SYNTHETIC APPROACHES
TO
NEW HETEROCYCLES
CONTAINING
TWO PHOSPHORUS ATOMS

BY

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ABSTRACT

Reactions involving nucleophilic attack of tertiary phosphines and related compounds upon acetylenic systems have been reviewed and the literature has been covered to the end of 1970.

In an extension of some of the work outlined in the above review, the bisphosphines 1,2-bis(diphenylphosphino)ethane, bis(diphenylphosphino)methane, *cis* 1,2-bis(diphenylphosphino)-ethylene and *trans* 1,2-bis(diphenylphosphino)-ethylene and the biphosphine derivative tetraphenylbiphosphine were treated with the powerful electrophile dimethyl acetylenedicarboxylate in attempts to synthesize new cyclic phosphonium ylides containing two phosphorus atoms.

On reaction with the acetylenic ester, the first three of these bisphosphosphines produced in high yield, cyclic phosphonium ylides characterized as dimethyl 1,1,4,4-tetraphenyl-1,4-diphosphacyclohexa-1,3-diene-2,3-dicarboxylate, dimethyl 1,1,3,3-tetraphenyl-5*H*-1,3-diphosph(V)ole-4,5-dicarboxylate and dimethyl 1,1,4,4-tetraphenyl-

1,4-diphosphorin-2,3-dicarboxylate respectively. The adducts were found to be extremely sensitive to water and they were characterized largely by extensive spectroscopic (mainly NMR) investigations although certain chemical reactions assisted in the structure determinations. Dimethyl 1,1,4,4-tetraphenyl-1,4-diphosphorin-2,3-dicarboxylate showed some evidence of aromatic character.

The fourth of the bisphosphines, *trans* 1,2-bis(diphenylphosphino)ethylene, was found to react with dimethyl acetylenedicarboxylate to give a 1:1 adduct. NMR evidence suggests that this adduct has a zwitterionic rather than an ylidic structure while protonation experiments, hydrolyses and deuterolyses are consistent with an ylidic structure. The sum of the evidence suggested that the adduct in solution is an equilibrium of two or more isomers in which a zwitterionic form is the major component while an ylidic form is the most reactive component of the mixture. Hydrolysis of the adduct led to an unusual reaction in which one of the diphenylphosphino groups was eliminated to give a product identical to the 1:1:1 adduct formed from diphenylvinylphosphine, dimethyl acetylenedicarboxylate and water. A mechanism has been

postulated for this reaction and deuterium labelling studies gave some support to this mechanism.

Tetraphenylbiphosphine gave a derivative of the *cis* 1,2-bis(diphenylphosphino)ethylene system on reaction with the acetylenic ester.

ACKNOWLEDGEMENTS

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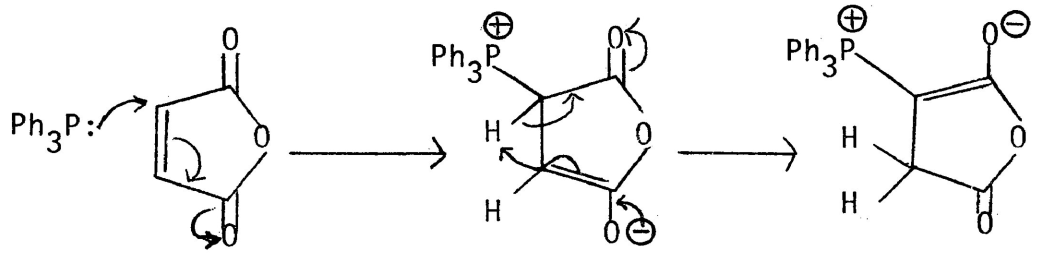
INTRODUCTION

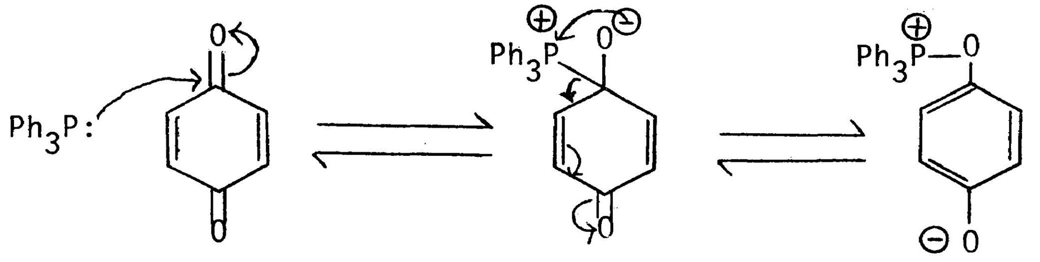
NUCLEOPHILIC ATTACK OF TERTIARY PHOSPHINES UPON ACETYLENIC SYSTEMS

Most tervalent phosphorus compounds are good nucleophiles although nucleophilic attack upon phosphorus is also relatively common-particularly when good leaving groups such as halogen atoms are attached to the phosphorus atom. Radical reactions of tervalent phosphorus compounds are also known. The dual nucleophilic-electrophilic nature of phosphorus in tervalent phosphorus compounds, therefore, leads to a wide variety of reactions but this survey is limited to the nucleophilic attack of phosphines upon carbon-carbon triple bond systems.

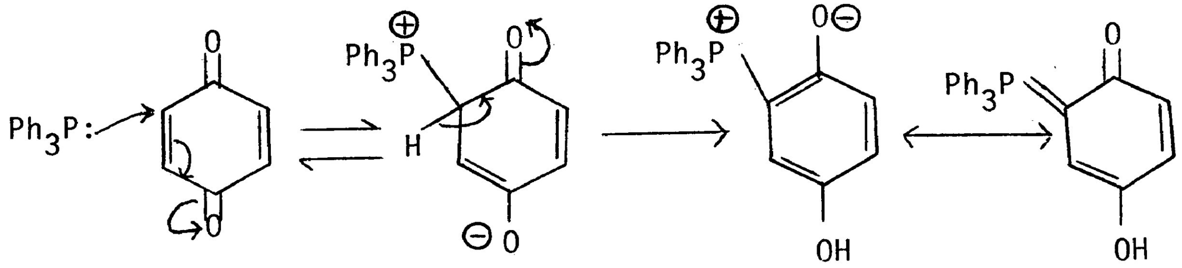
The first study[1] of the reaction of a tertiary phosphine with a carbon-carbon multiple bond system was carried out about thirty years ago. Thus, when triphenylphosphine is treated with maleic anhydride, a 1:1 adduct is formed which was originally given a quasi-phosphonium structure. Later, the structure was corrected[2] and the adduct was assigned the stable phosphobetaine structure (I). This is formed *via* a Michael type of


Ph3P:
O
O
O
Ph3P
H
H
O
O
O
Ph3P
H
H
O
O
O

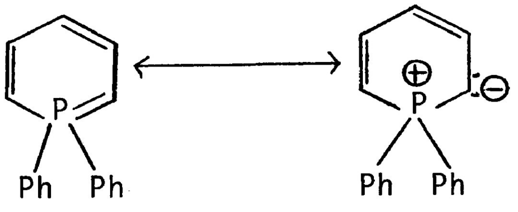
I


Ph3P:
O
O
Ph3P
O
O
Ph3P
O
O

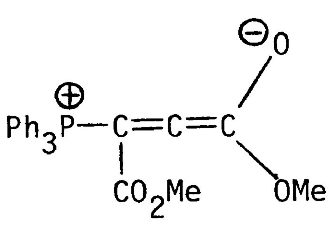
II


Ph3P:
O
O
Ph3P
H
O
O
Ph3P
O
OH
Ph3P
O
OH

III


P
Ph
Ph
P
Ph
Ph

IV


Ph3P
C
C
C
O
CO2Me
OMe

V

addition followed by the 1,2-migration of a proton. A related reaction is that which occurs between triphenylphosphine and *p*-benzoquinone. This reaction was first investigated by Davies and Walters[3] who proposed the structure II for the adduct. Their proposed structure and mechanism were later corrected[4] and it was shown that the initial product is in fact a phosphobetaine which gives the final adduct III through a proton transfer very similar to that involved in the formation of I.

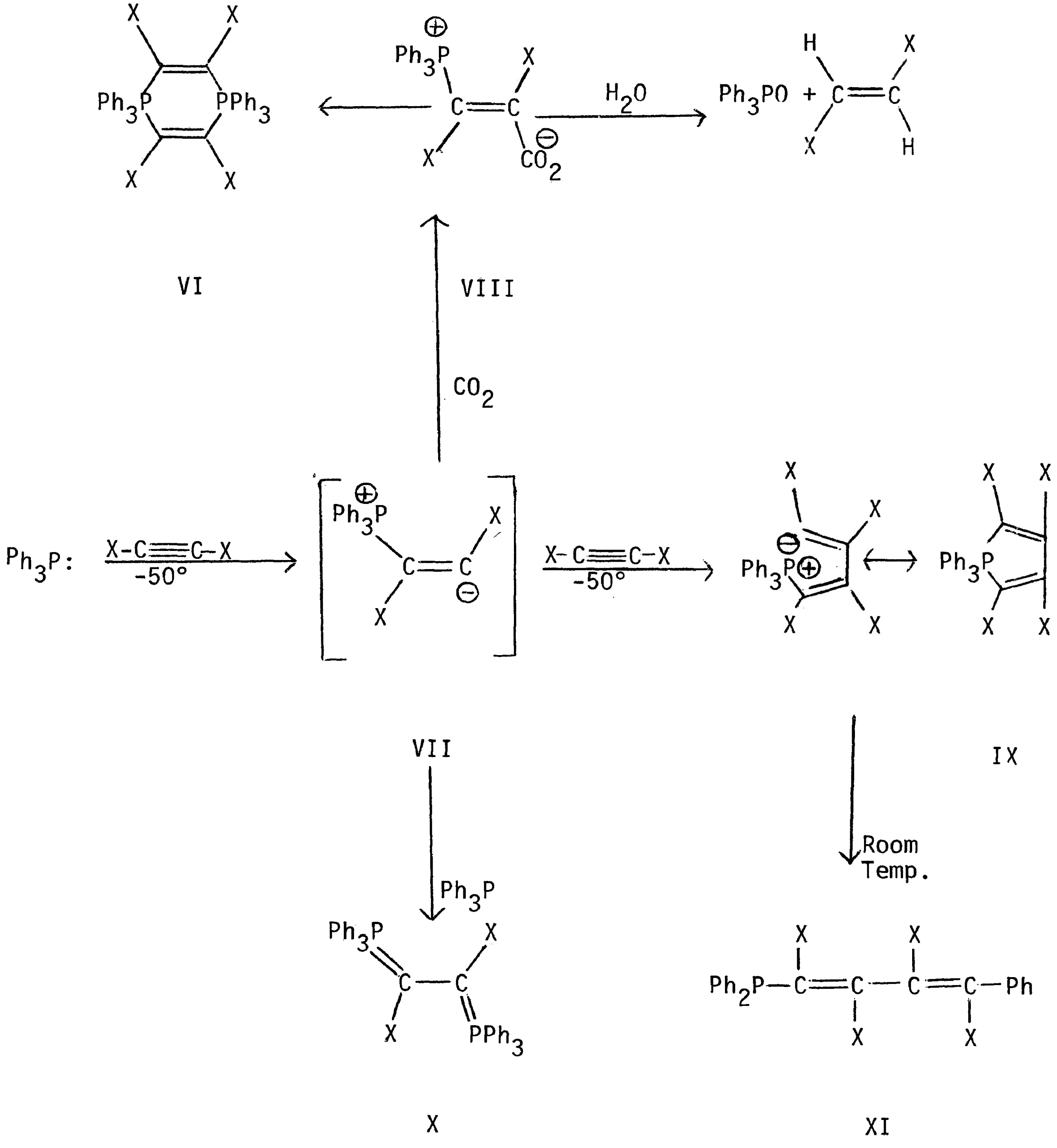
Systematic study of the reactions of phosphines with alkynes has, however, only been undertaken in the last decade and the reactions are of interest for several reasons. For example, the study of these reactions is of value in the investigation of the nucleophilic and donor properties of the various organic phosphines including open chain and cyclic unsaturated phosphines. Furthermore, a number of these reactions are known to lead to the formation of phosphorus heterocycles containing three or five valent phosphorus atoms. The chemistry and stereochemistry of these phosphorus heterocycles is of considerable interest. Moreover, some of these compounds are cyclic phosphonium ylides which, apart from the phosphabenzenes[5] (*e.g.* IV), have not yet been extensively studied.

The following is, therefore, a review of the reactions of phosphines, mainly tertiary phosphines, with acetylenic systems. It is not an exhaustive account, rather it offers a survey of the principal developments in the field. Reactions of phosphines containing phosphorus-oxygen and phosphorus-nitrogen bonds are considered to be outside the scope of the present discussion.

Reactions of Triphenylphosphine With Acetylenic Systems

The first reaction of a tertiary phosphine with an acetylenic system was reported by Horner and Hoffman[6] who treated triphenylphosphine with dimethyl acetylenedicarboxylate and isolated an adduct which they thought to be the zwitterionic 1:1 adduct V. Johnson and Tebby[7] carried out similar studies but were unable to isolate a 1:1 adduct. However, they did isolate several products and the reaction scheme they proposed (together with the various postulated products) is outlined in Scheme A. For various reasons, these workers preferred the zwitterionic version of IX to the pentacovalent version. Hendrickson and his co-workers[8,9] reported similar results but suggested that the yellow 1:2 adduct formed at -50°C had the pentacovalent structure IX. This suggestion was made largely on the basis of NMR studies on very fresh samples of the adduct which showed two methoxy signals in the NMR spectrum. However, the stereochemistry about a pentacovalent phosphorus atom and pseudorotational processes do not appear to have been considered.

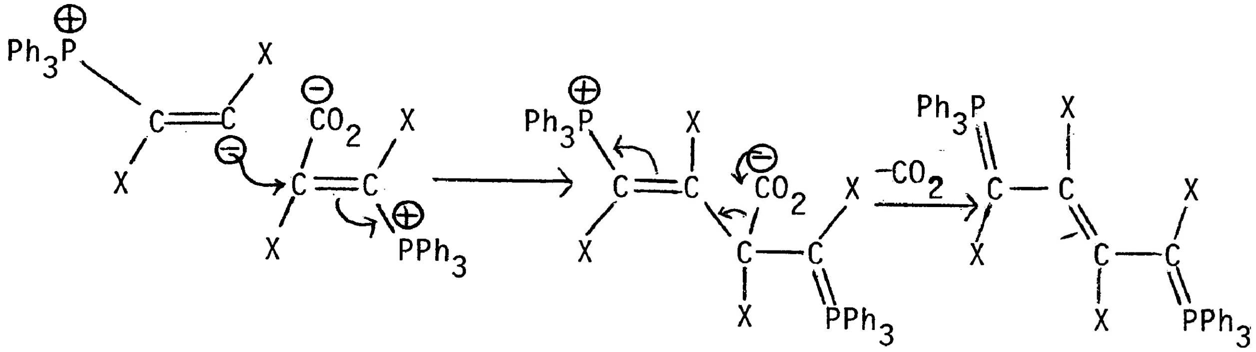
SCHEME A



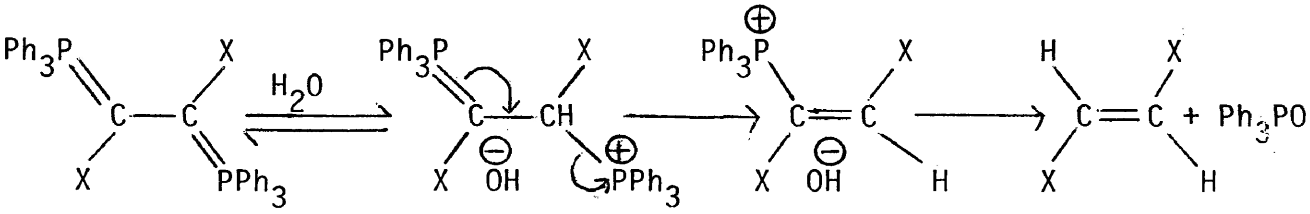
$X = CO_2Me$

In recent years, Tebby and his co-workers have carried out extensive investigations of the reactions of triphenylphosphine with dimethyl acetylenedicarboxylate. As already mentioned[7], they reported the formation of the 2:2 orange adduct VI. The structure of this orange adduct was later reinvestigated by Tebby[10] who found the compound to be soluble in acidic media yielding colourless solutions. On basification of these colourless solutions, the original compound was recovered. The diphosphorane structure VI could not account for this property and Tebby[10] suggested that the intermediate VII might be reacting with itself in a head-to-head manner to give XIII rather than the head-to-tail manner required to produce VI. The intermediate VII could also attack the stabilized intermediate VIII as shown to give XII which gives the bis-ylide XIII by loss of a molecule of carbon dioxide. The structure XIII would account for the behaviour of the adduct in acid and the structure was confirmed[10] by preparation of its bisperchlorate salt, by reductive cleavage with zinc and acetic acid and by a number of other experiments.

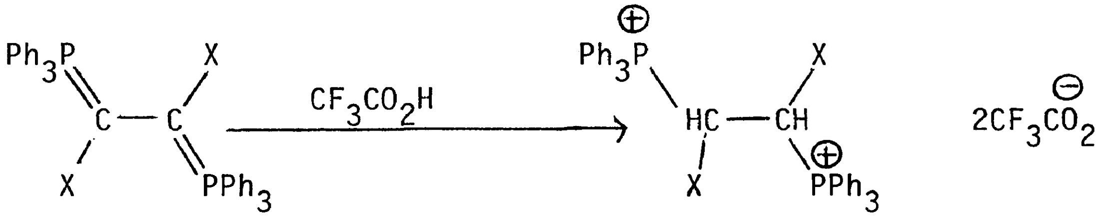
In Johnson's original paper[7], the structure X was tentatively assigned to the 1:2 yellow adduct of dimethylacetylenedicarboxylate with triphenylphosphine, as outlined in the Scheme A. The structure of this solid yellow adduct was further investigated by Tebby[11] and



VII VIII XII XIII



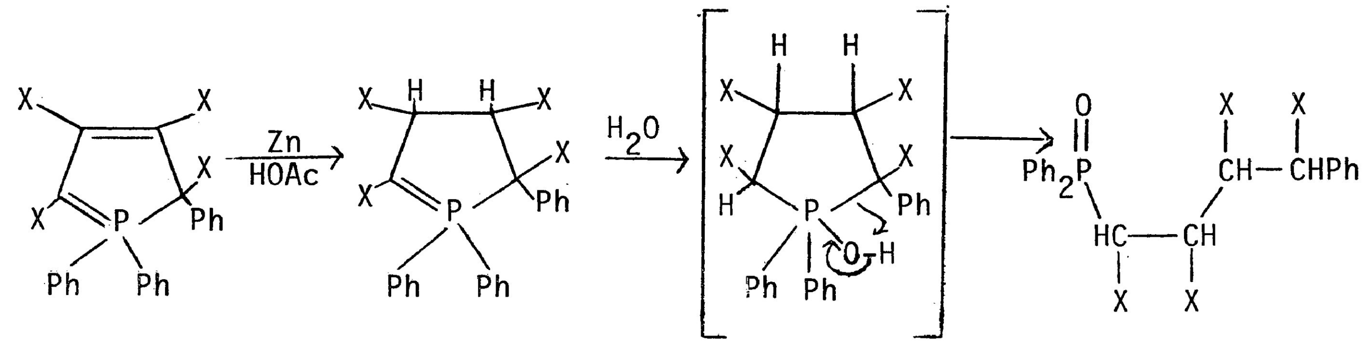
X XIV



X XV

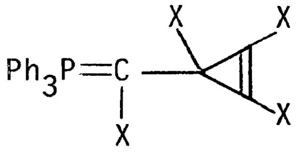
X = CO_2Me

his co-workers. They confirmed the structure X by a number of experiments including mass spectrometry which showed a molecular ion at *m/e* 666 and a fragmentation pattern consistent with X. Reductive cleavage with zinc and acetic acid gave triphenylphosphine and dimethyl succinate while molecular quantities of triphenylphosphine, triphenylphosphine oxide and dimethyl fumarate (XIV) were obtained on hydrolysis of X with boiling water. NMR studies also supported structure X. Thus, the spectrum of X in trifluoroacetic acid (corresponding to the bis-salt XV) was found to contain a 15 proton resonance in the τ2.2-2.1 region, a 1 proton doublet (J = 16 Hz) centred at τ4.62; and a sharp 3 proton singlet at τ7.02. The signals correspond to the aromatic, methine and methoxy-protons, respectively. In a more recent paper[12] Tebby has reported that the stable yellow 1:2 adduct of triphenylphosphine with dimethyl acetylenedicarboxylate is not the open-chain phosphine XI as previously reported[7-9] but is the phosph(V)ole derivative XVI. In addition to the physical evidence (*e.g.* variable temperature NMR studies of deuteriochloroform solutions and trifluoroacetic acid solutions of the adduct together with IR spectra) which supports the structure XVI, the chemical evidence also favours structure XVI. Thus, when the adduct XVI was treated with zinc and acetic acid, a colourless crystalline product was isolated which, on

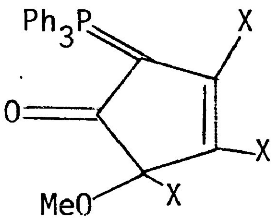


XVI

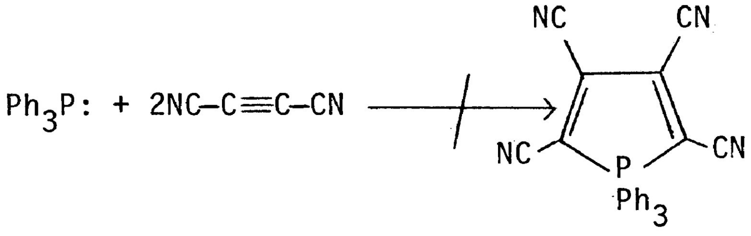
XVII

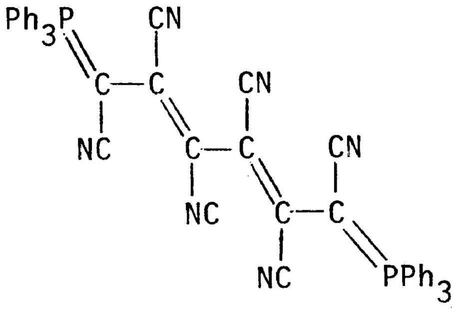


XVIII



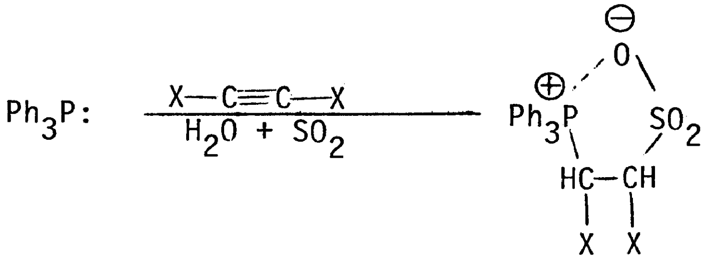
XIX





XX

XXI



X = CO_2Me

XXII

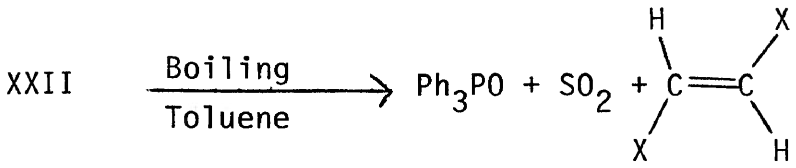
the basis of mass spectral evidence, was assigned the structure XVII. Formation of the adduct was thought to follow the sequence XVI → XVII as shown.

