (17) attempted to prepare the cyclic ylide XXXVIII from the phosphonium salt XXXIX by treatment with hydroxide ion but they obtained only the phosphine XL 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 XLI by treatment of the homocubylphosphonium salt XLII with phenyllithium. In most phosphonium salts containing an  $\alpha$ -hydrogen atom, this type of reaction readily yields a phosphonium ylide but in this case, the homocubyltriphenylphosphorane XLIII is formed - *i.e.* the salt XLII 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*  $\alpha$ -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 XLVI which arises from the abstraction of a proton from the methiodide XLIV followed by cyclization of the initially formed acyclic ylide XLV. The products XLVII and XLVIII are both formed by a Wittig reaction of the ylidic solution with the appropriate aldehyde. This supports the intermediacy of the ylide XLVI which, on this and other evidence, appears to be in equilibrium with the tautomers XLV, XLIX, and L.

$\alpha$ -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 (LI) 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  $\text{Ph}_4\text{P}^+\text{Br}^- \rightarrow \text{LII} \rightarrow \text{LIII} \rightarrow \text{LI}$  and the intermediate LIII is a cyclic ylide of the 3H-phosphole type. Similar results were obtained by Seyferth (21). The work has been extended by using other organometallic bases and greatly improved

yields of LI (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 *t*-butyltriphenylphosphonium ion LIV with lithium piperidide still gives LI as the major product whereas proton abstraction from the *t*-butyl group followed by elimination of triphenylphosphine might have been expected.

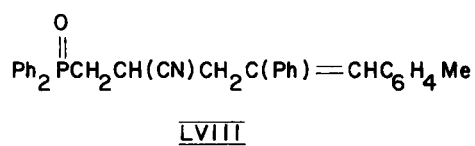
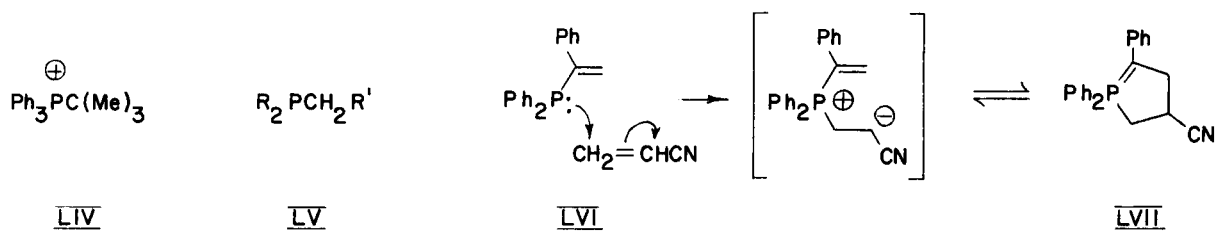
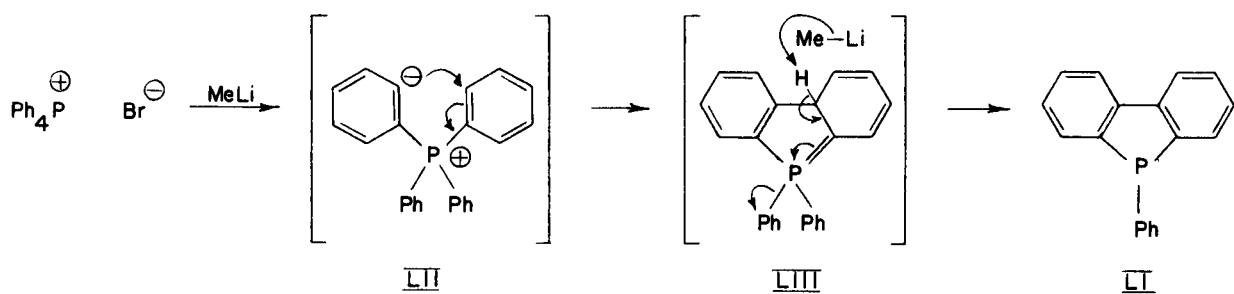
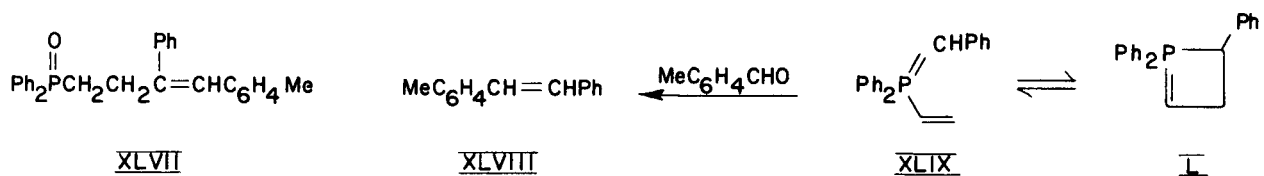
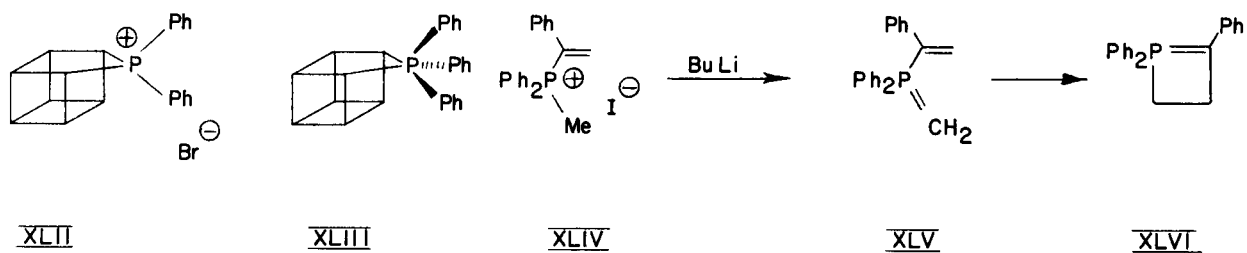
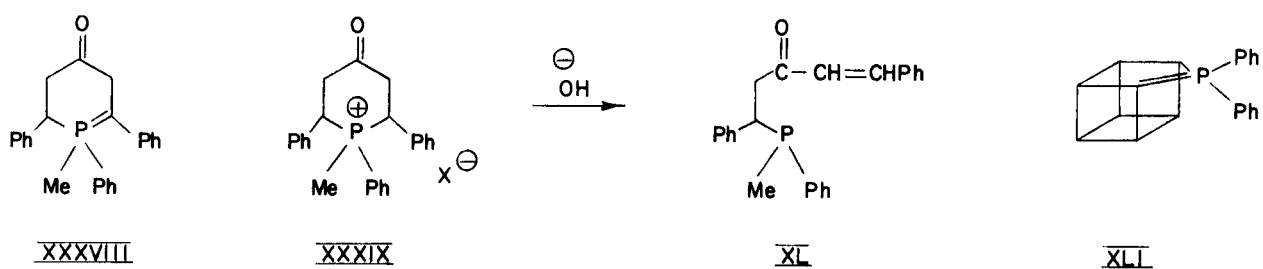
In a related reaction, Wittig (19b) found that treatment of triphenylphosphine itself with phenylsodium gives a low yield of LI by *o*-proton abstraction. However, in this case, it is unlikely that a cyclic ylide is involved.