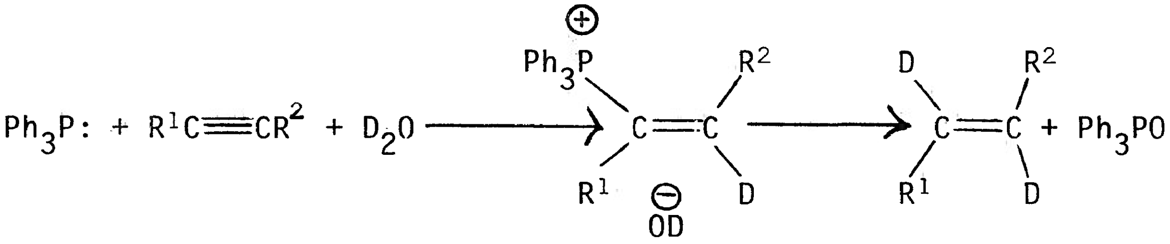
Tebby[13] has recently reported that the initial low-temperature 1:2 adduct of triphenylphosphine and dimethyl acetylenedicarboxylate is in fact XVIII and not IX as originally postulated.[7-9] Furthermore, the adduct XVIII rearranges at room temperature to give not only the methanol-insoluble product XVI but also the previously unreported methanol-soluble adduct XIX. All of the carbonyl groups in the adduct, assigned structure XIX, were found to have the normal stretching frequency in the infrared spectrum, *i.e.* none of the ester groups are ylidic as in XVI. Compound XIX is formed in 40% yield and its structure has been further confirmed by X-ray single crystal studies.[13]

Johnson's and Tebby's original experiments on the reactions of triphenylphosphine with dimethyl acetylenedicarboxylate[7] led Reddy and Weis[14] to react triphenylphosphine with dicyanoacetylene. An orange-coloured crystalline compound was isolated to which was assigned the structure XX. This structure assignment was made largely on the basis of ^{31}P studies and pyrolysis studies on the adduct. Tebby and his co-workers[15] re-examined the reaction and the product using mainly NMR and mass spectrometric techniques. Thus, it was quickly shown that the originally postulated stoichiometry is incorrect as well as the structure. For example, the adduct showed a molecular ion at *m/e* 752, for which the composition was determined by high resolution measurements as $C_{48}H_{30}N_6P_2$. This peak was found to be the most intense peak above *m/e* 262 (Ph_3P^+) and this indicates that the adduct is formed from three molecules of the dicyanoacetylene and two molecules of triphenylphosphine. This evidence alone excluded the structure XX. Several chemical analyses were also consistent with a 3:2 adduct. Further, the U.V. absorption spectrum [λ_{max} (EtOH) 485 mμ (ε21,800), 378mμ (13,900) and 315 mμ (7,700)] established that the molecule contains an extended conjugated system. This requirement also casts doubt on structure XX. In the light of the above results Tebby concluded[15] that the correct structure of this orange adduct is the bis-ylide structure XXI and not the phosphorane structure XX as claimed by Reddy and Weis.[14] Chemical evidence also supports this structure.

Reactions of Triphenylphosphine with Acetylenic Linkages in the Presence of Other Reagents

As already mentioned, when triphenylphosphine and dimethyl acetylenedicarboxylate are mixed in equimolar amounts,[10] the intermediate VII is formed. This has been successfully trapped[10] by carrying out the reaction in the presence of carbon dioxide, to give the adduct VIII.

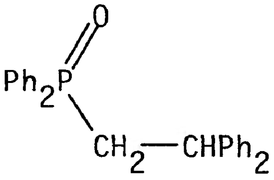




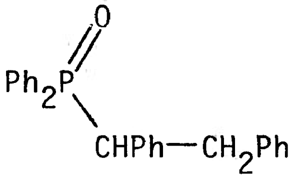
XXIII XXIV XXV

X = CO_2Me

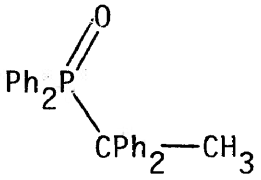
R^1 = CO_2Me or Ph; R^2 = CO_2Me or Benzoyl



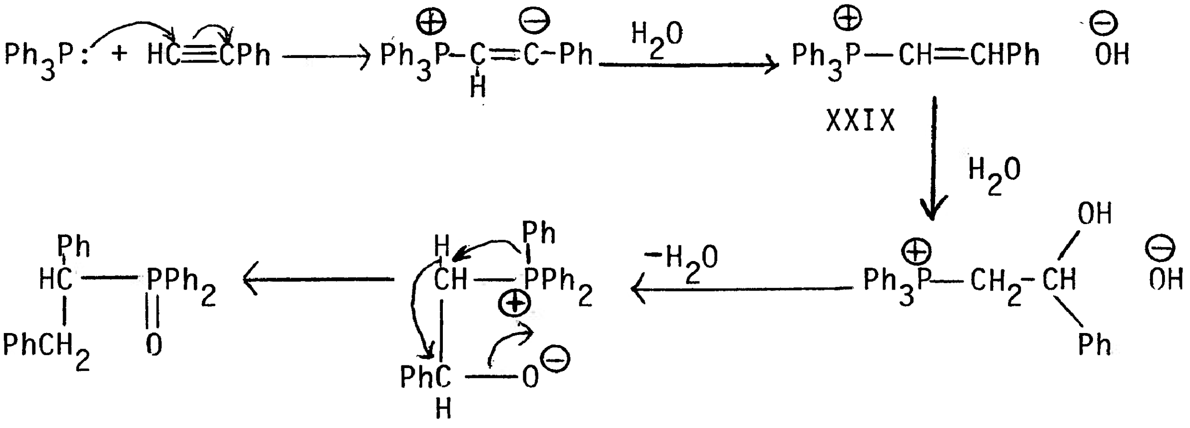
XXVI



XXVII



XXVIII



XXIX

XXVII XXXI XXX

In the presence of water,[16] the 1:1 intermediate VII hydrates and fragments to give triphenylphosphine oxide and dimethyl fumarate. However, if sulphur dioxide is also present in addition to water, fragmentation is avoided[16] and the adduct XXII is formed which has been found[16] to fragment readily in boiling toluene, giving triphenylphosphine oxide, sulphur dioxide and dimethyl fumarate.

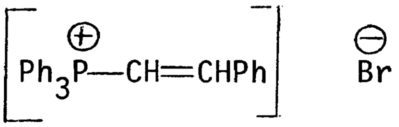
As mentioned above, triphenylphosphine and dimethyl acetylenedicarboxylate react together in the presence of water to give triphenylphosphine oxide and dimethyl fumarate. This reaction provides an easy and cheap method for the preparation of 1,2-disubstituted olefins. Tebby and his collaborators have utilized this reaction to prepare a number of 1,2-disubstituted olefins labelled with deuterium at the α- and β- positions as shown in the sequence XXIII → XXIV → XXV. It was also observed[17] that disubstituted acetylenes (XXIII) bearing groups such as methoxycarbonyl, benzoyl and phenyl, react with triphenylphosphine in the presence of deuterium oxide to give mainly *trans*-olefins in 40-70% yield. The structures of the deuterated olefins were confirmed by mass spectrometry and also by NMR measurements which confirmed the absence of olefinic proton signals. The reaction is thought to proceed *via* the the vinylphosphonium deuteroxide intermediate XXIV as outlined in the sequence

XXIII → XXIV → XXV. In a typical reaction, dimethyl acetylenedicarboxylate (XXIII, $R^1 = R^2 = CO_2Me$), triphenylphosphine and deuterium oxide when heated under reflux in tetrahydrofuran for several hours, gave dimethyl[α,β $^2H_2$]fumarate in 70% yield. On the other hand, diphenylacetylene required four weeks under reflux in deuterated diethylene glycol to give a 10% yield of partially deuterated stilbene.

The reaction of triphenylphosphine with phenylacetylene in the presence of water has been studied in detail by Allen and Tebby.[18] The reaction was carried out in boiling digol and a product with the molecular formula $C_{26}H_{23}OP$ was obtained. The adduct was found to be very stable and non-basic in character. It was recovered unchanged from boiling dilute aqueous sodium hydroxide and dilute hydrochloric acid and also from boiling hydrogen peroxide in glacial acetic acid. The IR spectrum showed the presence of a P=O stretching frequency. This evidence together with the UV spectrum led Allen and Tebby to propose the three possible structures XXVI, XXVII and XXVIII for the product. The structure XXVIII was rejected on the basis of ^1H NMR studies. A number of chemical derivatives of the adduct were prepared and the results obtained showed that the product has the structure XXVII. This structure was further confirmed by comparison of the product with an authentic[19] sample of 1,2-diphenylethyldiphenylphosphine oxide.

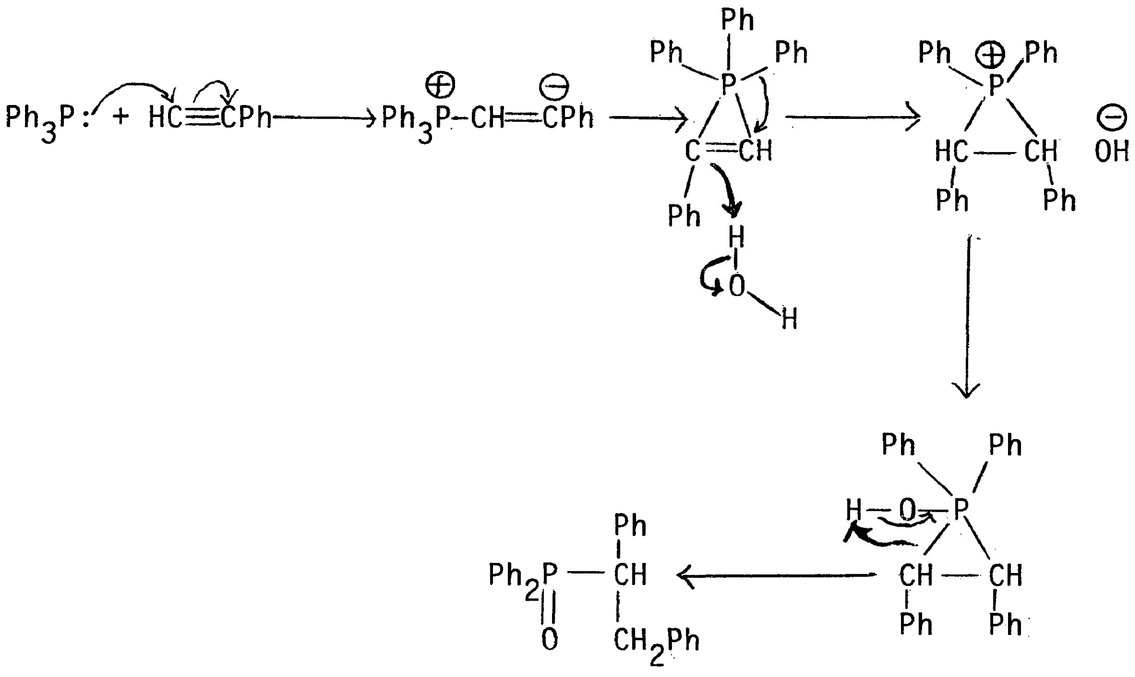
Allen and Tebby[18] also considered possible mechanisms for the reaction such as that shown in the sequence Ph_3P + H—C≡C-Ph → XXIX → XXX → XXXI → XXVII, and they argued as follows. Trippett and Walker[20] had previously succeeded in preparing the oxide XXVII from the reaction of triphenylmethylenephosphorane with benzaldehyde in ethanol and also from the reaction of triphenylphosphine with styrene oxide. They showed that the betaine XXXI is an important intermediate and Tebby and Allen,[18] therefore, investigated the possibility of this betaine being also a key intermediate in the reaction of triphenylphosphine with phenylacetylene and water. This was attempted by carrying out the reaction using deuterium oxide in place of water. The products were analyzed by mass spectrometry but the results[18a] were not conclusive due to migrations which occurred after electron impact in the mass spectrometer. Allen and Tebby, therefore, sought further evidence to establish the reaction pathways and they attempted to prepare the proposed intermediate hydroxide XXIX.

β-Styryltriphenylphosphonium bromide XXXII was prepared by reacting triphenylphosphine and phenylacetylene in the presence of hydrogen bromide in boiling diethyleneglycol. An attempt to prepare the phosphonium hydroxide XXIX was then made by treating the bromide XXXII with freshly prepared silver oxide. After removing silver bromide and upon concentration of the solution, a colourless

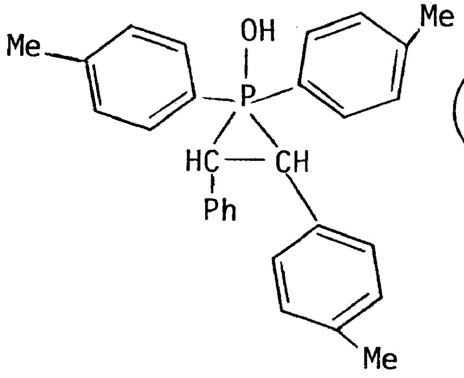


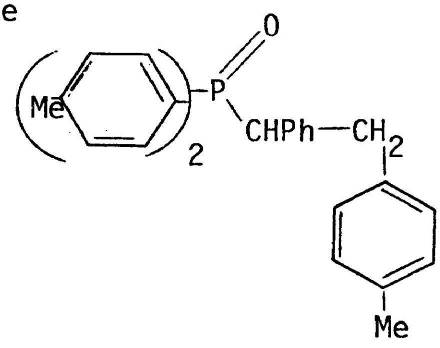
$[\overset{\oplus}{Ph_3P}\text{—CH=CHPh}]\ \overset{\ominus}{Br}$

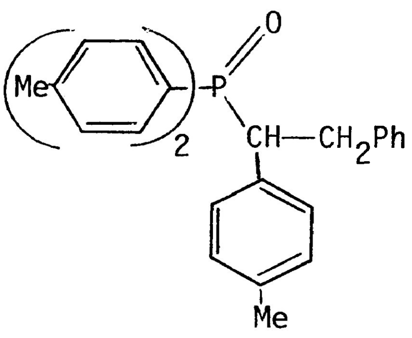
XXXII



XXVII XXXIII

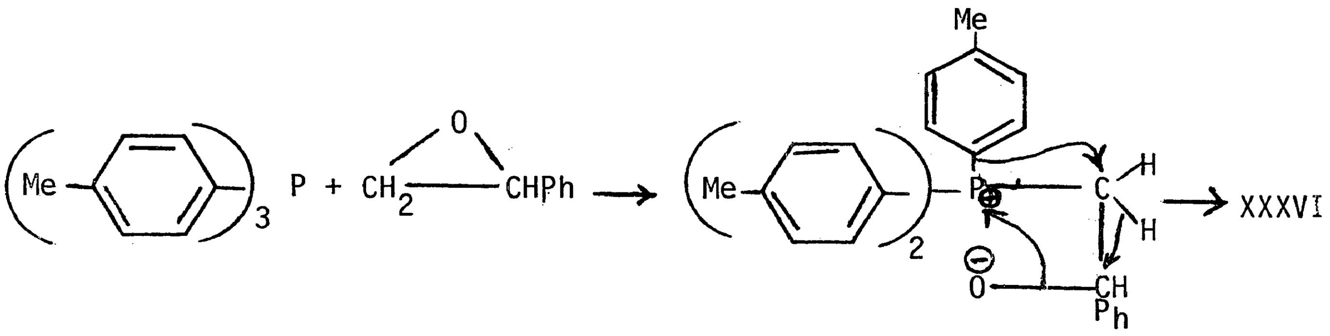






XXXIV XXXV XXXVI

oil was obtained which could not be converted into a crystalline picrate and it was suggested that this could have been due to hydration of the β-styryltriphenylphosphonium hydroxide XXIX to form some of the next possible intermediate XXX. When this colourless oil was heated in wet digol, no 1,2-diphenylethyldiphenylphosphine oxide (XXVII) was obtained. No direct confirmation of the proposed reaction scheme could, therefore, be obtained. An alternative pathway shown in the sequence $Ph_3P + H—C≡C—Ph \rightarrow XXXIII \rightarrow XXVII$, involving a cyclic phosphorane intermediate, was also proposed.[18] The intermediate in this case is the phosphonium hydroxide XXXIII in which either of the P-C bonds of the three-membered ring can break to give the oxide XXVII. To test this hypothesis, Tebby reacted tri-*p*-tolylphosphine with phenylacetylene and water reasoning that if the unsymmetrical intermediate XXXIV were formed, it would on cleavage afford the two isomeric phosphine oxides XXXV and XXXVI. However, no such mixture was found. Rather, the only product was found to be the phosphine oxide XXXVI which was also obtained from the reaction of tri-*p*-tolylphosphine XXXVII with styrene oxide. Thus, it was concluded that the sequence $Ph_3P + H-C≡C-Ph \rightarrow XXXIII \rightarrow XXVII$ was not the correct pathway for the reaction and that the most likely scheme is that outlined in the sequence $Ph_3P + H-C≡C-Ph \rightarrow XXIX \rightarrow XXX \rightarrow XXXI \rightarrow XXVII$. However, no mechanism has yet been conclusively established.



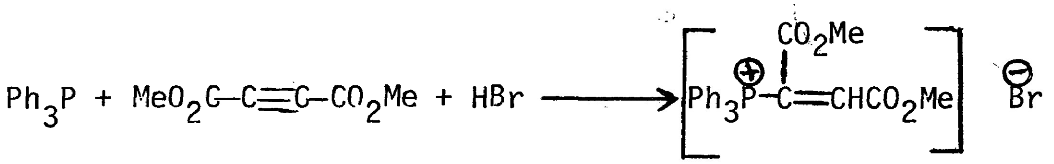
XXXVII

$$Ph_3P + HO_2C{-}C{\equiv}C{-}CO_2H + HBr \longrightarrow \left[Ph_3\overset{\oplus}{P}{-}CH{=}CH{-}CO_2H\right]\overset{\ominus}{Br} + CO_2$$

XXXVIII

$$Ph_3P + HC{\equiv}C{-}CO_2H + HBr \longrightarrow \left[Ph_3\overset{\oplus}{P}{-}CH{=}CH{-}CO_2H\right]\overset{\ominus}{Br}$$

XXXIX



$$Ph_3P + MeO_2C{-}C{\equiv}C{-}CO_2Me + HBr \longrightarrow \left[Ph_3\overset{\oplus}{P}{-}\overset{\overset{CO_2Me}{|}}{C}{=}CHCO_2Me\right]\overset{\ominus}{Br}$$

XL

Finally, a number of vinylphosphonium salts such as XXXVIII, XXXIX and XL have been prepared by Hoffman and Diehr[21] in good yield from reactions of triphenylphosphine with acceptor-substituted acetylene derivatives in the presence of mineral acids. Some other simple products such as XLI, XLII and XLIII, were also obtained by reactions of secondary phosphines with acetylenic systems.

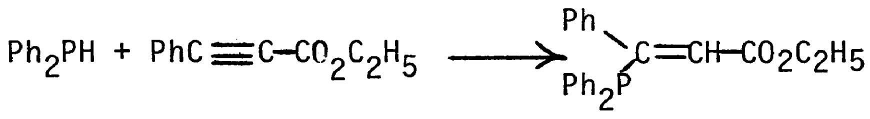
Reactions of Vinyl and Cyclopropylphosphines with Acetylenic Systems

Diphenylvinylphosphine has been found[22] to react with dimethyl acetylenedicarboxylate, at room temperature in undried ether under nitrogen, to give two products. When a dilute solution of the ester was added to a dilute solution of the phosphine, 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 was found to be in the ratio of 1:2:1 respectively.

The incorporation of water into the two products suggests that both of the compounds are formed by hydrolysis of highly reactive cyclic ylides. The base peak in the mass spectra of both adducts was found to be *m/e* 201 which suggests the presence of the $Ph_2P=O$ grouping.

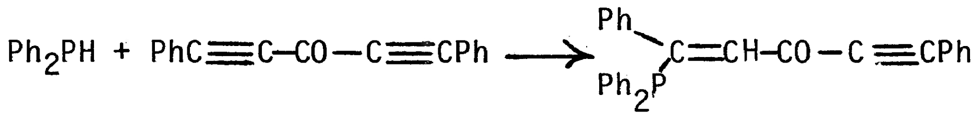
$Ph_2PH + HC\equiv C-Ph \longrightarrow Ph_2P-HC=CHPh$

XLI



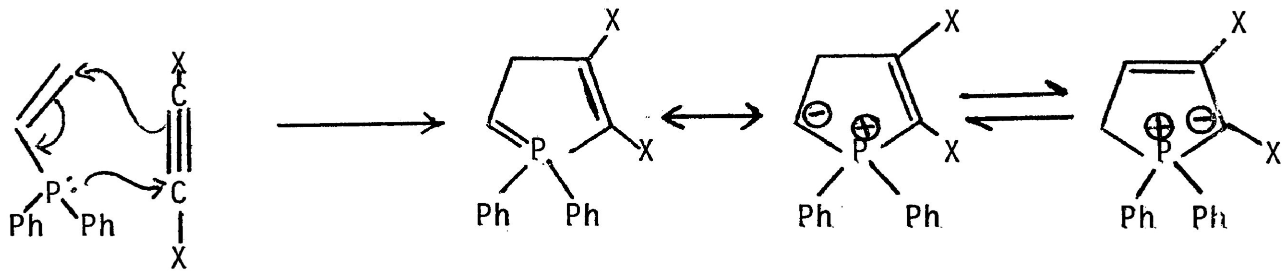
$Ph_2PH + PhC\equiv C-CO_2C_2H_5 \longrightarrow \begin{matrix}Ph\\ Ph_2P\end{matrix}\!\!>C=CH-CO_2C_2H_5$

XLII



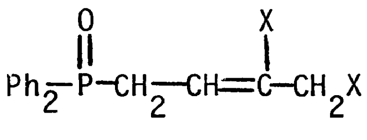
$Ph_2PH + PhC\equiv C-CO-C\equiv CPh \longrightarrow \begin{matrix}Ph\\ Ph_2P\end{matrix}\!\!>C=CH-CO-C\equiv CPh$

XLIII



XLIV

XLV



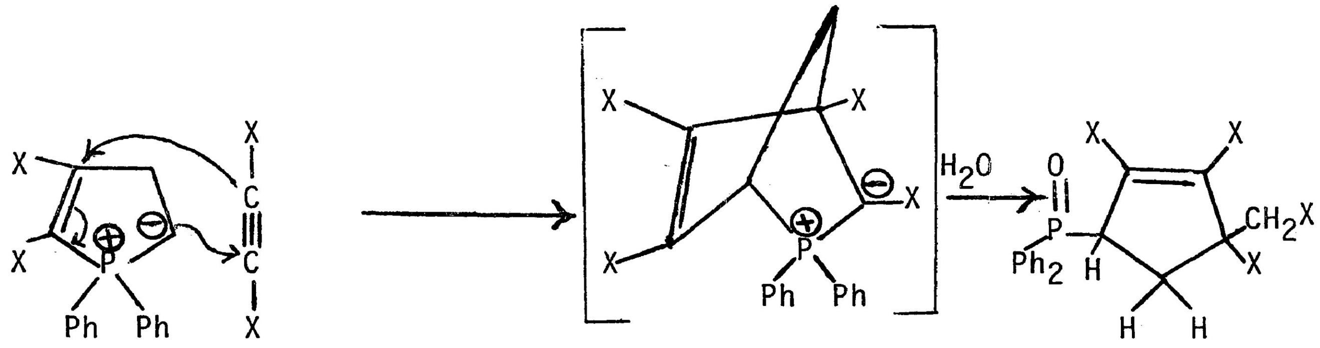
$Ph_2-\overset{\overset{O}{\|}}{P}-CH_2-CH=\overset{\overset{X}{|}}{C}-CH_2X$

XLVI

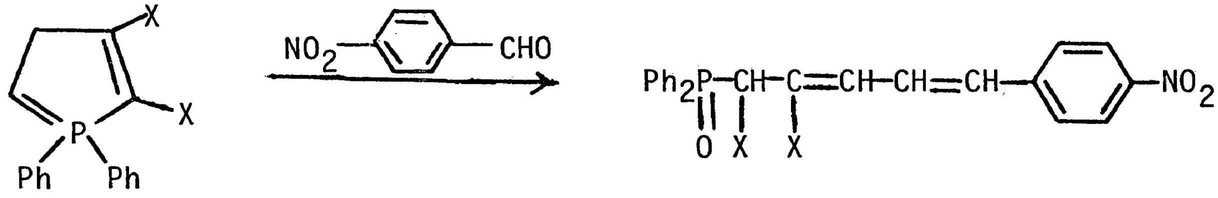
$X = CO_2Me$

Thus, the first stage in the reaction between the phosphine and the ester was, therefore, considered to be the formation of the highly reactive ylide XLIV which is in equilibrium with its tautomer XLV. Hydrolysis of the more stable tautomer XLV gives the adduct XLVI of which the structure was deduced by NMR and mass spectrometric measurements. However, when the reaction was carried out in the presence of an excess of ester, the initially formed ylide XLIV was found to react with another molecule of the ester to give the bicyclic ylide XLVII. This was isolated as its hydrolysis product XLVIII and again, NMR and mass spectral evidence were in good agreement with this structure. The adduct XLIV has also been trapped[23] in a Wittig reaction with *p*-nitrobenzaldehyde to give the product XLIX which is presumably formed from the expected product L by proton migration to give the more conjugated structure XLIX. The proton NMR assignments in the hydrolysis products XLVI and XLVIII have been confirmed[24] by carrying out the hydrolyses in the presence of deuterium oxide. Thus, when the adduct XLV was formed in the presence of D_2O, it hydrolyzed to give the deuterated adduct LI.

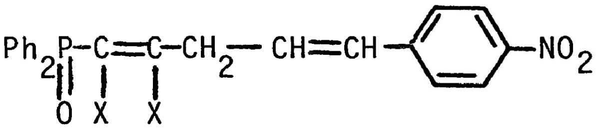
Recently, it has been observed[24] that cyclopropyldiphenylphosphine reacts with dimethyl acetylenedicarboxylate to give the ylide LII which is analogous to the methanol-insoluble stable adduct formed in the



XLIV XLVII XLVIII

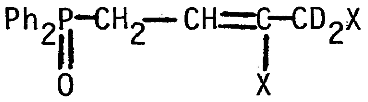


XLIV XLIX



$Ph_2P(=O)-C(X)=C(X)-CH_2-CH=CH-C_6H_4-NO_2$

L



$Ph_2P(=O)-CH_2-CH=C(X)-CD_2X$

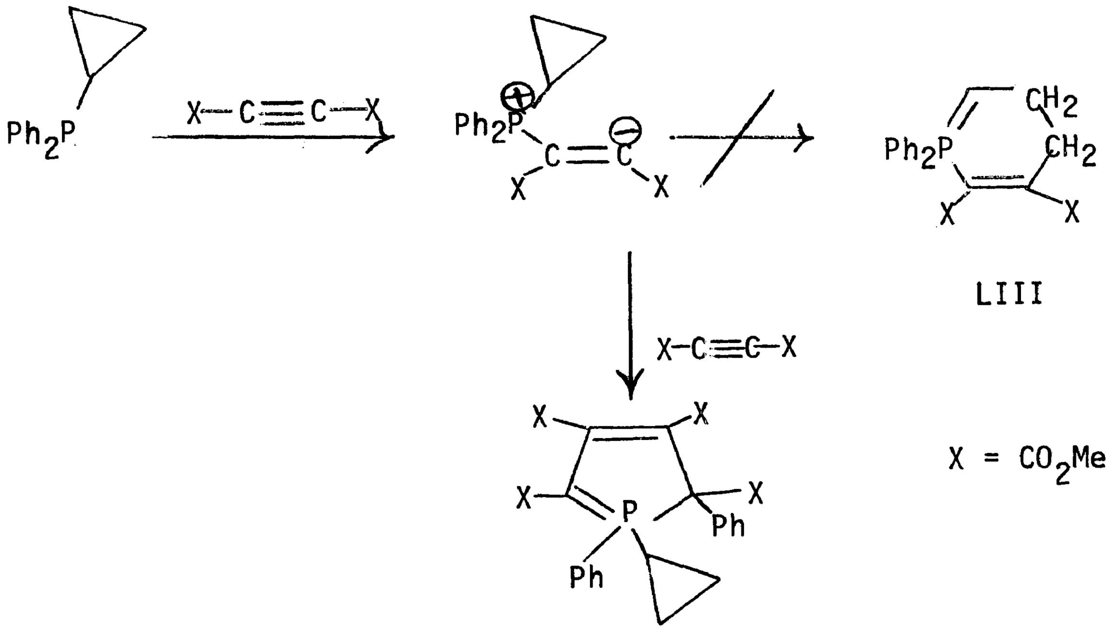
LI

X = CO_2Me

reaction of triphenylphosphine with the same ester,[12] *i.e.* in both cases a phenyl shift has occurred. No trace of the possible product LIII (in which ring opening of the cyclopropyl group has occurred) was observed.

Diphenylvinylphosphine on treatment with *o*-benzenediazonium carboxylate[24] gives the bisphosphine LIV. The mechanism of this reaction is not yet clear.

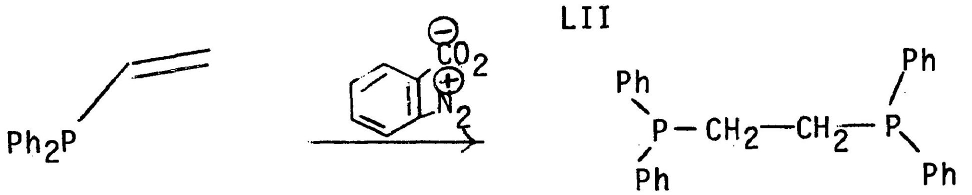
In related reactions, Savage and Trippett[25] have also carried out certain reactions of diphenyl-1-phenylvinylphosphine with activated C-C double bonds. Thus, when the phosphine LV was heated under reflux with acrylonitrile in the presence of *p*-tolualdehyde, an oxide having the molecular formula $C_{31}H_{28}NOP$ was obtained. Physical measurements on the adduct supported the structure LVII which was thought to be formed *via* the five-membered ylide LVI. The formation of the cyclic ylide LVI led Trippett[25] to assume that the methylene phosphorane LVIII would cyclize to give the four-membered ylide LIX. The phosphorane LVIII was generated from the methiodide of diphenyl-1-phenylvinylphosphine using butyllithium and when the ylide solution was treated with *p*-tolualdehyde, *trans*-4-methylstilbene (10%), the *cis*-and *trans*-oxide LXII (13%) and methyldiphenylphosphine oxide (23%) were obtained. The formation of these products indicated that the ylide solution was in fact an equilibrium mixture of the



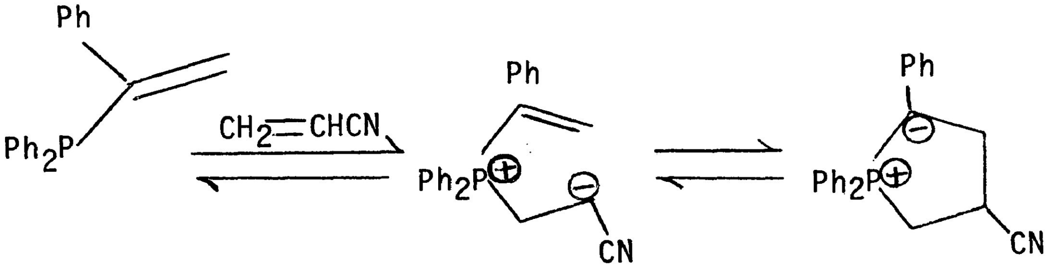
LIII

X = CO$_2$Me

LII



LIV



LV

LVI

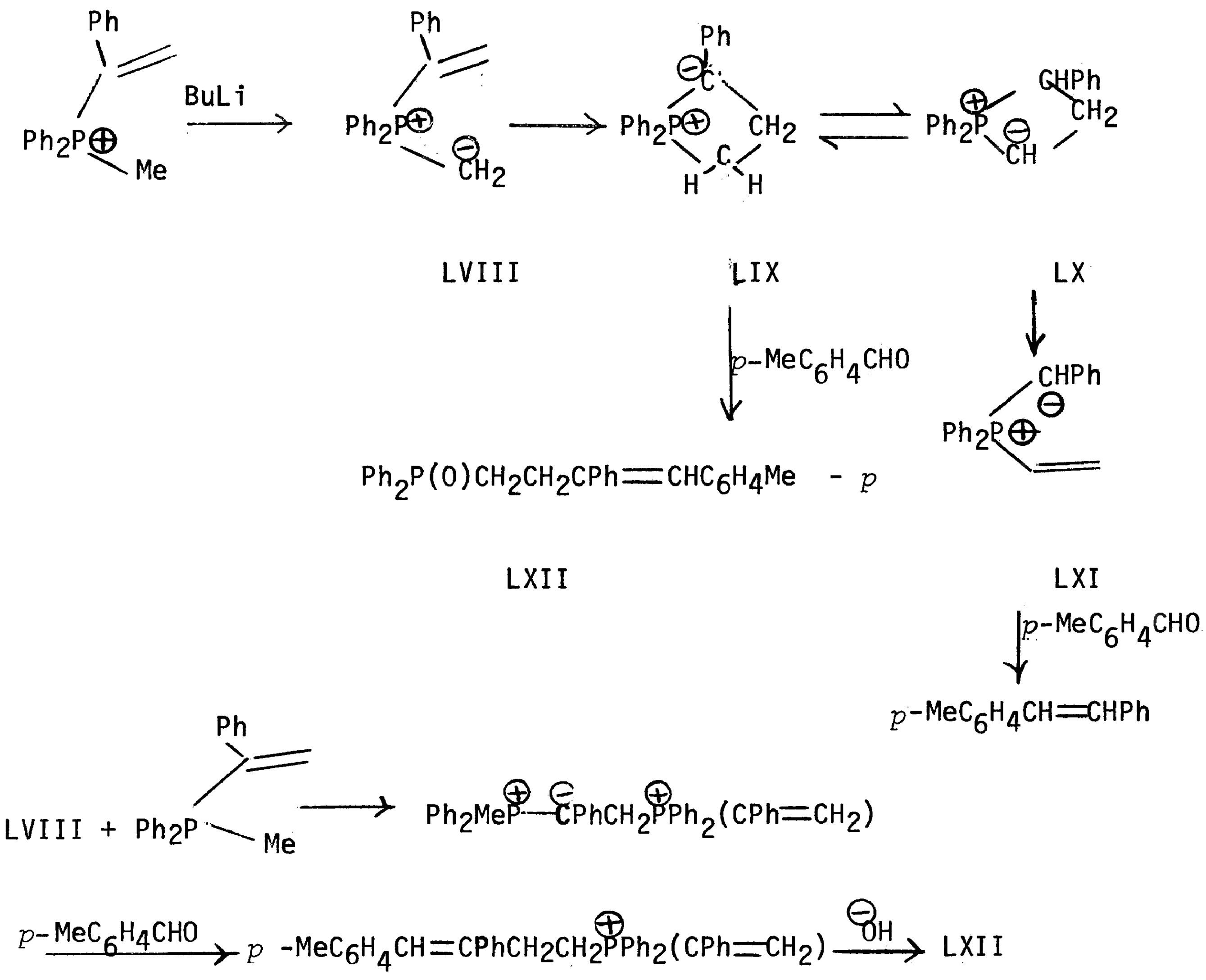
LVI $\xrightarrow{p\text{-MeC}_6\text{H}_4\text{CHO}}$ $\text{Ph}_2\text{P(O)CH}_2\text{CHCNCH}_2\text{CPh=CHC}_6\text{H}_4\text{Me}$ - *p*

LVII

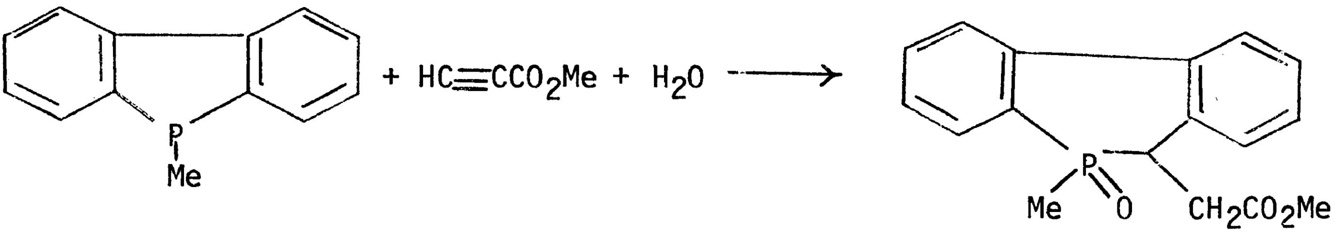
ylides LIX, LX and LXI. However, the major product was a non-crystalline phosphonium salt or mixture of salts which, on alkaline hydrolysis, gave the *trans*-oxide LXII, and which might have contained the salt LXII formed *via* Michael addition of the ylide LVIII to the unreacted vinylphosphonium salt. It should be noted that the two groups of workers[22-25] have both failed to isolate the intermediate ylides formed in the reaction of vinylphosphines with C-C multiple bonds. Rather, they have postulated the ylidic structures on the basis of the end products which they managed to isolate by carrying out the reaction in the presence of various trapping reagents such as water, or aldehydes. While Savage and Trippett reported[25] only 1:1 adducts, Hughes and Davies reported[22] both 1:1 and 1:2 adducts, although in both cases tautomeric equilibria between ylides were postulated.