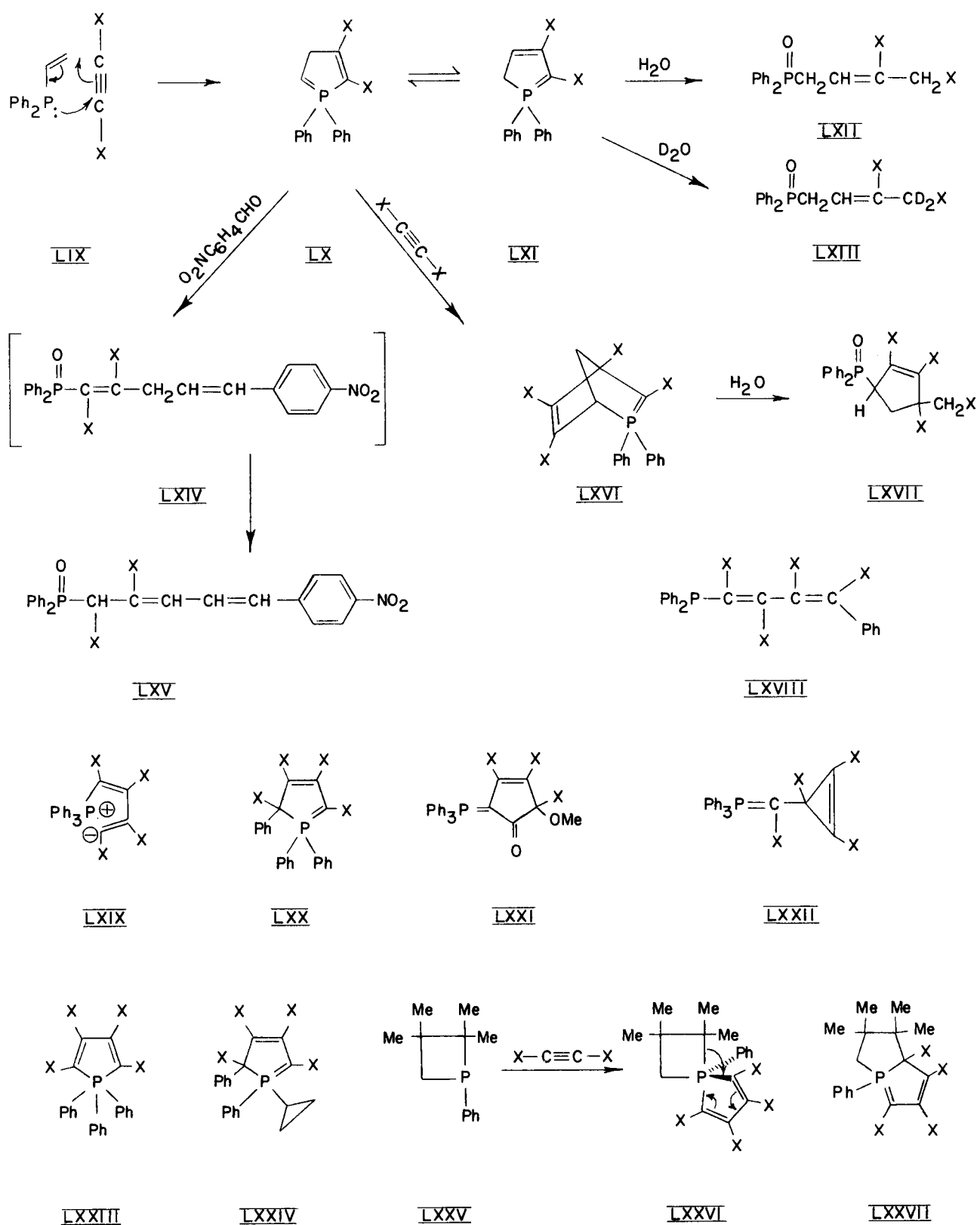
#### (b) Nucleophilic Addition to Activated Alkenes, Alkynes and Arynes.

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 LV 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 (LVI) with acrylonitrile in the presence of *p*-tolualdehyde (20) and obtained the phosphine oxide LVIII, the structure of which (established by nmr and mass spectral data) indicated that it was formed *via* the five-membered cyclic ylide LVII. When benzaldehyde was used in place of *p*-tolualdehyde, an analogous oxide was obtained.

There are numerous reports of the reactions of phosphines of various types with acetylene derivatives to give cyclic phosphonium ylides. One recent example of this (1) is closely related to the reaction of diphenyl-1-phenylvinylphosphine (LVI) with acrylonitrile as studied by Trippett (20) and was carried out at about the same time. Thus, diphenylvinylphosphine (LIX) has been found to react (1) with dimethyl acetylenedicarboxylate at room temperature in undried ether under nitrogen to give two





X = CO<sub>2</sub> Me



products. On addition of the acetylenic ester in ether to the phosphine in ether, an adduct was formed containing the phosphine, the ester and water in the ratio 1:1:1. On the other hand, a second adduct was formed when a dilute solution of the phosphine was added to a dilute solution of the ester. The proportions of the phosphine, the ester and water in this adduct were found to be in the ratio 1:2:1 respectively.

By a detailed chemical and spectroscopic investigation it was shown that the 1:1:1 adducts are LXII and LXVII respectively, and that these are derived from the ylides LXI and LXVI respectively. Furthermore, LXVI is derived from the cyclic ylide LX and therefore LXI is derived from LX by tautomerization. Independent evidence for the intermediate ylide LX was obtained by trapping it as the adduct LXV with *p*-nitrobenzaldehyde (28). The structure LXV is presumably formed from the expected adduct LXIV by proton migration to give a more highly conjugated structure. Confirmation of the nmr assignments in LXII was obtained by deuterolysis of LXI to give LXIII (28).

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 (29) 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 (30) revised the structure of the product. In 1961, Johnson and Tebby (29) had assigned the open-chain structure LXVIII to the methanol-insoluble product formed after the reaction mixture warmed from  $-50^{\circ}$  to room temperature. They also proposed that it is a rearrangement product of an intermediate formed initially at  $-50^{\circ}$  and to which they assigned the zwitterionic structure LXIX. In 1969, Tebby and his co-workers (30) revised the structure of the methanol-insoluble adduct to that of the stable ylide LXX 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 (31,32) has elaborated on this work. He now believes that the adduct LXX and another previously uncharacterized methanol-soluble 1:2 adduct formed in twenty percent yield and to which he has assigned the structure LXXI (32) may both be formed *via* the intermediate LXXII and perhaps LXXIII which are formed initially at  $-50^{\circ}$ .

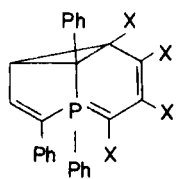
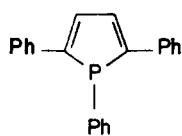
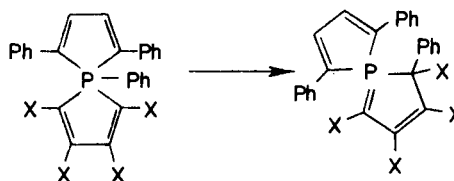
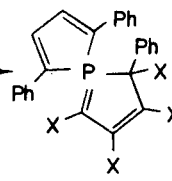
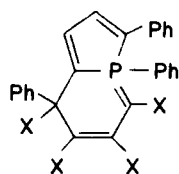
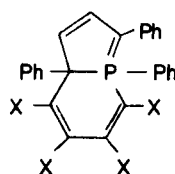
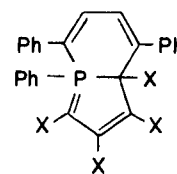
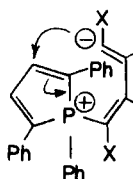
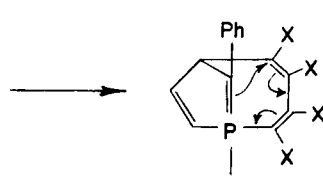
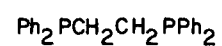
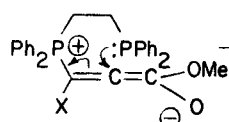
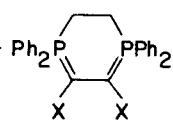
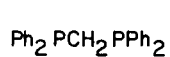
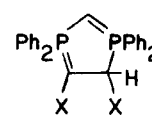
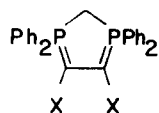
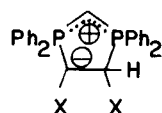
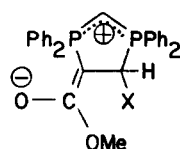
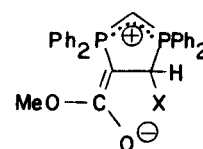
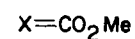
Similar reactions occur between tri-*p*-tolylphosphine and the ester (30-32) and a stable cyclic ylide LXXIV, analogous to LXX, is formed in the reaction of cyclopropyldiphenylphosphine with dimethyl acetylenedicarboxylate (28).

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 (30), Trippett and his co-workers (36) investigated the reaction of the phosphetan LXXV with the acetylenic ester. As with other phosphines, a stable cyclic ylide LXXVII is formed in 44% yield and the reaction presumably proceeds *via* the trigonal bipyramidal spiroporphorane LXXVI in which the four-membered ring occupies the apical-equatorial arrangement. This arrangement would favour the migration of the  $\text{CMe}_2$  group from the apical position to the carbon atom adjacent to the phosphorus atom in the five-membered ring.