Reactions of Phosphorus Heterocycles with Acetylenic Systems

As already mentioned, it has been reported[18] that triphenylphosphine reacts with phenylacetylene and water in boiling diethyleneglycol to give the phosphine oxide XXVII. In this reaction, it was observed that a phenyl group migrates from the phosphorus atom to the adjacent carbon atom *i.e.* a 1,2-phenyl shift occurs. This type



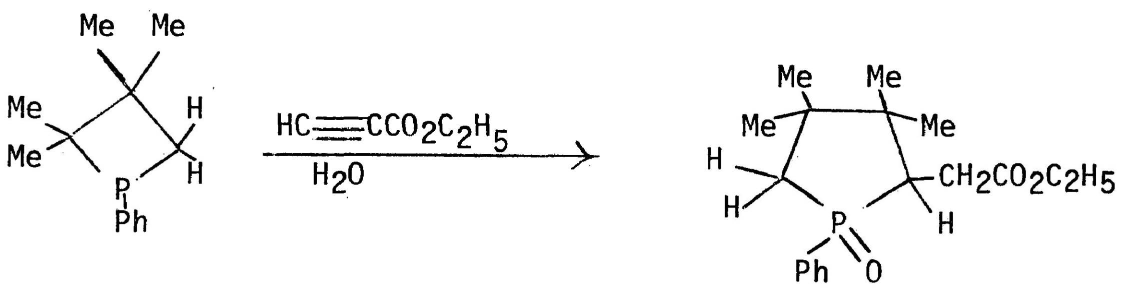
LXIII



LXIV

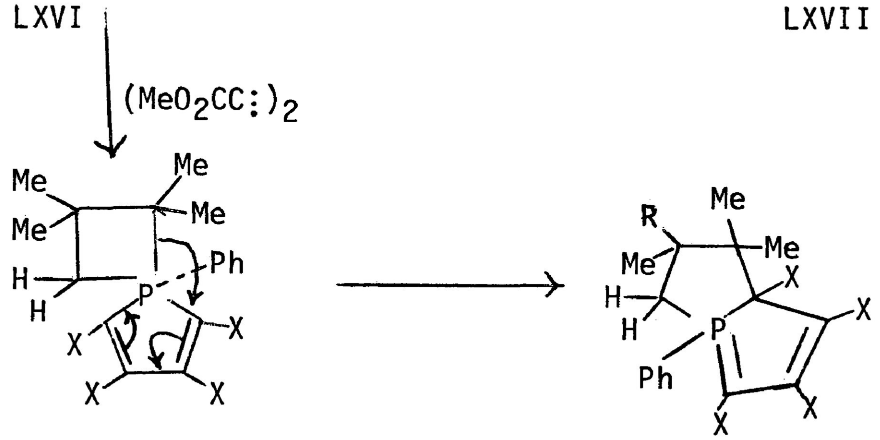
LXV

of migration in the above reaction has been exploited by Tebby[26] to achieve the ring expansion of 9-phosphafluorenes (LXIV) to give 9,10-dihydro-9-phosphaphenanthrene oxides. Thus, 9-methyl-9-phosphafluorene, methyl propiolate and water in tetrahydrofuran react to form a product, m.p. 145-148°, which has been shown[26] to be 9-methyl-10-methoxycarbonyl-9,10-dihydro-9-phosphaphenanthrene-9-oxide (LXV). A ring expansion therefore occurs. Preliminary investigations have also shown that the reaction can be used when R=Ph or $PhCH_2$ in LXIV. Trippett[27] and his co-workers have recently reported their investigations of the reactions of some phosphetans with C-C multiple bond systems. For example, when 2,2,3,3-tetramethyl-1-phenylphosphetan (LXVI) is treated with ethyl propiolate in wet ether, ring expansion occurs with the migration of the CMe_2 group to give the oxide LXVII together with a little of the isomer obtained by CH_2 migration. Similarly, reaction of the phosphetan LXVI with dimethyl acetylenedicarboxylate gives an ylide (LXIX; R=Me) *via* the phosphorane LXVIII. Again, the CMe_2 group migrates from an apical position. Ring expansion is also observed in the reactions of 2,2,3-trimethyl-1-phenylphosphetans and C-C multiple bond systems. Here too, the ring expansions involve migration of both the CH_2 and CMe_2 groups, but the situation is complicated by asymmetry about the phosphorus atom. A 19:1 mixture of the isomers of LXX



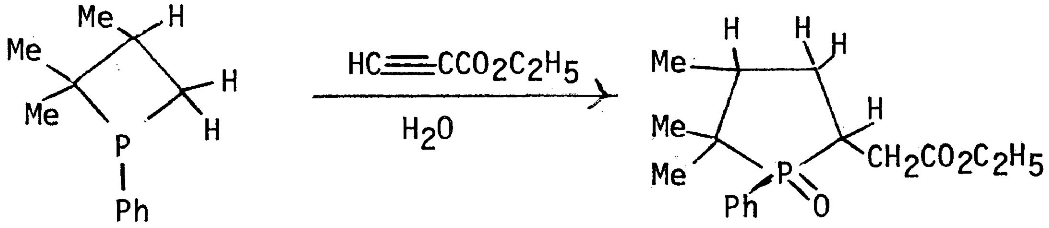
LXVI

LXVII



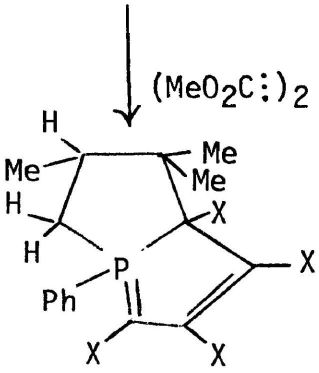
LXVIII

LXIX (R=Me)



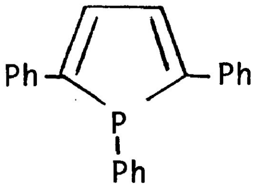
LXX

LXXI

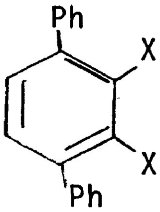


LXIX

(R = H)



LXXII



LXXIII

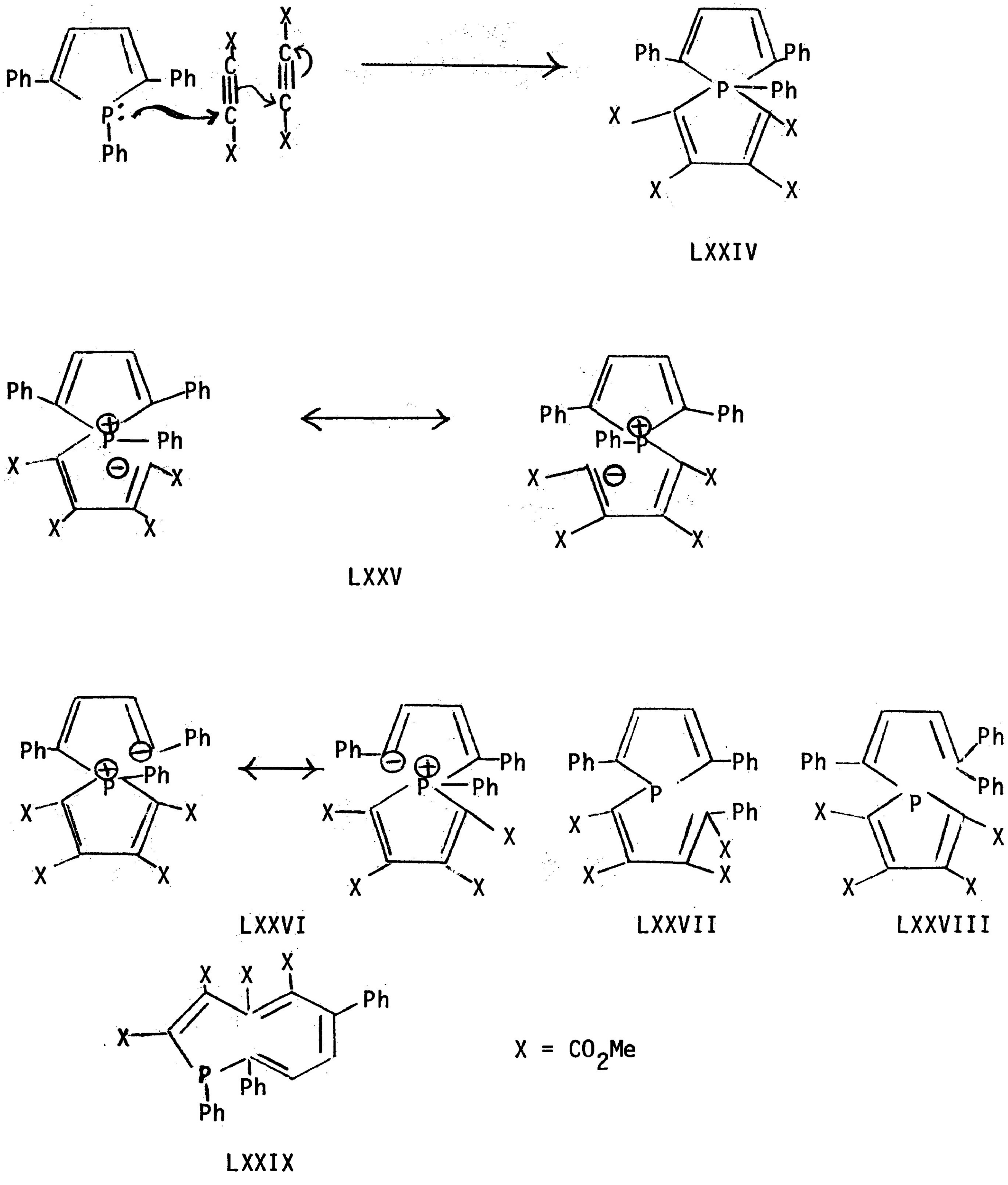
X= CO_2Me

gives, with ethyl propiolate in wet ether, a mixture of the product LXXI (formed by apical CH_2 migration) together with the product formed by CMe_2 migration. The same mixture of isomeric phosphetans with dimethyl acetylenedicarboxylate, gives a crystalline 1:2 adduct which was considered to be the ylide LXXIX (R=H) formed by migration of the CMe_2 group.

Hughes and Uaboonkul[28] have investigated the reaction of dimethyl acetylenedicarboxylate with 1,2,5-triphenylphosphole (LXXII). The phosphole was found to react with a large excess of the undiluted ester at room temperature under nitrogen to give three products. The first product (9% yield) is a colourless crystalline compound which proved to be the *p*-terphenyl derivative LXXIII. The major product (37% yield) is a yellow crystalline 2:1 adduct of the ester with the phosphole LXXII. The third product was obtained as red crystals in very low yield (2.5%) and it was shown to be a 4:1 adduct of the ester and the phosphole.

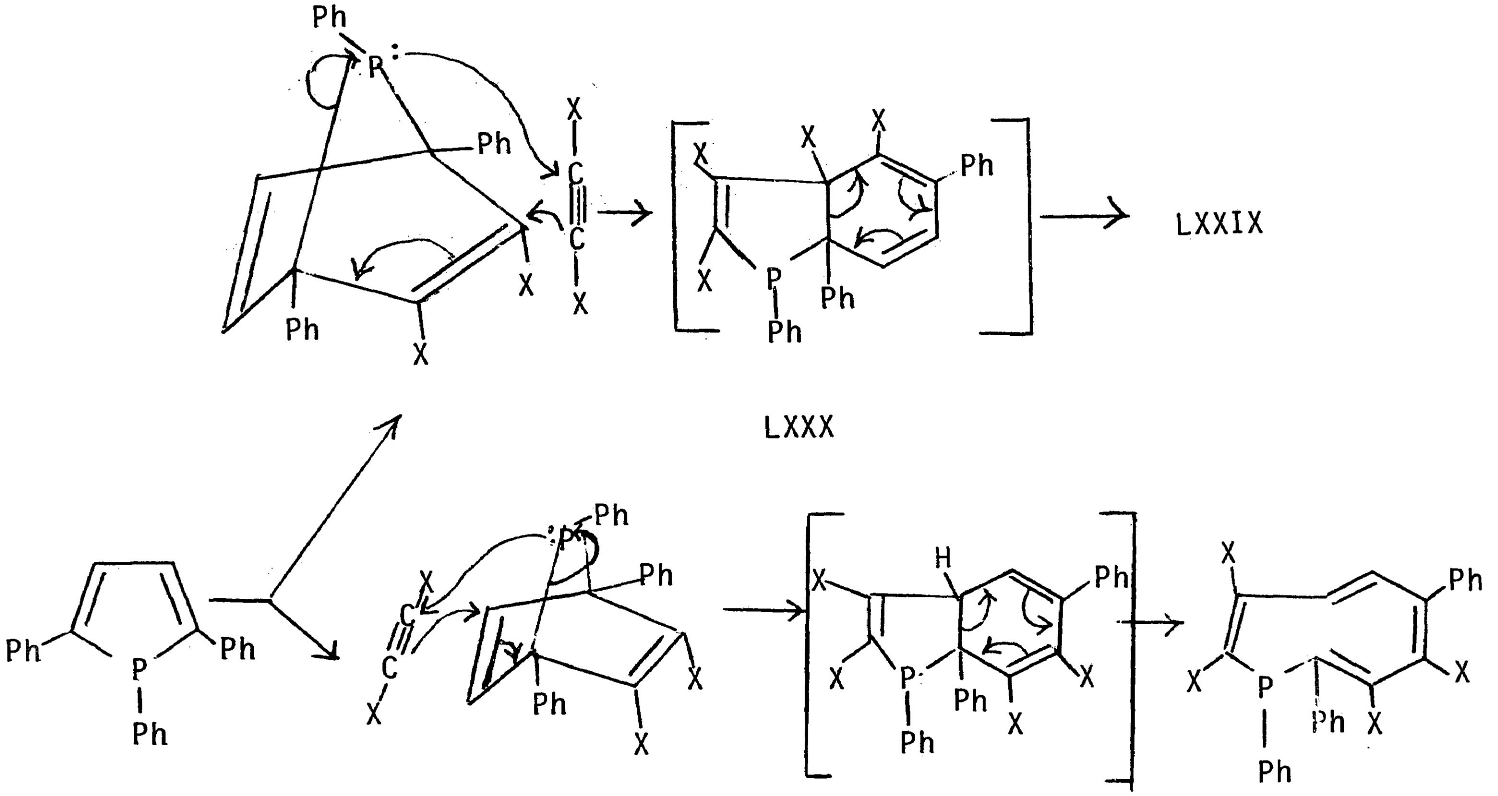
Hughes and Uaboonkul carried out an attempted structure determination of the second yellow (2:1) crystalline adduct and they proposed a number of possible structures for this 2:1 product as shown in the Schemes B,C and D. Scheme B illustrates the possible products which could be obtained if the initial reaction occurs by attack of the lone-pair of electrons of the phosphorus atom of LXXII on the ester. Scheme C represents an

SCHEME B



X = CO_2Me

SCHEME C



LXXIX

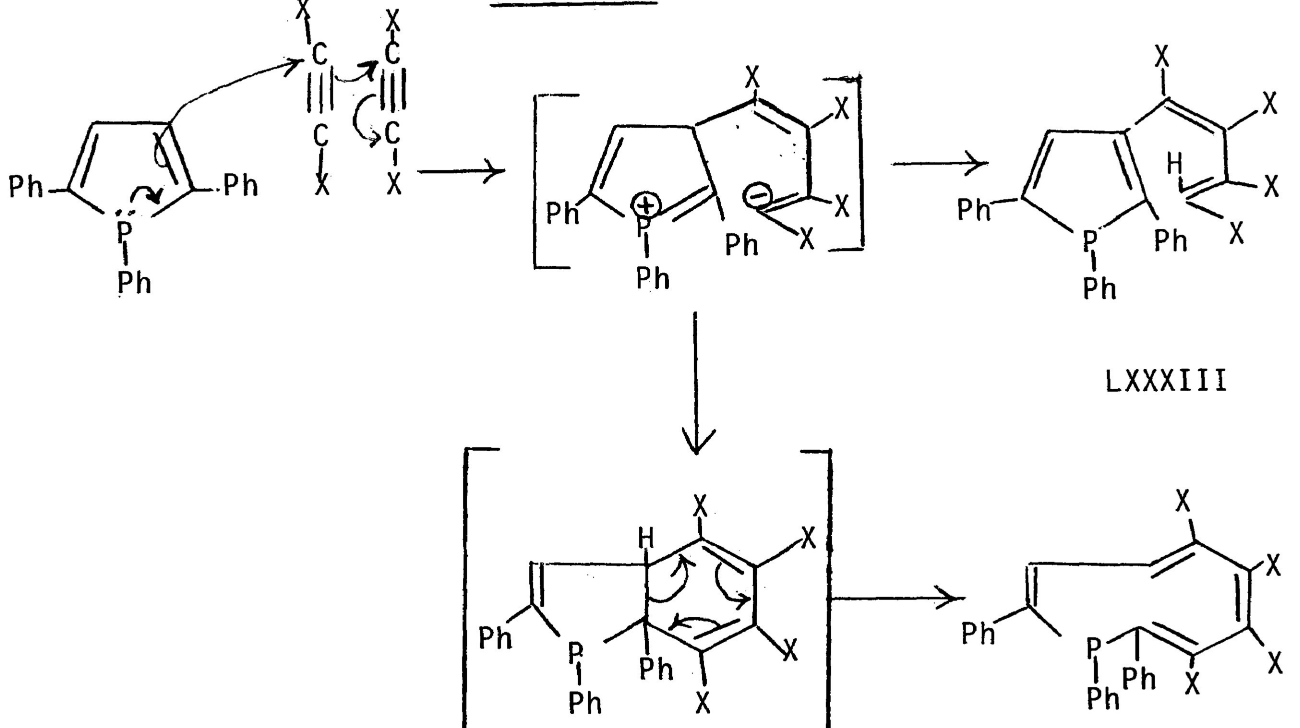
LXXX

LXXII

LXXXI

LXXXII

SCHEME D



LXXXIII

X = CO_2Me

LXXXIV

LXXXV

initial diene reaction of the phosphole LXXII with the ester and Scheme D represents the reaction of an electron-rich aromatic phosphole ring with the ester. Most of the possible structures were eliminated on the basis of spectroscopic evidence. Thus, spectroscopic results conclusively eliminated the structures LXXV, LXXVI, LXXVIII, LXXX, LXXXI, LXXXIII and LXXXIV. On the basis of the chemical evidence, all of the other structures considered, except LXXIV, were eliminated. This spirobiphosphole structure was considered as the most likely structure on the evidence available and supporting evidence came from the fact that the adduct slowly rearranges over several hours in boiling chloroform or alcohol to give a colourless isomer which possesses tertiary phosphine characteristics. Therefore, the pentacovalent structure LXXIV was suggested for this adduct.

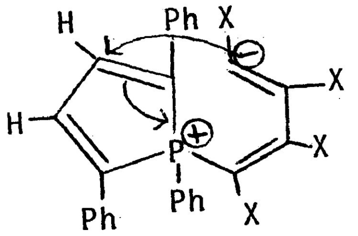
However, very recently Tebby and Waite[29] reinvestigated the reaction and the structure LXXIV was shown to be incorrect. The presence of an alkylidenephosphorane was indicated by the ^{31}P NMR spectrum which shows a resonance at -37 p.p.m. relative to external 85% orthophosphoric acid. This clearly shows that the phosphorus atom in the adduct is not pentacovalent, since Hellwinkel[30] has shown that phosphorus atoms having five single bonds to carbon have ^{31}P shifts in the region +80 to +100 p.p.m. relative to the same external standard. Tebby, therefore, suggested that first an intermediate LXXXVI is formed which cyclizes to give LXXXVII which further rearranges to give the final adduct LXXXVIII.

Confirmation of an ylidic structure comes from the protonation of the adduct with acid and the regeneration of the adduct upon basification of the acidic solution. The structure LXXXVIII is also supported by comparison of its UV and NMR spectra with those of the related phosphine oxide LXXXIX.

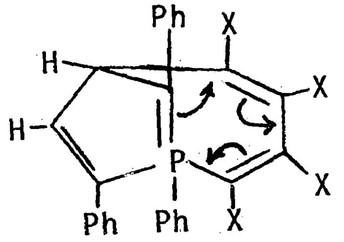
Reactions of Tertiary Phosphines with Arynes

Wittig and Benz[31] obtained (in less than 20% yield) 9-phenyl-9-phosphafluorene (XCI) by treating triphenylphosphine with benzyne. In this reaction, nucleophilic attack of triphenylphosphine upon benzyne occurs to give initially the intermediate XC followed by spontaneous elimination of benzene. Benzyne here was generated by treating *o*-bromofluorobenzene with magnesium in the presence of triphenylphosphine.

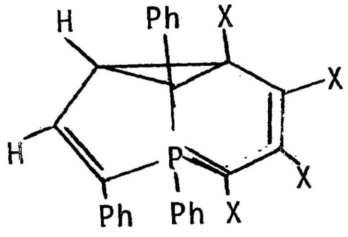
Zbiral[32] obtained, in 40% yield, 9-phenyl-9-phosphafluorene (XCI) by treating triphenylphosphine with benzyne, while triphenylphosphine on treatment with 1-methoxy-2,3-dehydrobenzene gave, in 50% yield, 4-methoxy-9-phenyl-9-phosphafluorene (XCII). When XCI was further treated with 1-methoxybenzyne the adduct XCIII was obtained.



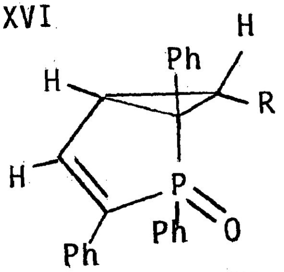
LXXXVI



LXXXVII

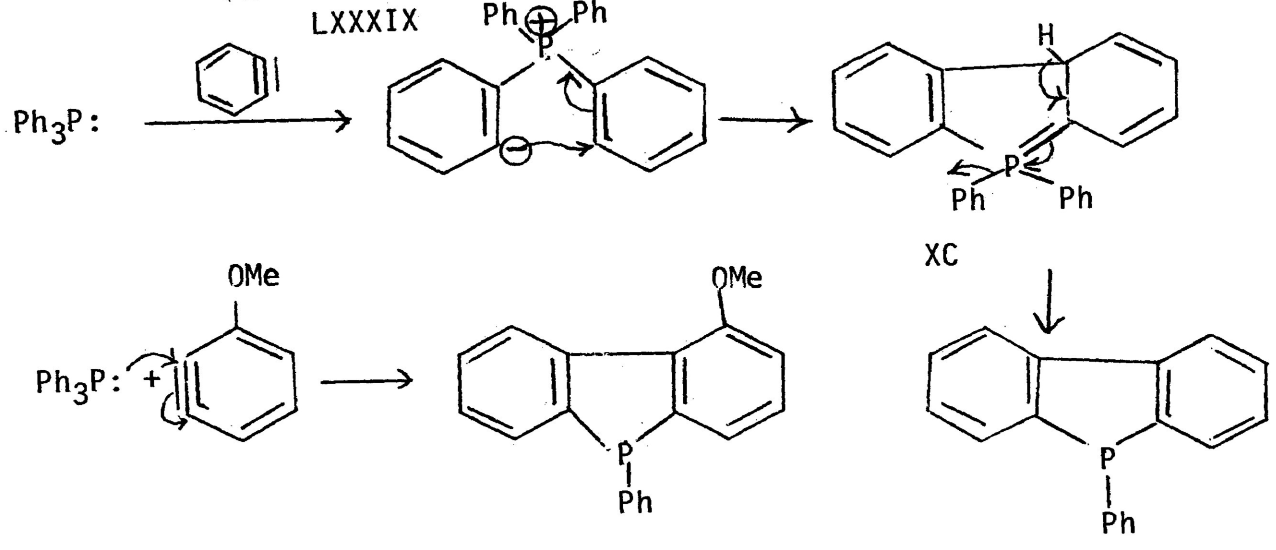


LXXXVIII



R = H, $-CO_2Me$, or -COOH

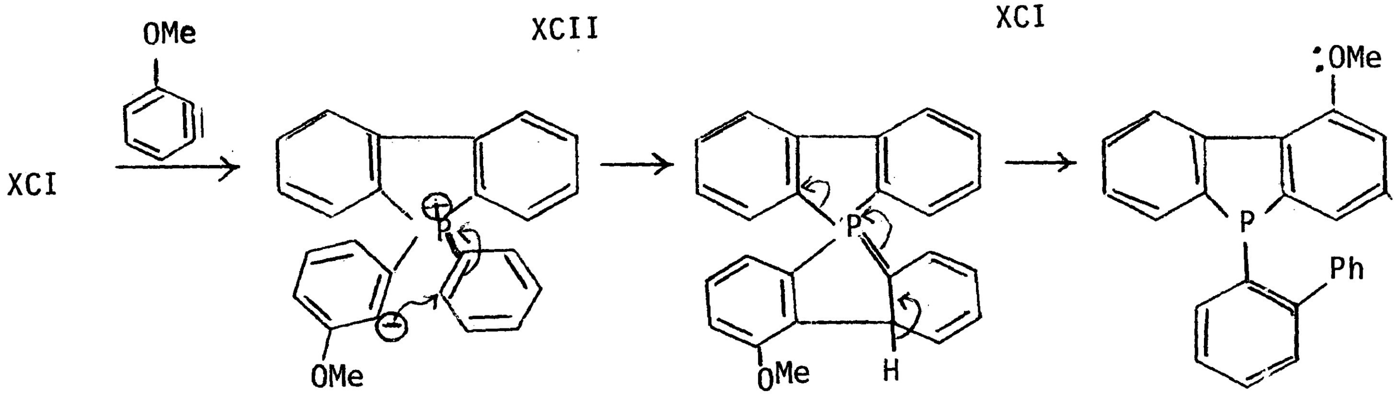
LXXXIX



XC

XCII

XCI



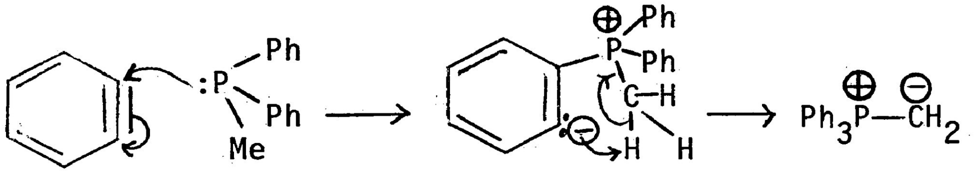
XCIII

Methyldiphenylphosphine, when treated[33] with benzyne, gives the 1:1 adduct XCIV which behaves as a normal ylide and enters into a successful Wittig reaction with cyclohexanone.