Another related stable ylide LXXVIII has recently been reported by Waite and Tebby (37). It is a revised structure, which they assigned to a 1:2 adduct of 1,2,5-triphenylphosphole LXXIX and dimethyl acetylenedicarboxylate which was originally isolated by Hughes and Uaboonkul (38) who proposed the spirobiphosphole structure LXXX for this adduct. However, on the basis of the  $^{31}\text{P}$  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 LXXX. Several rearrangement products of the spirobiphosphole leading to the ylides LXXXI, LXXXII and LXXXIII, the last one formed from LXXXIV 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 LXXX is formed as an intermediate and considered other methods by which the dipolar intermediate LXXXV, which is presumably formed, could cyclize. They finally decided on a mechanism (the sequence LXXXV  $\rightarrow$  LXXXVI  $\rightarrow$  LXXXVIII) very similar to the one proposed for the reaction of diphenylvinylphosphine with dimethyl acetylenedicarboxylate (1). Waite and Tebby confirmed the structure LXXVIII 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 (2) studied the reaction of the ester with bis(diphenylphosphino)ethane LXXXVII. On the basis of spectroscopic evidence, the product was shown to have the structure LXXXIX. This is supported by the fact that the ylidic product forms a bisperchlorate on treatment with perchloric acid and the dioxide of LXXXVII on hydrolysis. The formation of LXXXIX is thought to follow the sequence LXXXVII  $\rightarrow$  LXXXVIII  $\rightarrow$  LXXXIX.

At about the same time, Tebby and his co-workers (39)

LXXXVIIILXXXIXLXXXLXXXILXXXIIILXXXIVLXXXIILXXXVLXXXVILXXXVIIILXXXVIILXXXVIIILXXXIXXCXCIXCIIXCIIIXCIVXCV

reported the synthesis of the bis-ylide XCI from the reaction between bis(diphenylphosphino)methane (XC) and dimethyl acetylenedicarboxylate. They proposed that the ylide XCI is the preferred structure in a tautomeric equilibrium of XCI and XCII although XCII is probably formed first in the reaction. They further proposed that the electronic structure of XCI may best be represented by XCIII and that XCIII is an equilibrium mixture of the two conformers XCIV and XCV. 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 XCIII was based upon ir data and a consideration of the  $pK_a$  values (40) of the model alkylidenephosphoranes  $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$  ( $pK_a=9.2$ ) and  $\text{Ph}_3\text{P}=\text{CH}-\overset{+}{\text{P}}\text{Ph}_3 \leftrightarrow \text{Ph}_3\overset{+}{\text{P}}-\text{CH}-\overset{+}{\text{P}}\text{Ph}_3$  ( $pK_a=5.4$ ). Variable temperature nmr studies indicated the equilibrium  $\text{XCIV} \rightleftharpoons \text{XCV}$ .

In the same publication (39) Tebby and his co-workers presented some evidence for the successful synthesis of the 1,4-diphosph(V)orin XCVII from *cis*-1,2-bis(diphenylphosphino)ethylene (XCVI). Although the solid product was reported to be too unstable for complete characterization, the ir and mass spectral data supported the structure XCVII. In particular the ester groups are clearly both attached to ylidic carbon atoms since the carbonyl stretching frequencies occur well below  $1700\text{ cm}^{-1}$ . Moreover, hydrolysis of the adduct gives the dioxide of XCVI.

These and related reactions were being studied simultaneously by Hughes and Jafry (41). Their conclusions were the same for the structure of the ylide XCI produced by the reaction of XC with dimethyl acetylenedicarboxylate. However, they did manage to synthesize the monoperochlorate XCVIII but, on hydrolysis of the original adduct, only bis(diphenylphosphino)methane monoxide was obtained whereas Tebby also obtained the dioxide. Hughes and Jafry (41) also studied the reaction between XCVI 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 XCVII is indeed formed and, although the adduct is readily hydrolyzed, it appears to have some aromatic character. This will be discussed in a later section.

Hughes and Jafry (41) have also investigated the reaction of the bisphosphine *trans*-1,2-bis(diphenylphosphino)ethylene (XCIX) 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 deuteriochloroform indicates that the adduct exists largely in the form C which may be

in tautomeric equilibrium with the ylidic structures CI, CII, and possibly CIII. The nmr spectrum in trifluoroacetic acid shows that a mixture of protonated ylides is formed but, over a period of time, the protonated form CIV of CII 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 CIV.

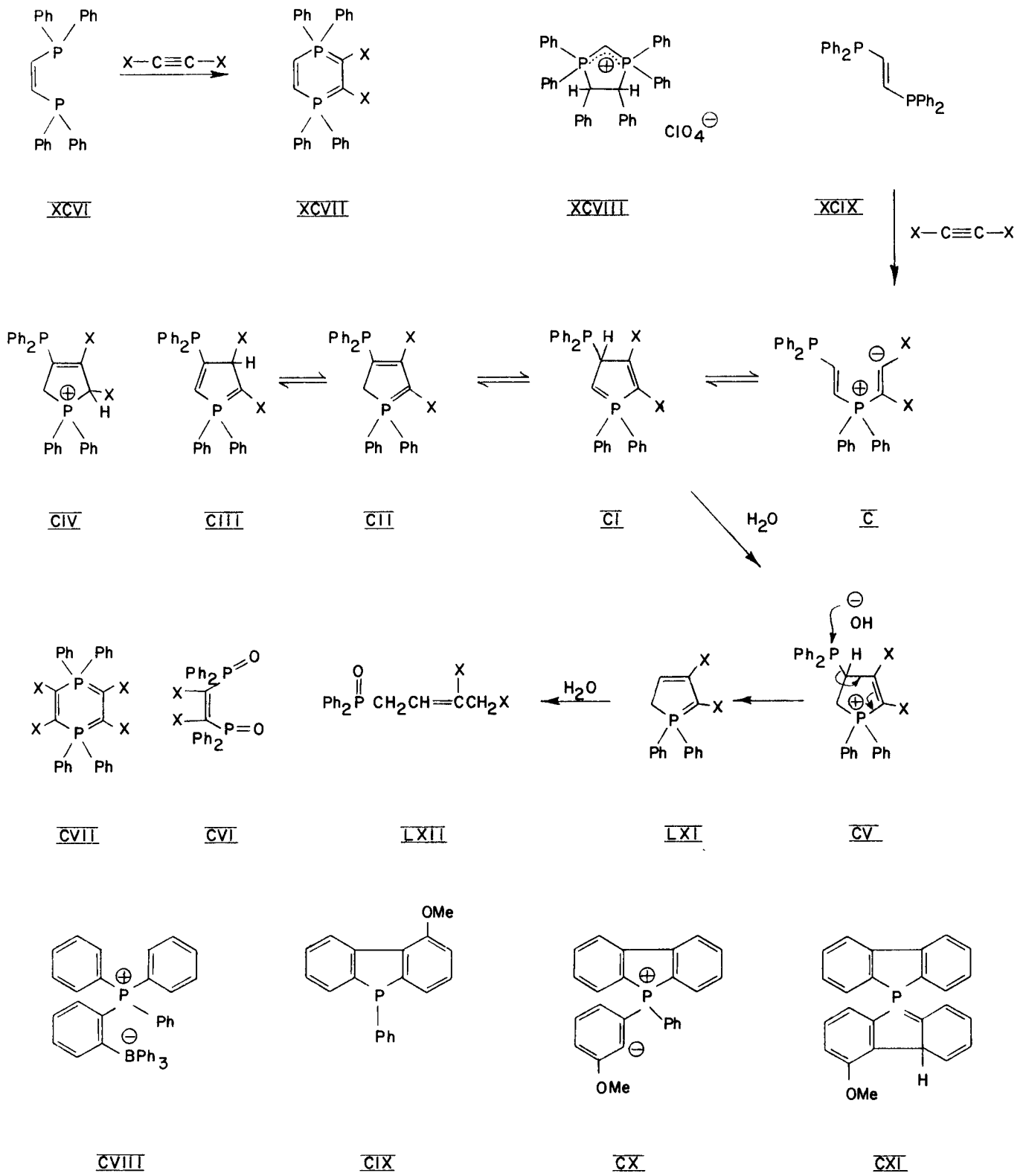
The behaviour of the adduct C towards hydrolysis is very surprising. Thus, on treatment with water (41) the adduct rapidly hydrolyzes to give the phosphine LXII which was previously obtained by hydrolysis of the cyclic ylide LXI - *i.e.* one of the diphenylphosphino groups has been eliminated. The mechanism of this reaction is obscure but a possible (though unconfirmed) scheme is outlined in the sequence  $\text{C} \rightleftharpoons \text{CI} \rightarrow \text{CV} \rightarrow \text{LXI} \rightarrow \text{LXII}$ . Deuterolysis experiments support this tentatively proposed mechanism (41).

Treatment of tetraphenylbiphosphine ( $\text{Ph}_2\text{PPH}_2$ ) with an excess of dimethyl acetylenedicarboxylate has given CVI - possibly by hydrolysis of the bis-ylide CVII (41).

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 (42) investigated the reaction of triphenylphosphine with benzyne and obtained 9-phenyl-9-phosphafluorene (LI) in low yield. Wittig (42) postulated the zwitterionic and cyclic ylidic intermediates LII and LIII as intermediates in the reaction and was able to trap the zwitterion LII as the adduct CVIII 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 (43) have extensively investigated the properties of the zwitterion LII at low temperature and similar zwitterions generated from triphenylphosphine and arynes derived from a variety of *o*-lithiofluoroaromatics.

Zbiral (44) reinvestigated the reaction of triphenylphosphine with benzyne and was able to obtain up to 40% of LI from these reactions. He also studied the reaction of 1-methoxy-2-benzyne with triphenylphosphine and obtained 4-methoxy-9-phenyl-9-phosphafluorene (CIX) *via* a cyclic ylide mechanism. Similarly, 9-phenyl-9-phosphafluorene (LI) was found to react with 1-methoxy-2-benzyne in a reaction involving a cyclic ylide intermediate. Two possible cyclizations of the zwitterion CX were considered to give the ylides CXI or CXII respectively followed by elimination of benzene to give CXIII or CXIV. It was found that only the reaction path  $\text{LI} \rightarrow \text{CX} \rightarrow \text{CXI} \rightarrow \text{CXIII}$  operates in this reaction.

Very recently, Märkl (45) has investigated the reactions of phosphorins of type CXV with arynes to give benzo-



X = CO<sub>2</sub> Me

phosphabarrelenes such as CXVI. This is an extension of his earlier investigations of the reactions of phosphorins with alkynes to give phosphabarrelenes (46). Märkl found (45) that 2,4,6-triphenylphosphorin (CXV, 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 CXVII which subsequently cyclizes to give the benzophosphabarrelene CXVI. 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 CXVIII (to be discussed in the next section) and on the basis of its uv spectrum, it was assigned structure CXIX.

(c) Radical and Ionic Addition to Phosphorin Derivatives.

Although phosphorins of type CXV are poor nucleophilic donors, they will readily undergo radical addition to give stable and isolable cyclic phosphonium ylides. Thus, Dimroth and his co-workers (47) have found that oxidation of 2,4,6-triphenylphosphorin (CXV, 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 (CXX, R = alkyl or aryl). The reaction is thought to proceed *via* the cation radical CXXI which has been detected by esr spectroscopy. In closely related experiments, the same group of workers has shown (48) that CXV (R = Ph) undergoes radical addition with the 2,4,6-triphenylphenoxy radical and the diphenylamino radical to give CXX (R = 2,4,6-triphenylphenyl) and CXXII respectively. Cyclic ylides of this type have proved to be remarkably stable and are protonated only by strong acids.