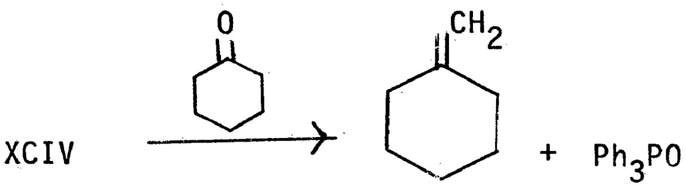
When triphenylphosphine, is treated[34] with benzyne in the presence of methyl iodide, the adduct XCV is obtained.

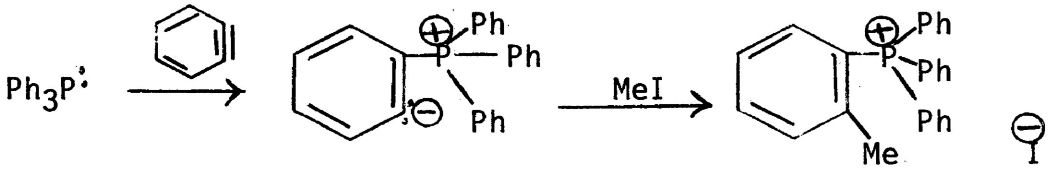
Miscellaneous Related Reactions

Märkl[35] has found that the potentially aromatic 2,4,6-trisubstituted phosphorins (XCVI) have very little diene or tertiary phosphine reactivity. For example, 2,4,6-triphenylphosphorin (XCVI, $R^1=R^2=R^3=Ph$) fails to react either with dimethyl acetylenedicarboxylate or with maleic anhydride. However, it was found[35] that the highly reactive dienophile hexafluoro-2-butyne reacts with 2,4,6-triaryl or 2,4,6-trialkyl substituted phosphorins at 100°C, although the analogous reaction with aromatic hydrocarbons such as benzene and durene[36] requires a temperature of 200°C. Cycloaddition of hexafluoro-2-butyne to the phosphorin XCVI occurs exclusively at the 1,4-positions to give the substituted 1-phosphabarrelenes XCVII. The ^1H NMR spectra confirmed the symmetrical nature of XCVII. It is not clear whether the reaction is a Diels-Alder type of 1,4-addition or whether the reaction goes *via* nucleophilic

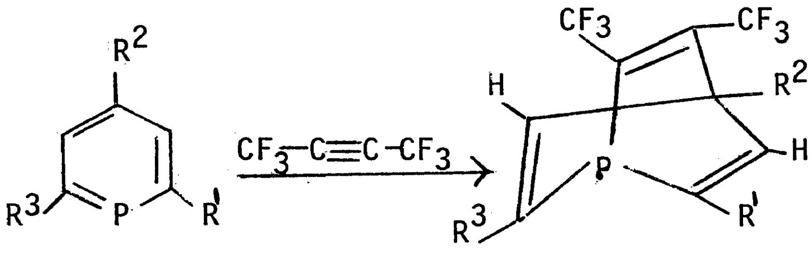


XCIV





XCV



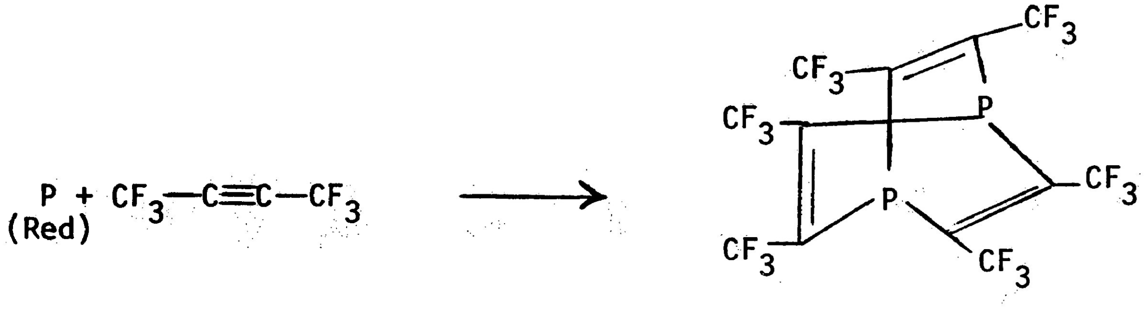
R^1 = Ph,Me; R^2= Ph,Me;
R^3= Ph,Me

XCVI XCVII

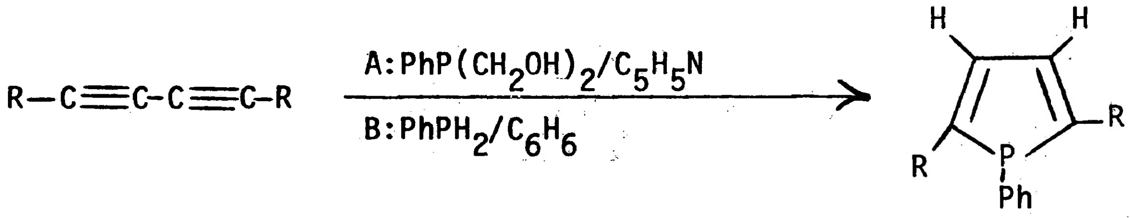
attack of the phosphorus atom upon the acetylenic linkage. A similar product is formed when red phosphorus is heated[37,38] at 200°C with hexafluoro-2-butyne in 2:1 molar ratio, for 5 hours in the presence of a small amount of iodine. The product, hexakis(trifluoromethyl)-1,4-diphosphabicyclo[2.2.2]octa-2,5,7-triene XCVIII, was obtained in 45% yield as a colourless solid m.p. 119° - 120°C.

Finally, Märkl[39] has developed a general method for the preparation of phospholes XCIX by treating butadiynes with phenylphosphine or bis(hydroxymethyl)-phenylphosphine. Thus, when bis(hydroxymethyl)phenylphosphine is treated with butadiyne in boiling pyridine (method A), a phosphole is formed. Similarly, phenylphosphine itself adds smoothly to butadiyne in benzene even at room temperature in the presence of a catalytic amount of PhLi (method B). In this way Märkl[39] prepared the first phosphole without any aryl substituents attached to the ring carbon atoms.

These reactions are, strictly speaking, not examples of nucleophilic attack of a normal tertiary phosphine upon an acetylenic linkage. However, they are related reactions of some importance and, as such, they should be included in this discussion.



XCVIII



R= Ph,2-Naphthyl,Me

XCIX

Conclusion

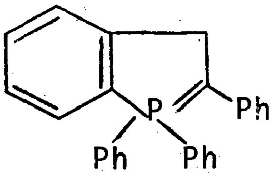
It can be seen from the foregoing discussion that a wide variety of reactions may occur between phosphines and acetylenic systems. Some of these reactions provide valuable routes to phosphorus heterocycles including cyclic phosphonium ylides. The next section of this thesis, therefore, reports the reactions of several bisphosphines and biphosphines with dimethyl acetylenedicarboxylate and outlines the possible value of such reactions in the synthesis of cyclic phosphonium ylides with particular emphasis upon those containing two ring phosphorus atoms.

RESULTS AND DISCUSSION

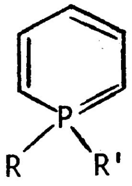
Introduction

There are relatively few cyclic phosphonium ylides known and some of these have been mentioned in the previous chapter. A comprehensive survey of cyclic phosphonium ylides (three-membered ring and higher) has recently been compiled by Davies.[40]

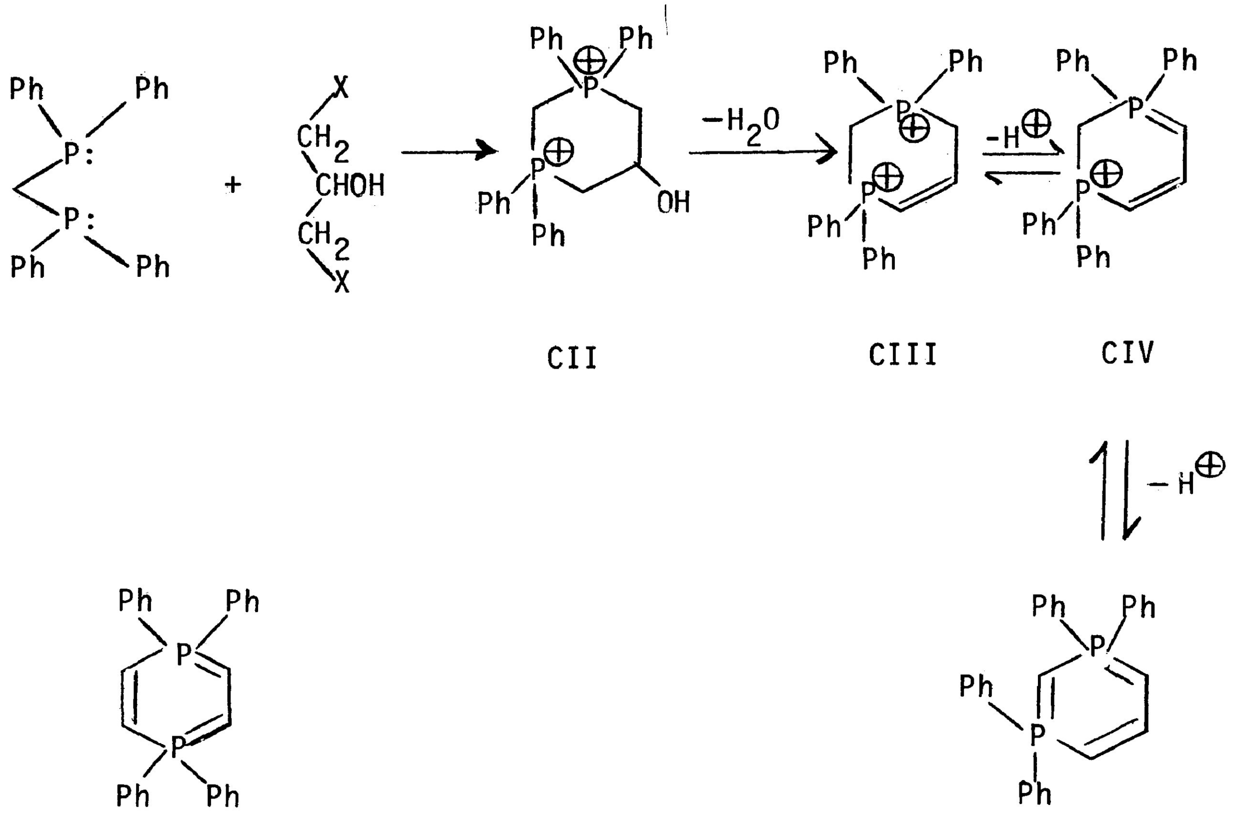
The best known and most studied cyclic ylides are the P,P-disubstituted phosphorins (phosphabenzenes) and the study of cyclic phosphonium ylides in general was pioneered by Märkl. For example, Märkl[41] reported the preparation of 2,3,3-triphenyl-3-phosphaindene (C) eight years ago. This compound was not isolated but could be studied in solution. It was found to undergo a Wittig reaction with benzaldehyde showing that the ylidic carbanion has normal nucleophilic character. Since the preparation of the ylide C, Märkl and other workers have succeeded in preparing and isolating a number of other cyclic phosphonium ylides particularly phosphorin derivatives such as CI. Recently, a review of phosphorus heterocycles including phosphorins has been published by Berlin and Hellwege.[5]



C



CI



CII

CIII

CIV

CV

CVI

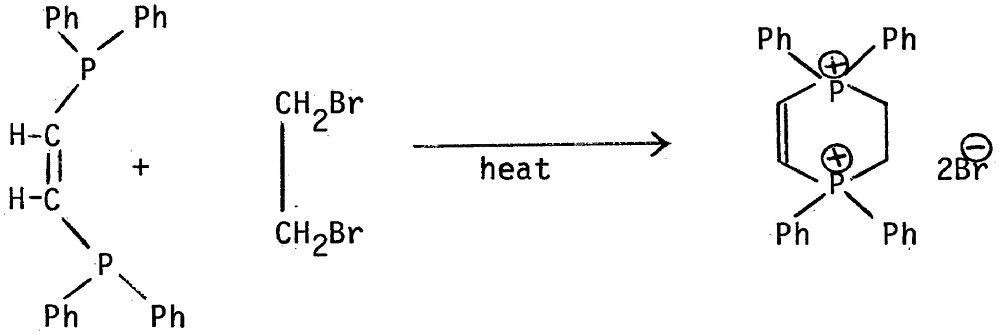
X = Halogen

While several cyclic phosphonium ylides with one phosphorus hetero atom are known, such compounds with two phosphorus hetero atoms in the ring, *i.e.* cyclic bis-ylides, are extremely rare. Again, Märkl[42] was the first to report the preparation of a compound of this type. Thus, 1,1,3,3-tetraphenyl-1,3-diphosphabenzene (CV) was prepared from the cyclic bisphosphonium salt CII which was in turn prepared by reaction of bis(diphenylphosphino)-methane[43] with the appropriate 1,3-dihalogeno compound. On treatment with polyphosphoric acid, the salt CII dehydrates to form the compound CIII. When CIII is deprotonated by sodium carbonate, the resonance stabilized cyclic ylide CIV is formed. When a stronger base such as aqueous sodium hydroxide is used, a second proton is removed and 1,1-3,3-tetraphenyl-1,3-diphosphabenzene (CV) separates out from aqueous solution as a yellow, non-crystalline precipitate.

On the other hand, Aguiar[44] unsuccessfully tried to prepare the potentially aromatic bis-ylide CVI. He heated *cis* 1,2-bis(diphenylphosphino)ethylene (CVII)[45] under reflux with an excess of 1,2-dibromoethane and obtained the cyclic bisphosphonium salt CVIII. However, all attempts to prepare the cyclic bis-ylide CVI by proton abstraction from CVIII with butyl lithium or phenyl lithium resulted only in ring rupture. Thus, the α-proton abstraction method which is so useful in the formation of acyclic ylides from phosphonium salts may have limitations in the synthesis of cyclic bis-ylides.

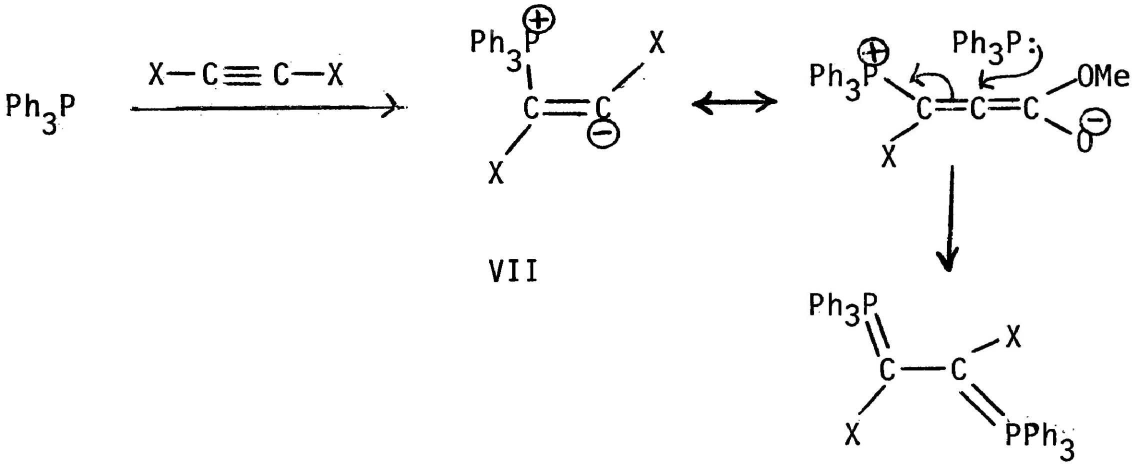
As already mentioned in the previous chapter, Tebby[7,11] and his co-workers investigated the reactions of triphenylphosphine with dimethyl acetylenedicarboxylate at low temperature and reported the isolation of the 2:1 bis-ylide X as one of the products. The probable mechanism of the reaction is outlined in the sequence $Ph_3P+MeO_2C-C\equiv C-CO_2Me \rightarrow$ VII → X. These observations of Tebby suggest that bisphosphines and biphosphines might, under suitable conditions, undergo cyclo-additions with dimethyl acetylenedicarboxylate to give cyclic phosphonium bis-ylides. For example, bisphosphines of the type CIX could react with the acetylenic ester to give cyclic bis-ylides of type CX by a mechanism similar to that postulated for the reaction of triphenylphosphine with the ester. This process could thus possibly lead to a general synthetic route to cyclic phosphonium bis-ylides. In this process, ring closure should be favoured because, although the first step in the reaction would be intermolecular, the second step would be intramolecular.

Reactions of several bisphosphines and biphosphines with dimethyl acetylenedicarboxylate have,



CVII

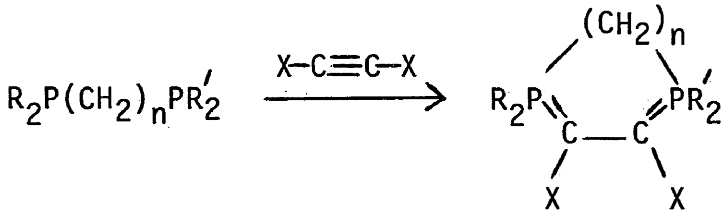
CVIII



VII

X = -CO$_2$Me

X



X = CO$_2$Me

R,R$'$ = Alkyl or Aryl

CIX

CX

therefore, been studied to investigate the possibility of the formation of cyclic phosphonium bis-ylides. The phosphines chosen were bis(diphenylphosphino)ethane (CXI), bis(diphenylphosphino)methane (CXII), *cis* 1,2-bis(diphenylphosphino)ethylene (CXIII), *trans* 1,2-bis(diphenylphosphino)ethylene (CXIV) and tetraphenylbiphosphine (CXV). The main reason for selecting these phosphines is because they are readily available commercially and/or readily synthesized. Additional reasons for the choice of the phosphine CXV will be discussed later.

The use of dimethyl acetylenedicarboxylate has two advantages. First, the triple bond is electron-poor and, therefore, very susceptible to nucleophilic attack. Second, any ylide formed should be stabilized to some extent by the delocalization of the ylidic carbon atom negative charge over the methoxycarbonyl group and may, therefore, be isolable. Further, products of some of the reactions should be fully unsaturated six-membered rings containing two phosphorus atoms and, therefore, potentially aromatic.

It was decided that the investigation should be largely exploratory and directed towards finding suitable conditions for the synthesis of new cyclic bis-ylides in high yield. Because of this, the more mechanistic aspects of the investigation have received only superficial discussion and experimental treatment.

A detailed discussion of the bonding in phosphonium ylides would not be appropriate here since the topic has already been very well treated elsewhere.[46] However, the fact that some of the ylides which could be synthesized by the proposed route could, at least superficially, have an aromatic structure suggests that a brief synopsis of current ideas on the bonding in phosphorins of type CI would be in order before discussion and interpretation of the results obtained in the investigation.