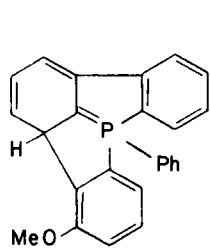
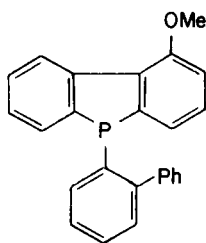
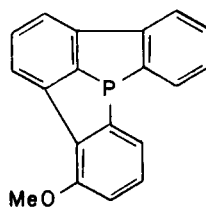
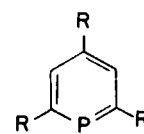
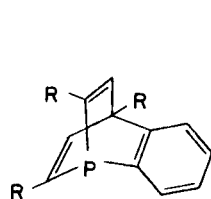
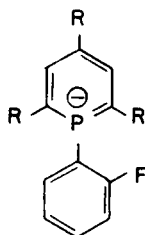
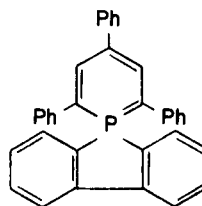
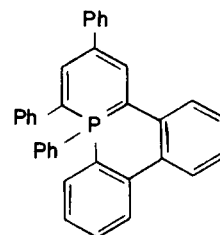
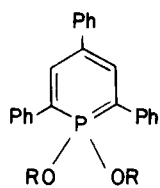
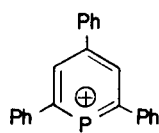
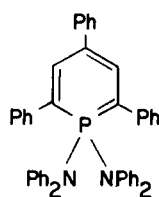
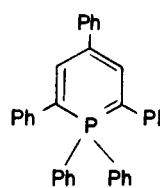
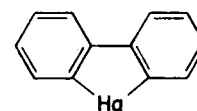
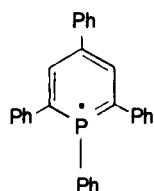
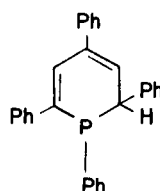
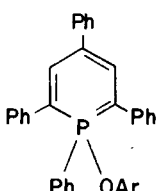
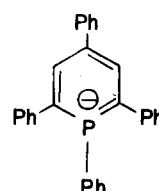
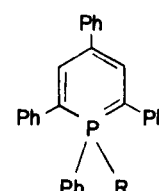
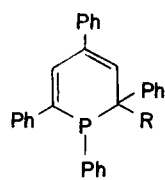
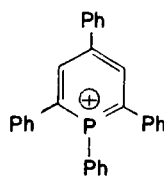
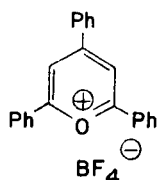
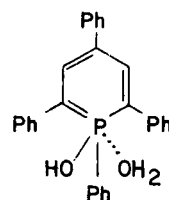
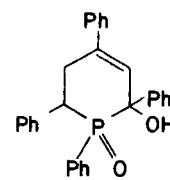
At about the same time, Märkl and his group were also investigating addition reactions of phosphorins and phosphorin derivatives. In particular, they investigated the generation of radical species in the presence of the phosphorin CXV (R = Ph) by the pyrolysis of organomercury compounds (49). By this method, they prepared 1,1,2,4,6-pentaphenylphosphorin (CXXIII) from the phosphorin CXV (R = Ph) and diphenylmercury and the spiran CXVIII from the phosphorin CXV (R = Ph) and 2,2'-biphenylmercury (CXXIV). In this case, the addition was thought to go *via* radicals of type CXXV and this radical (and subsequently the phosphorin CXXIII) could also be generated by treatment of CXXVI with diphenylmercury at 220° (49). Treatment of CXXVI with the 2,4,6-triphenylphenoxy radical leads to the formation of the phosphorin CXXVII (Ar = 2,4,6-triphenylphenyl) (49).

In a series of papers dealing with various aspects of the

electrophilic nature of 2,4,6-triphenylphosphorin (CXV), Märkl and his group (50-52) have found that CXV undergoes addition with organolithium (50-52) or Grignard reagents (52) to give anions of type CXXVIII. Furthermore, treatment of this anion with alkyl or benzyl halides can lead to the formation of the 1,1-disubstituted phosphorins CXXIX (R = alkyl or benzyl). Märkl (51) established that the nature of the solvent is quite important in the reaction. For example, the phosphorins CXXIX 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 CXXX. One exception to this generalization is the reaction of the anion CXXVIII with methyl iodide where the product is always CXXIX (R = Me) regardless of the nature of the solvent. The isomeric compound CXXX (R = Me) can be prepared from CXXVIII by treatment with trimethyloxonium fluoroborate (52). Märkl (52) has further generalized these observations by stating that the anion CXXVIII reacts with S<sub>N</sub>1 reactive halides to give the cyclic phosphines CXXX (*i.e.* reaction occurs at the site of highest electron density) whereas reaction with S<sub>N</sub>2 reactive halides yields the 1,1-disubstituted phosphorins CXXIX. It is also interesting to note that the anion CXXVIII can also be generated from the phosphorin CXXIII by treatment with Na/K alloy in tetrahydrofuran (49).

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

The first attempts to prepare CXXXI (as an intermediate in the proposed synthesis of CXXIII) were made by Price (53) who treated 2,4,6-triphenylpyrylium fluoroborate (CXXXII) with phenylphosphine in boiling pyridine. There is little doubt that the cation CXXXI 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 (53) assigned the structures CXXXIII and CXXXIV to these products and CXXXIII would be most unusual in that it would contain 5-coordinate hexacovalent phosphorus. More recently, Märkl (49,50) has repeated this work and has also obtained two similar products (49) to which he assigned the structures CXXXV and CXXXVI. Ultraviolet spectro-

CXIICXIIICXIVCXVCXVICXVIICXVIIICXIXCXXCXXICXXIICXXIIICXXIVCXXVCXXVICXXVIICXXVIIICXXIXCXXXCXXXICXXXIICXXXIIICXXXIV

photometric studies indicate that in methanol solution, CXXXV is in equilibrium with its tautomer CXXXVII (50). 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 CXXXI has been prepared by an alternative route (49) which involves the treatment of CXXVI with trityl perchlorate and subsequent treatment of CXXXI with phenyllithium does indeed give the 1,1-disubstituted phosphorin CXXIII. The product is obtained in excellent yield.

In a very recent paper, Märkl (54) has reported the investigation of three routes to 1,1-disubstituted phosphorins *via* cations of type CXXXIX. The first of these methods is direct treatment of pyrylium salts such as CXXXII with primary phosphines in the presence of alcohols, thioalcohols or phenols to give 1,1-disubstituted phosphorins such as CXL (R = Ph or CH<sub>2</sub>Ph, R' = alkyl or Ph), CXLI (R = Ph or CH<sub>2</sub>Ph, R' = alkyl) and CXLII (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<sub>2</sub> is replaced by the corresponding bis(hydroxymethyl)phosphine RP(CH<sub>2</sub>-OH)<sub>2</sub> and this greatly improves the yields.

The third method involves the oxidation of the cyclic phosphine CXXVI with mercuric acetate to give CXXXI which is then treated with an alcohol or phenol to give CXL (R = Ph, R' = Me or Ph). This reaction is reminiscent of Dimroth's experiments with phosphorins of type CXV in the presence of mercuric acetate and alcohols (47).

In connection with these studies, Märkl found (54) that treatment of 4-methyl substituted pyrylium salts with primary phosphines or bis(hydroxymethyl)phosphines gives compounds of type CXLIII *via* an unexpected base catalyzed condensation.

The recent synthesis (55) of the completely unsubstituted phosphorin CXV (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.

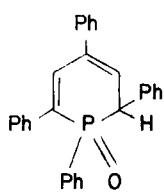
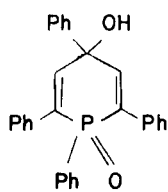
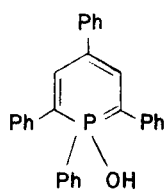
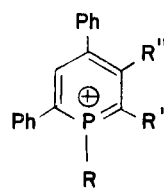
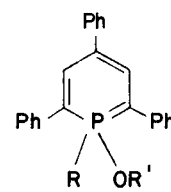
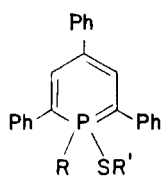
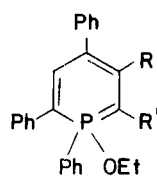
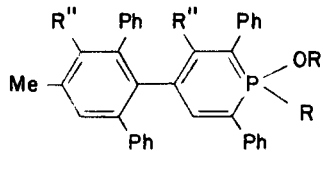
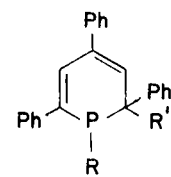
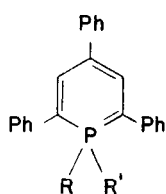
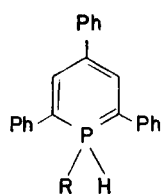
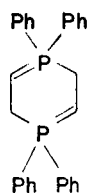
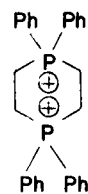
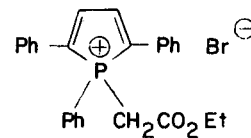
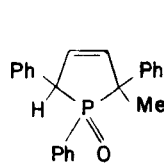
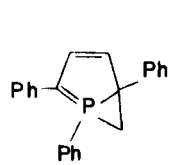
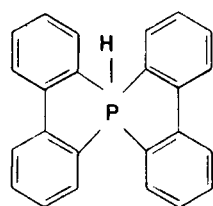
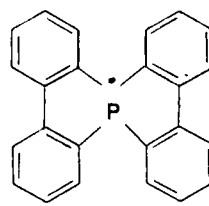
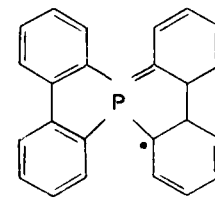
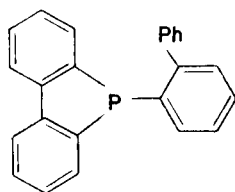
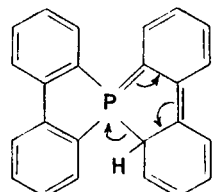
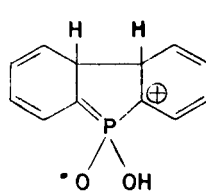
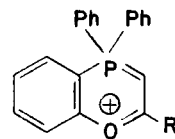
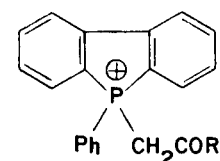
There appear in the literature several reports of the formation of cyclic phosphonium ylides by methods which do not fall into any of the three main categories already discussed and these are usually of limited scope.

One of these reactions which appears to have a good potential as a source of 1,1-disubstituted phosphorins is due to Märkl (52) and involves the controlled pyrolysis of 1,2-dihydrophosphorins of type CXLIV. Thus, it has

been found (52) that compounds of type CXLIV are smoothly converted into the corresponding phosphorins CXLV (R = Ph or CH<sub>2</sub>Ph, R' = CH<sub>2</sub>Ph or CH<sub>2</sub>CH=CH<sub>2</sub>) 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 CXLV (R = R' = CH<sub>2</sub>Ph) decomposes to give the phosphorin CXV (R = Ph) and at elevated temperatures, a number of 1,2-dihydrophosphorins similar to CXLIV decompose directly to give CXV (R = Ph) in high yield - presumably *via* the corresponding 1,1-disubstituted phosphorin CXLV. Certain of these decompositions may involve *1H*-1,1-disubstituted phosphorins such as CXLVI.