There is considerable evidence that there is a large degree of $p_\pi - d_\pi$ bonding in the ylide link of phosphonium ylides. If this is so, it is of interest to establish just how phosphorus d-orbitals are involved in the electronic structure of phosphorins of type CI.

Briefly, there have been three main suggestions regarding the bonding in phosphorins of type CI. The first two of these were put forward by Märkl[47] and Price[48] at about the same time and Märkl's proposal is similar to that put forward by Dewar[49] 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 towards an adjacent carbon atom (and its p_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 atom to form a p_π——d_π link. This would mean that the conjugation would not be complete since the phosphorus atom uses different d-orbitals to overlap with the orbitals of the adjacent carbon atoms. The arrangement is illustrated in structure CXVI.

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. This is illustrated in CXVII.

Recent X-ray diffraction studies on 1,1-dimethoxy-2,4,6-triphenylphosphorin[50] and 1,1-dimethyl-2,4,6-triphenylphosphorin[51] have confirmed that the heterocyclic ring is virtually planar and that the two P-C bonds are identical. Moreover, the C-C bond lengths are consistent with considerable delocalization in the system.

Very recently, Oehling and Schweig[52] have shown by CNDO/2 calculations that, for the phosphorus atom in compounds of type CI, there is a significant d-orbital contribution to the P-C σ-bonds and a significant $3p_z$ contribution to the π-bonds.

The Reaction of 1,2-Bis(diphenylphosphino)ethane with Dimethyl Acetylenedicarboxylate

When a solution of dimethyl acetylenedicarboxylate in dry benzene is added slowly with constant stirring at room temperature under nitrogen to a dry benzene solution of 1,2-bis(diphenylphosphino)-ethane, a bright yellow precipitate appears almost immediately.

The product is reasonably stable in the absence of air and moisture and can be filtered off under nitrogen without decomposition. However, care has to be taken to ensure that the benzene is rigorously dried, since the adduct is very sensitive to moisture - particularly in solution. The crude adduct can be crystallized from dry benzene under nitrogen to give yellow crystals of a 1:1 adduct of the phosphine and the ester (up to 80% yield) containing some benzene of crystallization. The

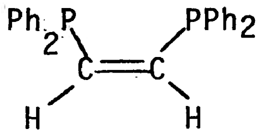
$Ph_2PCH_2CH_2PPh_2$

CXI

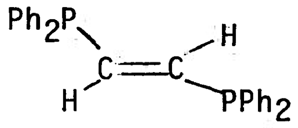
(LIV in previous Chapter)

$Ph_2PCH_2PPh_2$

CXII



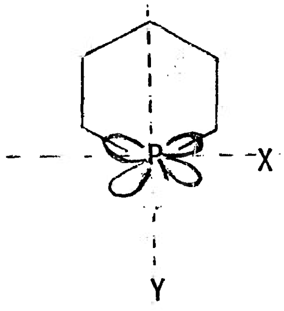
CXIII
(CVII)



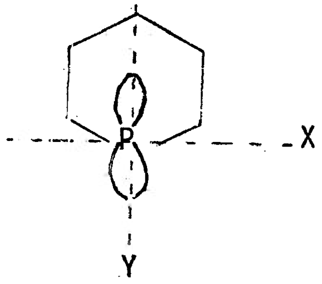
CXIV

$Ph_2P—PPh_2$

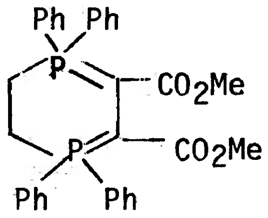
CXV



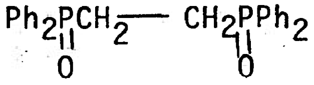
CXVI



CXVII

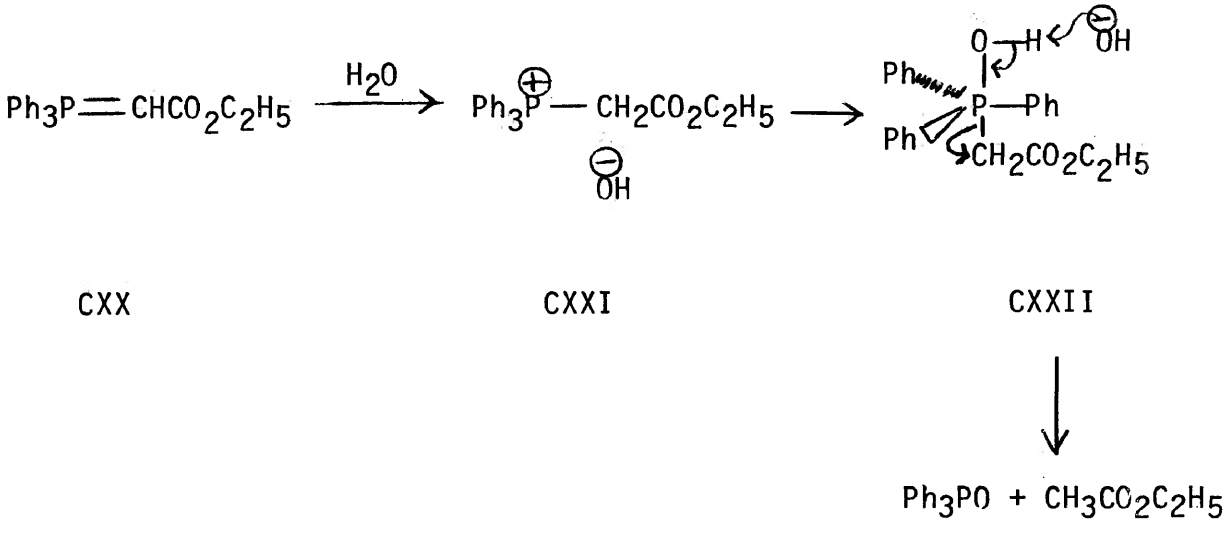


CXVIII



$Ph_2\overset{}{\underset{O}{\overset{\|}{P}}}CH_2—CH_2\underset{O}{\overset{\|}{P}}Ph_2$

CXIX



CXX

CXXI

CXXII

CXXIII

benzene cannot be completely removed even by pumping at 50°C and 8 x 10^{-6} Torr for several hours.

Elemental analyses of the adduct were found to be rather poor because of varying amounts of benzene trapped in the crystals. N.M.R. studies on fresh samples of the adduct show that initially about 1 molecule of benzene of crystallization is present but, with occasional pumping, this drops over a period of several months to about 0.3 molecules of benzene of crystallization. It is likely that benzene is occluded in the crystal lattice and is very slowly released. This is indicated by ^{1}H NMR spectral studies at various time intervals. Pumping at higher temperatures is not possible because the adduct slowly decomposes and the decomposition becomes very rapid at 140° - 150°C.

The adduct was shown to be the expected bisylide dimethyl 1,1,4,4-tetraphenyl-1,4-diphosphacyclohexa-1,3-diene-2,3-dicarboxylate (CXVIII) in the following manner. As already mentioned, elemental analyses suggested a 1:1 adduct containing a little benzene. Mass spectral studies were difficult because the benzene of crystallization is released suddenly at about 140°C and this endangers the filament in the mass spectrometer.

However, by using a direct inlet system and pumping the crystals at about 140°C with the filament current turned down until all of the benzene had been released and pumped out, a rather poor spectrum was obtained which showed a weak molecular ion peak at *m/e* 540.

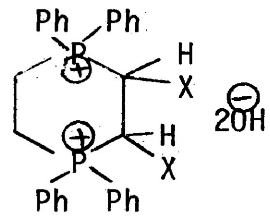
The adduct CXVIII slowly hydrolyzes in water to give the dioxide CXIX for which the identity was confirmed by IR, ^1H NMR and mass spectrometry. Elemental analyses of the hydrolysis product of the adduct CXVIII were also in agreement with the dioxide CXIX. Comparison (IR, ^1H NMR, m.p.) with an authentic sample of the dioxide, prepared by the oxidation of bis(diphenylphosphino)-ethane with acetic acid and hydrogen peroxide, further confirmed the identity of the hydrolysis product as CXIX.

The formation of the dioxide CXIX would be expected from an adduct such as CXVIII since it has been shown[46] that in the hydrolysis of ylides, the first step is the protonation of the ylidic carbon atom followed by the formation of a trigonal bipyramidal pentacovalent phosphorus intermediate which eliminates from the apical position the group which would form the most stable carbanion to give the corresponding phosphine oxide.

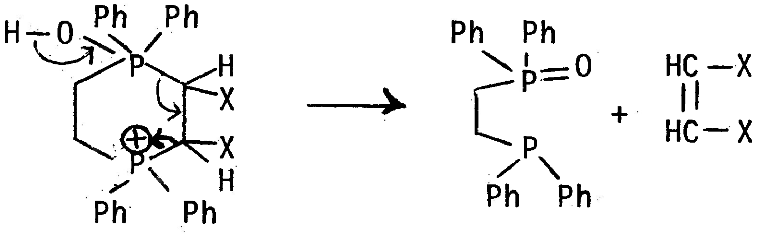
A typical example is shown in the sequence CXX → CXXI → CXXII → CXXIII.

As well as the formation of the dioxide CXIX, one might also possibly expect to obtain some of the monoxide CXXVI by decomposition of the intermediate bis-quaternary hydroxide CXXIV as shown in the sequence CXXIV → CXXVI. A similar reaction has been observed by Aguiar[44] in which the cyclic bisphosphonium bromide CXXVII hydrolyzes in dilute aqueous base to give the monoxide CXXVIII. This type of elimination has also been observed[53] in systems containing the 1,2-bisphosphoniaethylene (CXXIX) grouping as in CXXX.

Thus, the evidence so far suggests that the adduct, obtained by reacting dimethyl acetylenedicarboxylate and the bis(diphenylphosphino)ethane, is a cyclic compound containing two phosphonium ylide linkages. Confirmation of the two ylide linkages comes from the fact that on brief treatment of a solution of the adduct in methanol with perchloric acid, a bisperchlorate is formed. Elemental analyses of the perchlorate are in excellent agreement with the molecular formula $C_{32}H_{32}O_{12}$-P_2Cl_2. The IR spectrum of the perchlorate shows a typical broad perchlorate peak around 1100 cm^{-1},



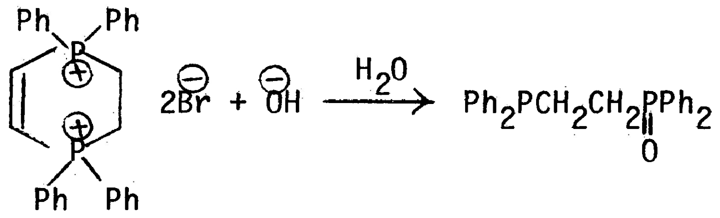
CXXIV



CXXV

CXXVI

X = CO_2Me



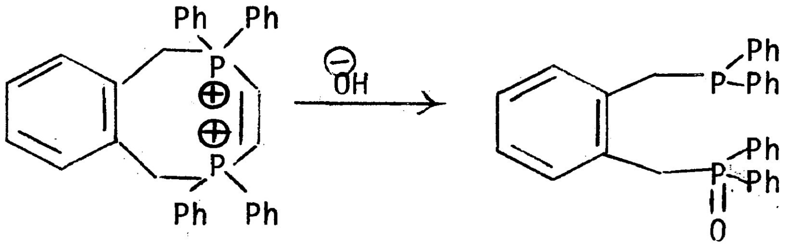
CXXVII

CXXVIII

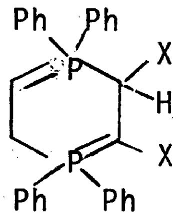
(CXXVI)

$(\equiv\overset{\oplus}{P}-CH=CH-\overset{\oplus}{P}\equiv)$

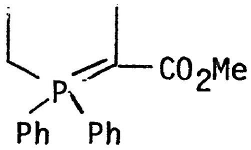
CXXIX



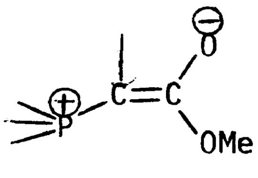
CXXX



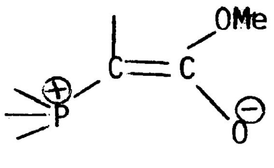
CXXXI



CXXXII



CXXXIII



CXXXIV

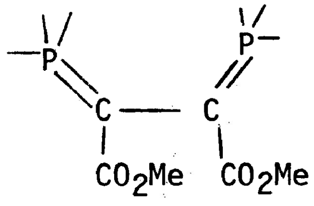
while the stretching of the $\geq$C=O group appears at higher frequency (1740 cm^{-1}) than in the original adduct which would be expected[12] on protonation of the ylidic carbanion.

Spectroscopic evidence further confirms the bis-ylide nature of the yellow adduct and also shows that the correct structure of the adduct is CXVIII rather than energetically less favoured isomers such as CXXXI. The infrared spectrum, for example, shows that the carbonyl frequency occurs at the unusually low value of 1585 cm^{-1} with shoulders at 1594 cm^{-1} and 1618 cm^{-1}. These unusually low values are typical[11,12] of α-carbonyl stabilized phosphonium ylides-*i.e.* both carbonyl groups are attached directly to ylidic carbon atoms.

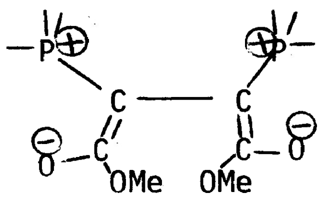
The ^1H NMR spectrum in $CDCl_3$ gives further information. The spectrum of the adduct varies slightly from one sample to the next because the amount of benzene of crystallization varies. Basically the spectra show 20 aromatic protons at τ2.0 - 2.85, between two and six benzene protons (close to six in very freshly prepared samples) as a very sharp singlet at τ2.68 and the methoxy and methylene protons as a very broad and poorly defined signal between τ6.1 and τ8.0.

At first sight, the absence of a sharp methoxy signal is unexpected bearing in mind the symmetrical nature of the adduct. However, it should be noted that in α-carbonyl stabilized ylides, there is extensive delocalization of the ylidic carbanion negative charge over the carbonyl group.[12] Thus, if one looks at the structure CXXXI it can be seen that, in this grouping, there should be substantial contributions from the structures CXXXIII and CXXXIV - *i.e.* the ester group has preferred conformations in that the carbonyl carbon of the ester, the carbonyl oxygen and the phosphorus atom tend to be co-planar. This gives rise to preferred conformers in which the carbonyl oxygen is either *cis*- or *trans*- to the phosphorus atom.[12] Such an ester group has been shown to give[12] two ^{1}H NMR signals corresponding to the two conformers and, since the two conformers are interconvertible, the signals are broader than normal.

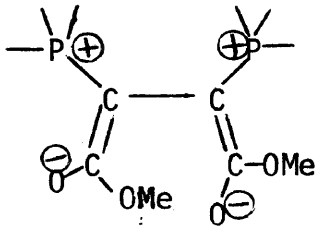
If the case of structure CXVIII is considered, there are two adjacent ylidic ester groups and the arrangements shown in CXXXV, CXXXVI, CXXXVII, and CXXXVIII are possible. This would generate at least four broad methoxy signals. Further, the protons of the ring methylene groups of the adduct would be in a variety of magnetic environments



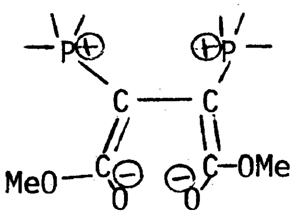
CXXXV



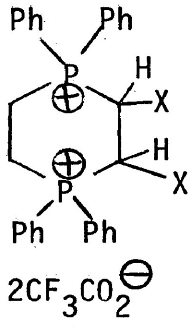
CXXXVI



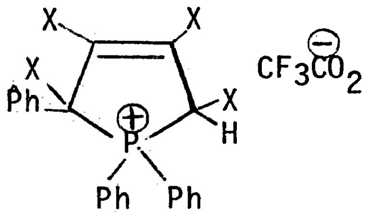
CXXXVII



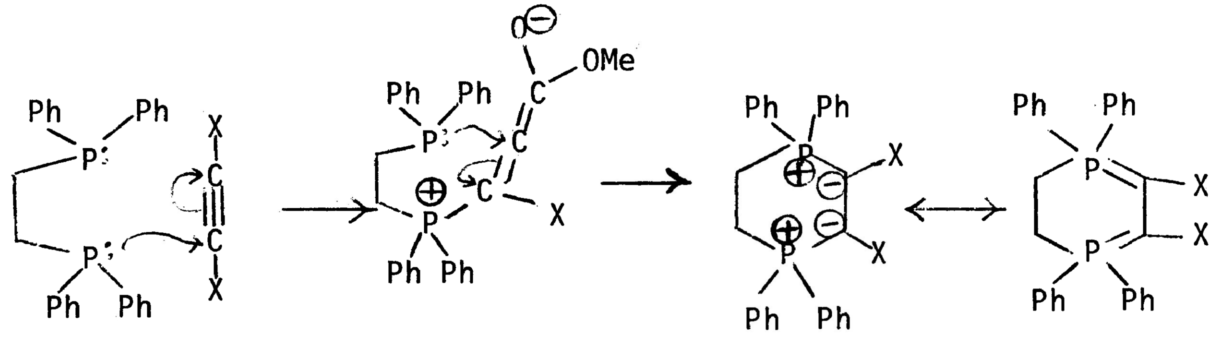
CXXXVIII



CXXXIX



CXL



CXI
(LIV)

CXLI

CXVIII

$X = CO_2Me$

corresponding to the above conformational arrangements. In some arrangements, the methylene groups would be virtually equivalent while in others, they would be non-equivalent and the two methylene groups would show spin-spin interactions. Finally, the ring methylene protons in some of the conformers would each couple unequally with the two phosphorus atoms. The overall result would be one very broad methylene-methoxy band in the ^{1}H NMR spectrum.

Some evidence for the preferred but interconvertible ester group arrangements suggested above comes from the ^{1}H NMR spectrum of the adduct at -40°C (where interconversion of conformers would be slow) which shows one large broad methoxy signal at τ6.35 together with one or two other smaller peaks superimposed upon the band envelope.

Addition of trifluoroacetic acid to the solution of the adduct in $CDCl_3$ supports the above suggestions. This causes the spectrum to be modified to show 20 aromatic protons at τ2.0 - 2.6, between 2 and 6 benzene protons (according to the age of the sample) at τ2.68, and ten methylene and methoxy protons at τ6.1 - 7.3 with the methoxy protons as a sharp singlet at τ6.57. There is apparently no trace of the two methine protons of the doubly protonated salt of the adduct to which the structure CXXXIX could be assigned, although the rest of the spectrum is consistent with the structure CXXXIX.

However, if the spectrum is recorded in pure trifluoroacetic acid (with TMS added as internal reference) then two protons appear as a broad hump at $\tau 4.67$ which is in good agreement with the chemical shift observed[12] for the similar proton in compound CXL. The rest of the spectrum remains the same except for a small downfield shift of the peaks. Presumably, the two protons are not observed in acidic $CDCl_3$ because the ylidic carbon atoms of the adduct are relatively weakly basic because of resonance stabilization and, consequently, in the salt CXXXIX there is a rapid exchange between the methine protons and the acid in the solvent.*

---

*Note:-The methine protons were originally thought[54] to be under the aromatic signal. This was because, initially, it was found that one molecule of benzene of crystallization was present and it was not recognized that the amount of benzene can in fact vary with the age of the sample. This gives rise to variable integrations in the aromatic region.

Some evidence for this comes from the fact that in trifluoroacetic acid, these protons become better defined (and at very slightly lower field) at 0°C where, presumably, exchange is slower.

The spectrum in CF_3CO_2D is virtually identical except that the methine protons, as expected, are not observed.

In the salt CXXXIX, the ring would probably adopt the chair conformation with the two ester groups in a *trans*-diequatorial arrangement, thus giving rise to a single methoxy signal. The methylene multiplet, therefore, comes from the different chemical shifts and couplings of the axial and equatorial methylene protons and also the coupling effect of the two phosphorus atoms. The U.V. spectrum of the yellow adduct shows λ_{max} at 375 mμ. This is similar to the spectra of related ylides.[12]

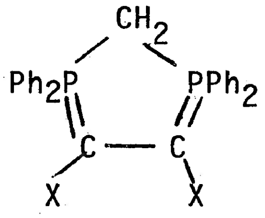
As already mentioned briefly, the adduct is quite stable and may be kept for several months without decomposition, in a well stoppered container under nitrogen although it reacts rapidly with perchloric acid and trifluoroacetic acid, as described, to give colourless salts, and with atmospheric water or wet solvents to give the corresponding bisphosphine dioxide.

From the foregoing discussion it can now be concluded that the yellow adduct, obtained by the reaction of bis(diphenylphosphino)ethane with dimethyl acetylenedicarboxylate, is a cyclic phosphonium bis-ylide with the structure CXVIII. The most probable reaction pathway for the formation of the adduct CXVIII is shown in the sequence CXI → CXLI → CXVIII. This is similar to the mechanism proposed by Tebby[11] for the formation of the 2:1 triphenylphosphine-dimethyl acetylenedicarboxylate adduct X.

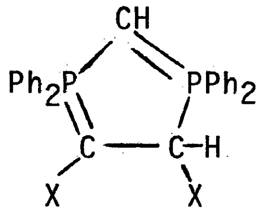
Some of the results described in this section have been published as a preliminary communication.[54]

The Reaction of Bis(diphenylphosphino)methane with Dimethyl Acetylenedicarboxylate.