Cyclic phosphonium ylides have been postulated as transient intermediates in a variety of other reactions. For example, Märkl (56) has postulated a cyclic bis-ylide intermediate - presumably CXLVII - in the proton catalyzed quantitative dimerization of diphenylvinylphosphine to give CXLVIII. Similarly, Campbell (57) reported that, on one occasion, treatment of the quaternary salt CXLIX with concentrated aqueous alkali gave CL and suggested that the intermediate in this reaction is the interesting bicyclic ylide CLI. Hellwinkel (58) found that solutions of the spirophosphorane CLII in dry, oxygen-free benzene rapidly take on a deep violet colour due to the formation of the radical CLIII. He also suggested that this radical is one contributor to a resonance hybrid to which the ylidic structure CLIV is also a significant contributor. Furthermore, when the phosphorane CLII 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 CLV is obtained. In Hellwinkel's opinion, it is likely that addition of a hydrogen atom to CLIV occurs in this reaction to give the ylidic structure CLVI which rearranges to CLV as shown.

There have also been reports (59,60) 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 (59) has postulated the formation of the ylidic radical cation CLVII as a cyclized form of the molecular ion of diphenylphosphinic acid. Similarly, Williams (60) suggested that in the mass spectra of acylphosphoranes (Ph<sub>3</sub>P=CHCOR), the (M-1)<sup>+</sup> ion could have the ylidic structure CLVIII or the alternative structure CLIX and presented arguments in favour of the latter. Very recently, these conclusions of Williams have been confirmed by Bowie and his group (61).

CXXXVCXXXVICXXXVIICXXXIXCXLCXLIICXLIIICXLIVCXLVCXLVICXLVIICXLVIIICXLIXCLCLICLIICLIIICLIVCLVCLVICLVIICLVIIICLIXCLX



### 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. 3 and several later papers). Moreover, many of the three-, four- and five-membered cyclic phosphonium ylides discussed in this review 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 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 (62, see also 56) and Price (63) and Märkl's proposal is similar to that put forward by Dewar (64) 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  $p_\pi$ - $d_\pi$  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 (65) discussed four types of cyclic  $\pi$ -bonding and suggested that both 1,1-diphenylphosphorin (XVIII) and the corresponding 1,3-diphosphorin XXXV are anti-Hückel Möbius type conjugated systems. This approach also suggests that the corresponding phosphorus analogues of cyclobutadiene and cyclooctatetraene would also have large resonance energies. However, Vilceanu (66) carried out HMO calculations on 1,1-diphenylphosphorin (XVIII) using various models for heteroatoms possessing 3d-orbitals. Among the models used was that of Fukui (67) which assumes a normal  $d_\pi$  orbital and one  $\pi$ -electron for the phosphorus

atom. A second model considered was that of Mason (65) and Craig and Paddock (68) which leads to an anti-Hückel system in which the  $\beta$ -integrals for the two ring P-C bonds are of opposite sign. A third model considered was that of Dewar (64) which has already been mentioned. Vilceanu also considered Fukui and anti-Hückel models involving weak interactions between the  $\pi$ -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 (67) and Dewar (64) models are consistent with the spectroscopic properties, the stability to water and the relatively weak basic character of XVIII.

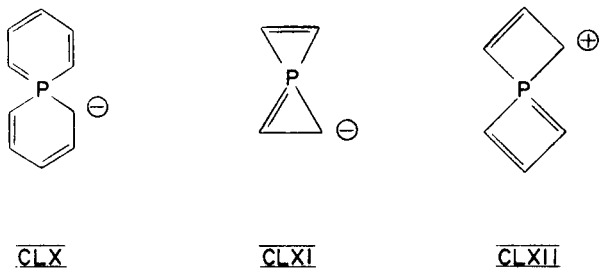
Very recently, Oehling and Schweig (69) have shown by CNDO/2 calculations that for the phosphorus atom in 1,1-disubstituted phosphorins, there is a significant d-orbital contribution to the P-C  $\sigma$ -bonds and a significant phosphorus  $3p_z$  orbital contribution to the  $\pi$ -bonding.

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 (70) determined the crystal and molecular structure of 1,1-dimethyl-2,4,6-triphenylphosphorin (CXLV, 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 (71). 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 (CXX, R = Me) (72) and 1,1-bis(dimethylamino)-2,4,6-triphenylphosphorin (the *N,N*-dimethyl analogue of CXXII) (73) 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 (65) and Vilceanu (66) have made brief mention of theoretical treatments of 1,1,3,3-tetraphenyl-1,3-diphosphorin (XXXV) and Vilceanu has predicted that XXXV and 1,1-diphenylphosphorin (XVIII) should have approximately the same  $\lambda_{\max}$  values. 1,4-Diphosphorins such as XXVIII and XCVII have received no theoretical treatment or X-ray diffraction studies but some evidence for a delocalized  $\pi$  system in XCVII is provided by the infrared spectrum which shows (41) the main carbonyl stretching frequencies at 1640 and 1650  $\text{cm}^{-1}$ . These frequencies are considerably higher than those of the analogous structure

LXXXIX ( $1600\text{ cm}^{-1}$ ) and suggest that there is less delocalization of the ylidic carbon atom negative charges over the ester groups and more participation in a delocalized  $\pi$  system in the ring. On the other hand, the system is highly sensitive to hydrolysis (41) unlike XVIII and XXXV which can be generated in aqueous media (9,14).



Finally, Ashe (74) has discussed the stability of certain  $(n+1)$ -phosphonia $[n,n]$ spirarenes such as the ylidic structures CLX, CLXI, and CLXII. These are potentially novel aromatic systems in which the two rings are at right angles to one another but fully conjugated through  $p\pi-d\pi$  interactions.

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*Note added in proof :*

Since this review was prepared, Bergerhoff (75) has published a full account of his studies on the cyclic phosphonium ylide XXXVII (R = Et, R' = Ph) which contains a P-P bond. The structure has been confirmed by chemical and spectroscopic measurements and it is suggested that XXXVII is formed from a proposed intermediate  $\text{PhP}=\text{C}(\text{CO}_2\text{Et})_2$  by a dimerization reaction accompanied by migration of an ethoxy group. This synthesis should, therefore, be classified under section (d) of the review.