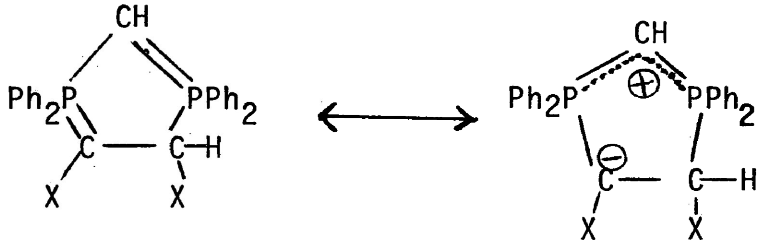
Since 1,2-bis(diphenylphosphino)ethane was found to react so readily and favourably with dimethyl acetylenedicarboxylate to give the expected cyclic bis-ylide in high yield, the reaction was extended to bis(diphenylphosphino)-methane CXII. The expected bis-ylide (CXLII) here would be somewhat more rigid than the bis-ylide CXVIII and this could be of interest from the point of view of how reactivity is affected.



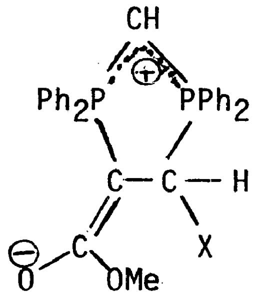
CXLII



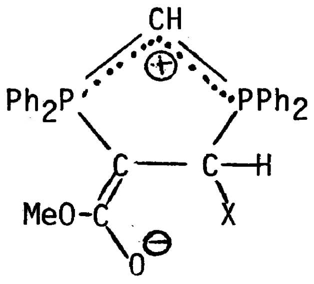
CXLIII



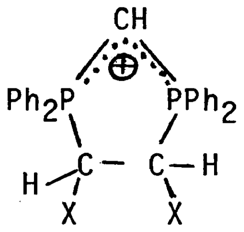
CXLIV



CXLV



CXLVI



CXLVII

$X = CO_2Me$

In a reaction similar to that already described in the previous section for the bisphosphine CXI, dimethyl acetylenedicarboxylate in ether (dried over $LiAlH_4$) was added slowly to an ethereal solution of the bisphosphine CXII, under nitrogen with constant stirring at room temperature. A light cream coloured precipitate at once settled down and was filtered off under nitrogen. The yield of the 1:1 adduct was found to be 67%. The adduct is quite sensitive to air and moisture so every effort was made to exclude them from the reaction mixture. The crude cream adduct was crystallized from dry benzene.

Element analyses agree well with a 1:1 adduct and the mass spectrum shows a molecular ion at *m/e* 526. The IR spectrum of the adduct is considerably different from that of the yellow adduct CXVIII, obtained from the bisphosphine CXI, since it shows one normal ester carbonyl stretching frequency at 1740 cm^{-1} and a strong carbonyl stretching frequency at 1605 cm^{-1} corresponding to an ester carbonyl group adjacent to an ylidic carbon atom.[11,12] It is, therefore, clear that the product is an ylide but not of structure CXLII, since this structure should show both ylidic ester carbonyl group stretching frequencies around 1600 cm^{-1} as in CXVIII. Moreover, the adduct is virtually colourless while the adduct of the phosphine CXI is bright yellow. The U.V. spectrum of the adduct shows a slight inflection at λ_{max} 299 mμ on the long wavelength side of the benzene solvent band which is quite consistent with the colour of the adduct.

The 1:1 composition of the adduct and its ylidic nature suggest that the isomeric structure CXLIII is possible since this also fits the IR spectrum. The structure CXLIII is further suppor-supported by the ^1H NMR spectrum of the adduct which shows 20 aromatic protons as a complex multiplet at τ1.6 - 3.0, one methine proton as a multiplet of at least five peaks centred on τ5.0, six methoxy protons as three peaks of unequal area at τ6.51, τ6.68 and τ6.86, and one other proton as a diffuse multiplet at τ8.75 at room temperature. There are also indications of small peaks (totalling much less than one proton) in the range τ6.2 - 7.2 which could be due to traces of the isomer CXLII or, possibly, to hydrolysis products of the ylide. The proton at τ5.0 is presumably the methine proton adjacent to the ester and phosphonium groupings while the signal at τ8.75 is probably due to the ylidic proton. Ylidic protons of this general type are highly shielded by the negative charge on the carbon atom and, therefore, would be expected to show signals at quite high field.

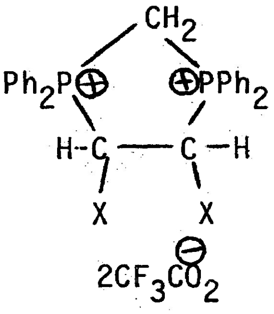
An approximate idea of where such a proton would be expected to resonate can be obtained from a consideration of the published data on structurally related alkylidenephosphoranes. For example, the ylidic proton in $Me_3P{=}CHR$ has been found[55] to resonate in the range τ10.8-11.0, while $Ph_3P{=}CH_2$ shows[56] methylene proton resonance at τ10.61. A more closely related system is the structure $Ph_3P{=}CH{-}\overset{\oplus}{P}Ph_3 \leftrightarrow Ph_3\overset{\oplus}{P}{-}CH{=}PPh_3 \equiv Ph_3P\overset{\cdot\cdot\cdot}{-}\overset{\oplus}{CH}\overset{\cdot\cdot\cdot}{-}PPh_3$ in which the ylidic proton is located between two phosphonium groups. In this system, the ylidic proton resonates[57] at τ8.0. In the proposed structure CXLIII, the ylidic proton would be in a similar, though not identical environment to that in $Ph_3P\overset{\cdot\cdot\cdot}{-}\overset{\oplus}{CH}\overset{\cdot\cdot\cdot}{-}PPh_3$, since in the system CXLIV one phosphorus atom is involved to some extent with two ylidic groupings and the CH group should be more highly shielded than in $Ph_3P\overset{\cdot\cdot\cdot}{-}\overset{\oplus}{CH}\overset{\cdot\cdot\cdot}{-}PPh_3$. The observed position of τ8.75 is in good agreement with this idea.

At 0°C the ^1H NMR spectrum of the adduct shows much the same pattern except that the methine and ylidic proton signals at τ5.1 and τ8.75 are much better defined as quintets and septets respectively with some peaks partially superimposed and the methoxy signal at τ6.86 is considerably broadened. At -20°C, no further improvement in the methine and ylidic proton signals is observed but the methoxy signal at τ6.86 is split into a very closely spaced doublet with a difference in chemical shift of less than 2Hz. Also at -20°C all peaks are shifted about 5Hz down field.

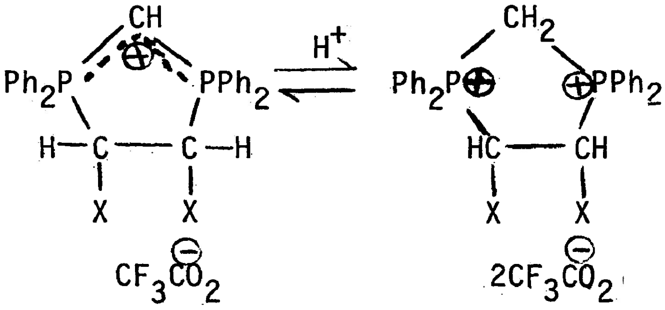
All of this is consistent with the structure CXLIII. Thus, rotational isomersof the type shown in CXLV and CXLVI would be expected to give rise to at least three and probably four methoxy signals. Furthermore, in the two rotational isomers, the normal ester group protons would be expected to have very similar chemical shifts. Further, because of the magnetic non-equivalence of the phosphorus atoms and rotational isomerism of the ylidic ester group, both the ylidic and methine protons would be expected to be octets and, in the ^{1}H NMR system at 0°C, both are observed as complex multiplets although, at 60MHz, resolution of these multiplets is poor. However, predictions of multiplicity in such bisphosphine or bisphosphonium systems should be treated with caution, since other workers have observed that, in these systems, $^{1}H-^{31}P$ couplings are frequently of lower multiplicity than expected.[58,59]

The ^{1}H NMR spectra in acidic solution are also of interest. Addition of two drops of trifluoroacetic acid to the solution of the adduct in $CDCl_3$ modifies the spectrum considerably. Both the methine and ylidic protons vanish from the spectrum and the ester protons are concentrated mainly in a singlet at $\tau 6.44$ although a low intensity doublet on the side of the main ester proton signal may be due to incomplete protonation of the ylide. Presumably in acid solution, the ylide CXLIII would protonate to CXLVII and a 2 proton signal corresponding to the methine protons would be expected at about $\tau 5.00$ by analogy with related systems.[12] However, in acidified $CDCl_3$ solution proton exchange is likely to be rapid and the signals would probably be very broad and diffuse. Examination of the ^{1}H NMR spectrum of the adduct thought to be CXLIII in $CDCl_3$ in the presence of a few drops of trifluoroacetic acid shows a very broad and very poorly defined multiplet at $\tau 5.1$ - 5.8 integrating for less than one proton.

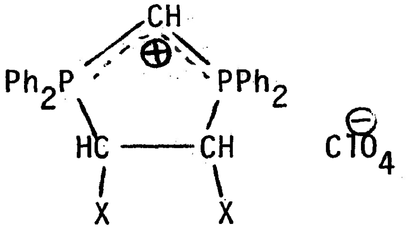
The ^{1}H NMR spectrum in pure trifluoroacetic acid (containing a little TMS as internal reference) at room temperature is different again. This spectrum shows 20 aromatic protons as a very broad hump



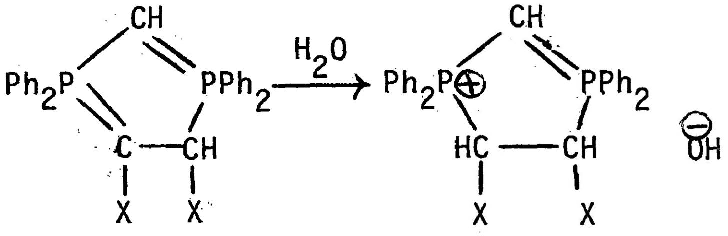
CXLVIII



CXLIX

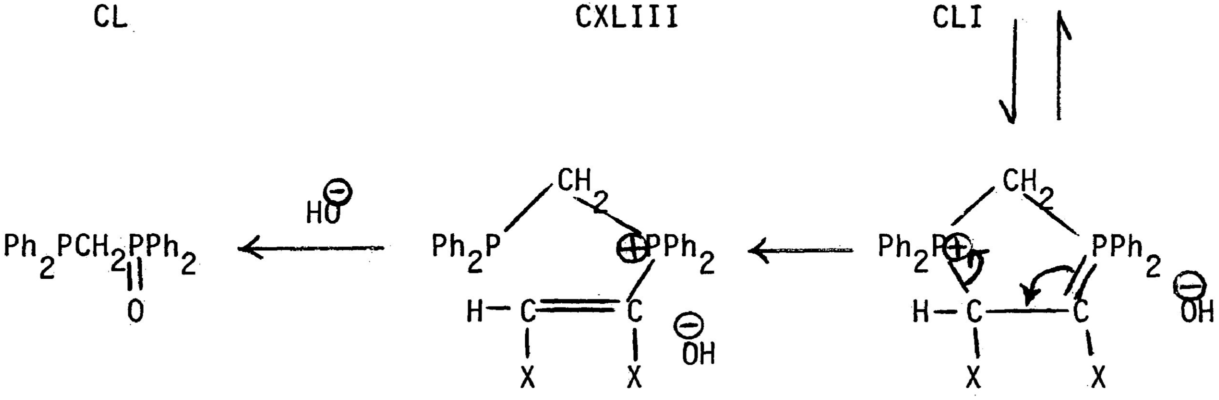


CL



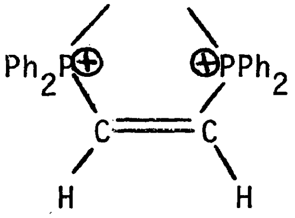
CXLIII

CLI



CLIII

CLII



X = CO_2Me

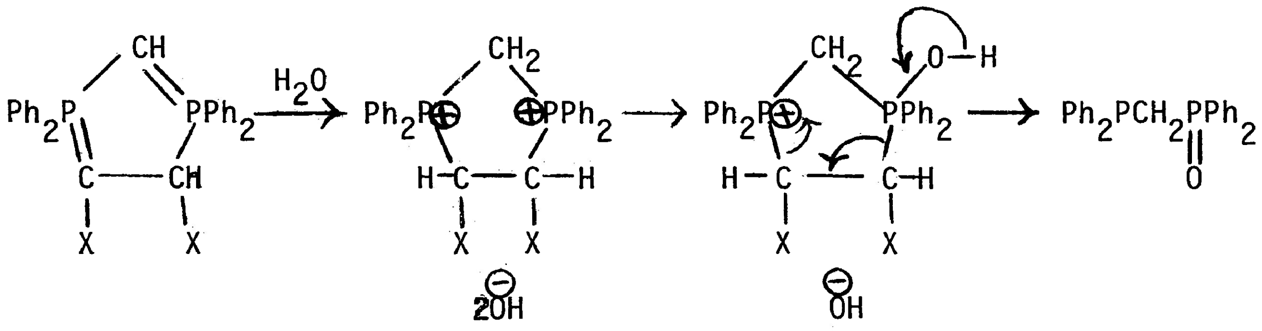
CLIV

at τ1.6 - 2.7, 6 methoxy protons as a sharp singlet at τ6.25 and between three and four protons as two very broad humps centred on τ4.34 and τ4.90 respectively with the first of these signals integrating for approximately 2 protons while the second is somewhat less intense. In strong acid solution, one would expect CXLIII to protonate to give the salt CXLVIII. This could account for the signals at τ4.34 and τ4.90, corresponding to the methine and methylene protons respectively. On the other hand, the $>P\overset{\cdots}{-}\overset{\oplus}{C}H\overset{\cdots}{-}P<$ grouping is quite resistant to protonation. Thus Driscoll^{57} found that $Ph_3P\overset{\cdots}{-}\overset{\oplus}{C}H\overset{\cdots}{-}PPh_3\ \overset{\ominus}{Cl}$ can be generated by addition of HCl to $Ph_3P{=}C{=}PPh_3$. Similarly, Hughes^{60} has found that the related system $Ph_3P\overset{\cdots}{-}\overset{\oplus}{N}\overset{\cdots}{-}PPh_3\ \overset{\ominus}{Cl}$ is converted into the corresponding perchlorate without protonation by addition of excess of perchloric acid. This suggests that, in strongly acid solutions of the adduct, the equilibrium CXLIX could be set up. This could account for the inequality of the signals at τ4.34 and τ4.90.

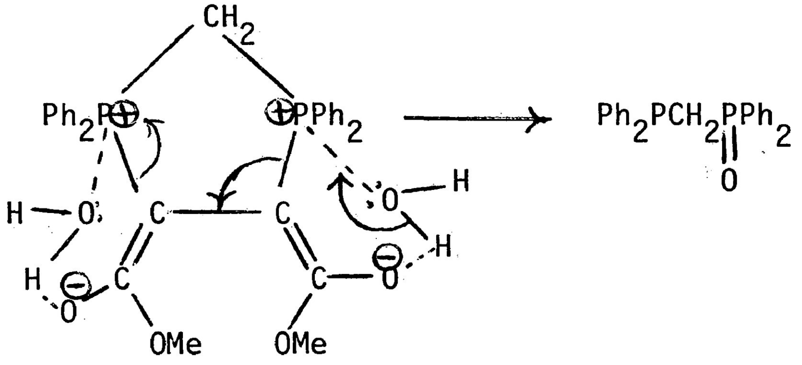
Some confirmation of this comes from the fact that on treatment with perchloric acid in methanol, the adduct forms a monoperchlorate corresponding to CL. Isolation of the perchlorate of the adduct in a pure crystalline state was achieved after much difficulty. A colourless sticky mass was obtained when perchloric acid was added to a solution of the adduct in various solvents such as benzene, methanol, and ethyl acetate. All efforts to crystallize this product failed. However, when the solid ylide was stirred with perchloric acid, a viscous liquid was initially obtained. After stirring the mixture for 2 hours at room temperature, aqueous methanol was added and the adduct was dissolved by warming the mixture. It was then left for crystallization. After allowing the mixture to stand for four days, white crystals were obtained. The IR spectrum shows the typical broad perchlorate peak around 1100cm^{-1} and only one carbonyl vibration at 1740 cm.$^{-1}$ Elemental analyses are in agreement with the monoperchlorate structure CL.

As expected in the ^{1}H NMR spectrum of the adduct in deuterotrifluoroacetic acid solution (with TMS as internal reference), only the aromatic and methoxy protons are observed.

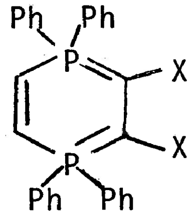
Some other chemical confirmation of the structure CXLIII for the adduct comes from the fact that on heating the adduct under reflux with aqueous methanol, the phosphine oxide CLIII (identified by its IR, ^{1}H NMR and mass spectrum) was obtained.



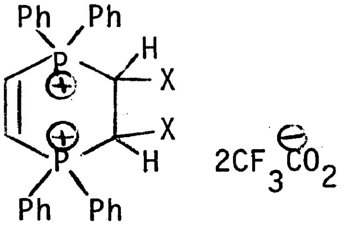
CXLIII CLV CLVI CLIII



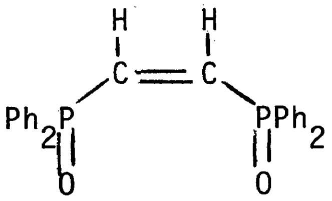
CLVII CLIII



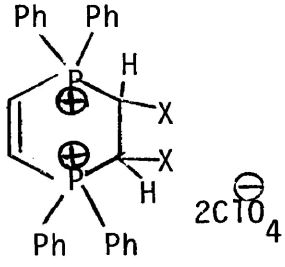
CLVIII



CLIX



CLX



CLXI

X = CO_2Me

Two possible mechanisms come to mind here. The first, shown in the sequence CXLIII → CLI → CLII → CLIII, is similar to that proposed by Tebby[11] for systems containing the $>P=C-C=P<$ linkage. The second, shown in the sequence CXLIII → CLV → CLVI → CLIII, is quite similar to the above and is also related to Aguiar's[44] mechanism for the elimination of acetylene from the bisphosphonia system CLIV on alkaline hydrolysis.

At this point, the investigation of the reaction of bis(diphenylphosphino)methane with dimethyl acetylenedicarboxylate was terminated (apart from completing experiments already in progress) since Tebby[61] published an account of essentially the same work.

There are only minor differences between the work described in this section and Tebby's account. For example, Tebby used 100 MHz ^1H NMR measurements and was able to show that in the ^1H NMR spectrum (in $CDCl_3$) of the adduct CXLIII, the signals at $\tau 5.0$ and $\tau 8.75$ are two overlapping triplets and an octet respectively. Further, in trifluoroacetic acid solution the adduct showed two clear 2 proton multiplets at $\tau 4.5$ and $\tau 5.05$ respectively ($\tau 4.34$ and $\tau 4.90$ in this account). Tebby also isolated the dioxide $Ph_2P(O)CH_2P(O)Ph_2$ as well as the monoxide CLIII from the hydrolysis of the adduct and also characterized the by-products dimethyl fumarate and dimethyl succinate among the hydrolysis products. On the basis of the formation of these products, he proposed an alternative mechanism for the hydrolysis as shown in the sequence CLVII → CLIII.

However, since the ylide CXVIII appears to produce only dioxide, this mechanism, if correct, is apparently not general. Tebby did not report the preparation of the perchlorate or any other salt of the adduct.

The Reaction of *cis* 1,2-Bis(diphenylphosphino) ethylene with Dimethyl Acetylenedicarboxylate

The rigid *cis* geometry of *cis* 1,2-bis(diphenylphosphino)ethylene (CXIII) suggested that conditions for a cyclization reaction with dimethyl acetylenedicarboxylate to give the bis-ylide CLVIII would be very favourable. This ylide would be particularly interesting since it is a potentially aromatic diphosphorin and the only other diphosphorin known to date is CV which was reported by Märkl.[42]

When a solution of dimethyl acetylenedicarboxylate in dry benzene was slowly added to a solution of the phosphine in dry benzene under nitrogen with constant stirring while maintaining the temperature of the reaction flask at about 8°C, a buff precipitate was obtained in 70% yield. Elemental analyses are consistent with a 1:1 adduct and the molecular weight of the adduct was confirmed as 538 by mass spectrometry.

The adduct is highly water sensitive and the IR spectrum shows only ylidic ester groupings, with ester carbonyl stretching frequencies at 1640 cm^{-1}, with lesser peaks at 1600 cm^{-1} and 1650 cm^{-1}. This is at somewhat higher wavenumber than the vibration of the carbonyl groups in the two ylides, CXVIII and CXLIII already described in this account.

This evidence so far is consistent with the structure CLVIII and this structure is further supported by the ^{1}H NMR spectrum in $CDCl_3$ at room temperature which shows 22 aromatic and olefinic protons as a broad complex multiplet at τ1.9 - 2.9 and six methoxy protons as a very broad unresolved hump at τ6.2 - 7.1. The appearance of the methoxy region is very similar to that of the ylide CXVIII although, because of the unsaturated nature of the *cis*-phosphine, it integrates for four protons less than for CXVIII.

At lower temperatures, the ^{1}H NMR spectrum becomes much clearer in the methoxy region. What is a broad hump at 42°C becomes at 20°C two very broad signals at τ6.47 and τ7.1 respectively with one or two other smaller peaks in the same general region. At 0° these two peaks are much sharper at τ6.37 and τ7.1 respectively, again with one or two other small peaks. Moreover, the two peaks are not of equal area and the peak at 6.37 has significantly greater area. At -40° the two peaks are further sharpened and occur at τ6.32 and τ7.1 respectively with the peak at τ6.32 almost twice the area of the other peak. Both peaks show signs of splitting into doublets although the splitting is unequal in the two signals.

This behaviour is consistent with the presence of a mixture of different conformational arrangements of the ester groups as outlined for the ylide CXVIII.

Addition of a few drops of trifluoroacetic acid to the ^{1}H NMR sample in $CDCl_3$ modifies the spectrum to show 22 aromatic and olefinic protons at τ1.8 - 2.8 and six methoxy protons at τ6.44. There is no sign of the methine protons which would be expected from the protonated structure CLIX and this is probably due to rapid exchange of these protons with the acid in the solvent. A few very weak peaks (much less than one proton) at the base of the methoxy peak suggests that protonation is incomplete.

The ^{1}H NMR spectrum in trifluoroacetic acid acid (with TMS as internal reference) is again different. This time, the 22 aromatic and olefinic protons occur as a multiplet at τ1.6 - 2.5 while the six methoxy protons appear as a singlet at τ6.27. The methine protons of CLIX occur as a broad hump at τ4.6 - 5.0. This picture is very similar to that presented by the ylide CXVIII in trifluoroacetic acid.

Thus, all spectroscopic evidence points to CLVIII as the structure for the adduct.

Chemical evidence also supports this structure. For example, on hydrolysis in aqueous ethanol, the adduct gives the dioxide CLX as the main product. The melting point and the IR, ^{1}H NMR and mass spectra of this dioxide were found to be identical with those of an authentic sample[45] of the dioxide. Further, the adduct forms a bisperchlorate analogous to that of the ylide CXVIII.

There is, therefore, no doubt that the structure of the adduct is as postulated-*i.e.* CLVIII.

As already noted, the carbonyl stretching frequencies of the adduct at 1640 cm^{-1} and 1650 cm^{-1} are at rather higher frequency than for CXVIII and at slightly higher frequency than for CXLIII. This suggests that there is somewhat less delocalization of the ylidic carbanion negative charge over the adjacent ester groups and this may imply that there is some delocalization of these electrons around the ring in an aromatic sextet. Furthermore, the ylide CXVI is bright yellow whereas the adduct CLVIII has a pale buff colour. On the other hand, CLVIII is more readily hydrolyzed than CXVIII and it is possible that the difference in spectra and reactivity are due to the small differences in molecular geometry causing minor differences in the efficiency of p_π-d_π overlap in the two cases.

^{31}P studies would be useful in considering the possible aromatic character of the ylide CLVIII.

Again, at this point, the investigation had to be terminated since Tebby[61] in his paper dealing with the bis-ylide CXLIII also published a brief account of the synthesis and reactivity of the ylide CLVIII by this method. However, there are minor differences between Tebby's results and those described here. For example, Tebby was unable to carry out any ^1H NMR studies, because of the reactivity of the adduct, whereas this author has found that the adduct is reasonably stable if kept under nitrogen. Further, Tebby did not report the formation of a perchlorate or any other salt of the ylide CLVIII.

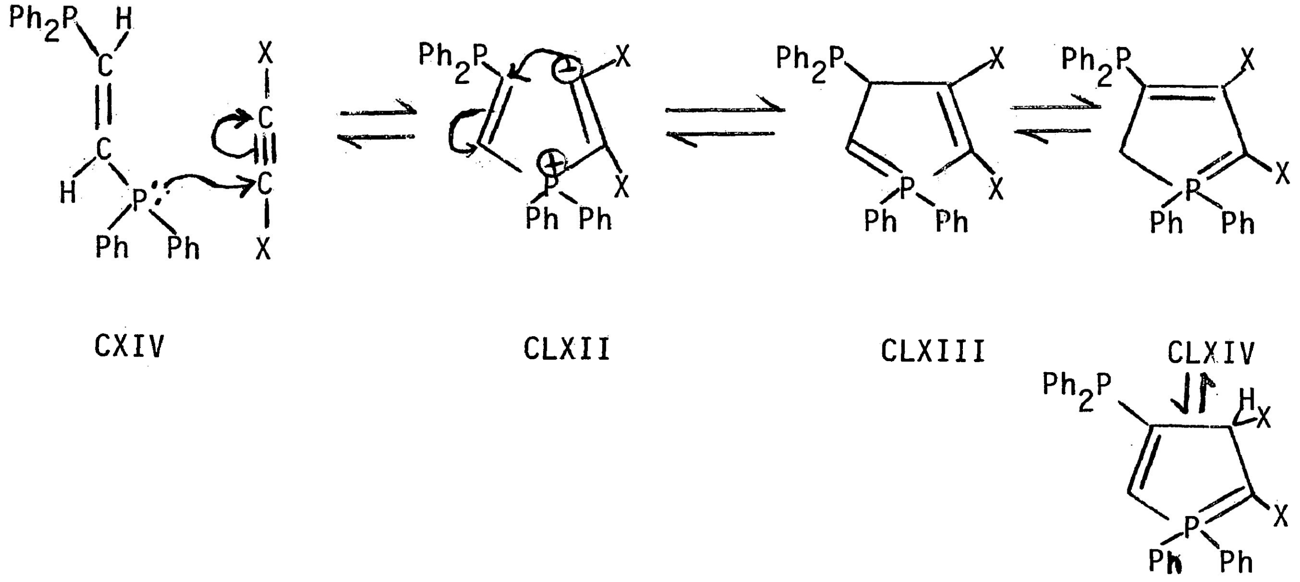
The Reaction of *Trans* 1,2-Bis(diphenylphosphino)-ethylene With Dimethyl Acetylenedicarboxylate

The results described in this section are unexpected and are quite difficult to interpret. Much of the discussion is, therefore, speculative. However, when all of the evidence is considered, it indicates that fairly positive conclusions can be drawn.

When a benzene solution of dimethyl acetylenedicarboxylate is added slowly, with constant stirring under a dry nitrogen stream, to a solution (in a benzene/pentane mixture) of the *trans* phosphine CXIV, keeping the temperature around 8°C, a light yellow precipitate is obtained. This adduct analyses well for a 1:1 adduct and is obtained in 69% yield. The mass spectrum confirms the 1:1 nature of the adduct and shows a molecular ion peak at *m/e* 538.

There are several possible modes of reaction which could give a 1:1 adduct. However, the *trans* geometry of the phosphine suggests that after attack of one phosphorus atom on the ester, it is unlikely that the second phosphorus atom will attack on the same ester to cause ring closure-*i.e.* the reaction should give a product different from the product CLVIII obtained from the *cis* phosphine CXIII, unless the *trans* geometry of the expected intermediate CLXV changes to *cis* before cyclization, if any, occurs. The IR spectrum of the adduct is totally different from that of the product CLVIII obtained from the *cis* phosphine CXIII.

The most likely reaction is cycloaddition of the type shown in the sequence CLXIV → CLXII ⇄ CLXIII ⇄ CLXIV ⇄ CLXV. This would be very similar to the reaction[22] between diphenylvinylphosphine and dimethyl acetylenedicarboxylate where similar tautomeric equilibria have been postulated. Furthermore, Trippett[25] has suggested equilibria of this type in the reaction of $Ph_2PCH(Ph){=}CH_2$ with acrylonitrile. Presumably, in any such equilibrium, the most stable tautomer would predominate.



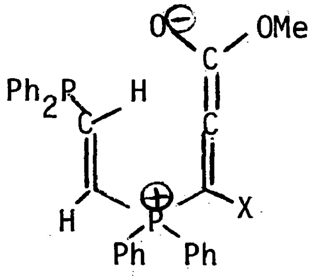
CXIV

CLXII

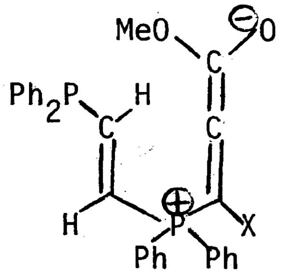
CLXIII

CLXIV

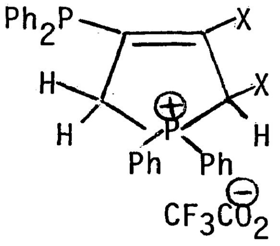
CLXV



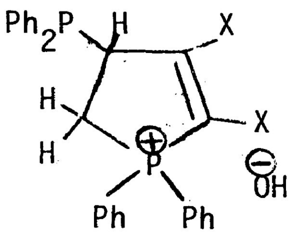
CLXVI



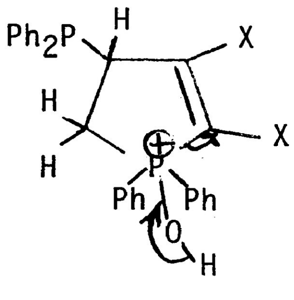
CLXVII



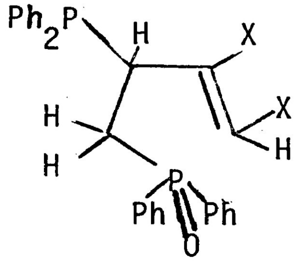
CLXVIII



CLXIX



CLXX



CLXXI

X = CO_2Me

As already mentioned earlier, the infrared spectrum of the adduct was found to be completely different from that of the *cis* phosphine adduct CLVIII. However, the IR spectrum does show two distinct carbonyl frequencies. One of these is at 1712 cm^{-1} and is clearly due to a normal ester carbonyl stretching vibration, while the other is at 1601 cm^{-1} with a smaller, though still intense, peak at 1585 cm^{-1}. These last peaks are, therefore, probably due to an ester carbonyl group adjacent to a carbon atom with appreciable carbanionic character. Superficially, this would suggest that the adduct is either CLXIV or CLXV with CLXIV the more likely by analogy[22] with the reaction of diphenylvinylphosphine and dimethyl acetylenedicarboxylate.

Unfortunately, the ^1H NMR spectrum of the adduct is definitely not consistent with CLXIV and probably not consistent with CLXV or CLXIII. The ^1H NMR spectrum shows 20 aromatic protons as a complex multiplet at τ2.18 - 3.32, one apparently olefinic proton as two poorly defined quartets centred on τ3.63 and τ4.04 respectively and six methoxy protons as three peaks of unequal area at τ6.15, τ6.28 and τ5.69. At -50°C, the spectrum is much the same apart from small downfield shifts and better definition of the two quartets except that the methoxy signal which occurs at τ6.15 in the room temperature spectrum appears as a very closely spaced doublet at τ6.01 and τ6.03.

The ^{1}H NMR spectrum in the methoxy region is consistent with the infrared spectrum in that it indicates that one of the ester groups is adjacent to a carbanionic centre and shows conformational preference as outlined previously in this thesis. However, this would also apply to CLXII where the only non-aromatic protons are olefinic and where one ester group is adjacent to a carbanionic centre. Major contributors to the resonance hybrid of CLXII would be CLXVI and its rotational isomer CLXVII.

The multiplicity of the olefinic proton signal is of interest. Presumably the two fairly widely separated quartets (*ca.* 25Hz) could be the result of the conformational preference of the methoxy carbonyl group as in CLXVI and CLXVII and its effect upon the proton β to the phosphonium centre. One might perhaps expect this proton to appear under the aromatic signal but it has been shown that in some related structures such as *trans* $Ph_2PCH=CHPPh_2$, *cis* $Ph_2P(O)CH=CH(O)PPh_2$ and *cis* $Ph_2P(S)CH=CH(S)PPh_2$, the ethylene bridge protons resonate[59] between τ3.0 and τ3.5. Further, the close proximity of the carbanion negative charge to this proton would be expected to shield it to some extent. In theory, ignoring conformational preference, an octet would be expected for this proton due to coupling with the other olefinic hydrogen and the two different phosphorus atoms but it is well known[58,59] that the protons on the bridging carbon atoms of bisphosphines show less that the normal multiplicity and, in the opinion of the author, the octet is probably due to conformational preference although the difference in chemical shift of the two quartets (25 Hz) is within the normal J_{PH} coupling range for similar[59] bridged phosphines.

Thus, of the possible structures considered so far, only CLXII (best represented as CLXVI or CLXVII) is fully consistent with both the ^1H NMR and IR spectra, although the reasons why this tautomer should be preferred over the other possible tautomers in the equilibrium are obscure.

The ^1H NMR spectrum of the adduct in trifluoroacetic acid gives further information although the spectrum itself is rather unexpected. The spectrum of a freshly prepared solution in CF_3CO_2H (with TMS added) shows, at room temperature, a ratio of approximately twenty aromatic protons at τ1.6 - 2.8 to approximately one proton as a diffuse multiplet at τ4.3 - 5.1 to approximately six methoxy and two methylene or methine protons as a complex multiplet between τ5.60 and τ6.65. One striking feature of this last region is that each of the two methoxy groups appears as a narrow doublet centred on τ6.98 and τ6.42 respectively. The peaks of each doublet are of unequal area. Clearly, these methoxy signals cannot be due to conformational preference relative to a carbanionic centre since the solution is strongly acidic. It seems likely then that the spectrum is caused by a mixture of isomers caused by protonation of two (or more) of the tautomers in the previously suggested equilibrium.

The ^1H NMR in CF_3CO_2D is similar except that the multiplet at τ4.3 - 5.1 is absent. Presumably these protons are provided by the acid or are rapidly exchanged with the acidic solvent.

Some evidence for the idea that the spectrum is caused by a mixture is given by the observation that if the acid solution is allowed to stand for several days, the spectrum is modified to show twenty aromatic protons as a multiplet at $\tau 1.5 - 2.8$, one methine proton as a doublet (J=13Hz) at $\tau 4.49$, two methoxy groups as singlets at $\tau 5.95$ and $\tau 6.45$ respectively and two methylene protons as a multiplet hidden under the methoxy protons in the range $\tau 5.6 - 6.3$. All of these peaks are present in the spectrum of the freshly prepared solution.

These observations are consistent with the idea that two or more of the postulated tautomers in the original ylide equilibrium are protonated by the trifluoroacetic acid but that further equilibria between ylide tautomers and protonated ylide tautomers lead to an increasing amount of the more stable protonated form.

Of the various protonated tautomers possible from the originally postulated equilibrium, only CLXVIII (derived from CLXIV) agrees in every respect with the ^1H NMR spectrum of solution of the adduct in CF_3CO_2H which has been allowed to stand for several days. Thus the methine proton at $\tau 4.49$ is virtually identical in location and splitting with the similar protons in CXXXIX, CLIX and CXLIX, while the multiplicity of the methylene protons is similar to that of the similar protons in CXXXIX.

To summarize, the IR and ^{1}H NMR evidence indicates that the 1:1 adduct of the *trans* 1,2-bis(diphenylphosphino)ethylene (CXIV), with dimethyl acetylenedicarboxylate is an equilibrium of the structures CLXII, CLXIII, CLXIV, and CLXV in which the zwitterionic form CLXII greatly predominates over the other forms. However, in the presence of acid, the ylidic contributors to the equilibrium are more reactive and are protonated more readily than the zwitterionic form. This may also be true in the reactions of 1-phenylvinyldiphenylphosphine (LV) with acrylonitrile[25] and of diphenylvinylphosphine with dimethyl acetylenedicarboxylate where[22] the initial 1:1 adduct has not been isolated and conclusions regarding the nature of the adducts have been drawn solely on the basis of their chemical reactions.

Chemical reactions indicate that an ylidic contributor is the reactive form present in the equilibrium but, again, very unexpected results were obtained and these have proved quite difficult to interpret.

If the adduct has appreciable ylidic character, it should hydrolyze in the manner of an ylide to give[46] a phosphine oxide. However, when the adduct was dissolved in aqueous ethanol and warmed with stirring for several hours, the oxide XLVI was formed which is identical with the hydrolysis product obtained from the 1:1 adduct of diphenylvinylphosphine with dimethyl acetylenedicarboxylate[22] *i.e.* one of the diphenylphosphino groups has been lost. The m.p. and the IR, ^{1}H NMR and mass spectra of this product are identical in all respects with those of an authentic sample.[23]

This reaction is completely unexpected and is very difficult to account for. However, one possible mechanism is as follows.

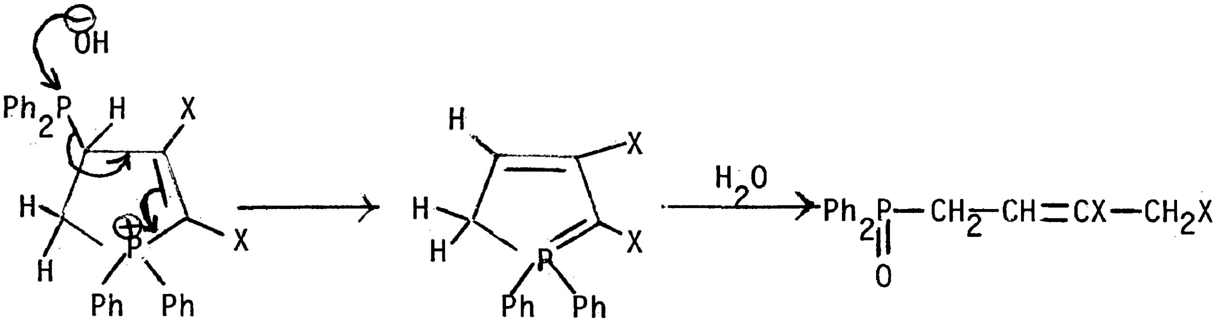
Presumably, the first step in the hydrolysis would be protonation of the most reactive tautomer to give a phosphonium hydroxide. In the proposed ylide/zwitterion equilibrium, the most reactive tautomer would probably be CLXIII, since in this case, the ylidic negative charge is stabilized only by overlap with the d-orbitals of the phosphorus atom and is not delocalized in any way. Protonation of this ylide by water would give CLXIX.

It would be expected that normal rearrangement of this phosphonium hydroxide would involve attack of hydroxide ion upon the phosphonium grouping followed by apical elimination of the most stable carbanion to give a phosphine oxide as shown in the sequence CLXX → CLXXI.

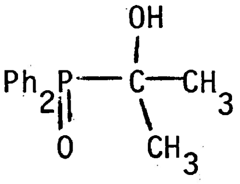
On the other hand, it is well known[62] that in phosphonium compounds, nucleophilic attack may take place at the atom β to the phosphorus atom as in the sequence $R_3\overset{+}{P}-X-Y\ \ddot{N}u \rightarrow R_3\overset{+}{P}-\overset{-}{X}$.

In the structure CLXIX the diphenylphosphino group is not β to the phosphonium group but is vinylogously β to this group and attack of the kind shown in the sequence CLXIX → XLV → XLVI could conceivably occur. This would generate the intermediate XLV which was also postulated[22] in the reaction of diphenylvinylphosphine with dimethyl acetylenedicarboxylate and which could hydrolyze as observed by Davies[22] to give the product XLVI. Again, it is not clear why hydroxide ion should prefer, in this case, to attack by the postulated route rather than by the more conventional route of attack on the phosphonium centre.

Deuterolysis experiments give some support to this mechanism since the compound CLXXII is

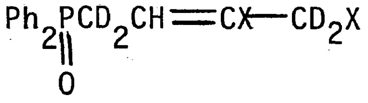


CLXIX XLV XLVI



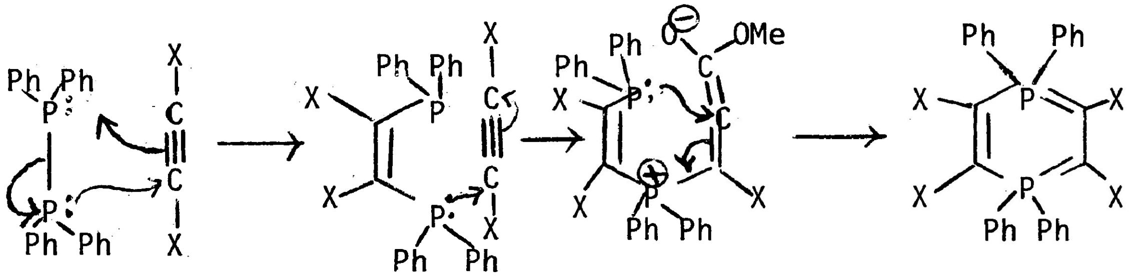
$Ph_2P(O){-}C(OH)(CH_3){-}CH_3$

CLXXIII

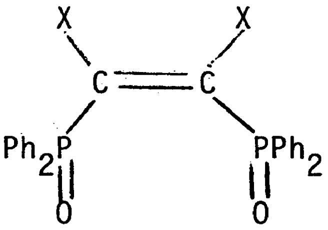


$Ph_2P(O)CD_2CH{=}CX{-}CD_2X$

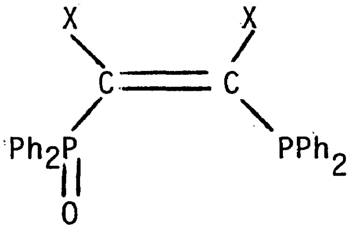
CLXXII



CXV CLXXIV CLXXV



CLXXVI



CLXXVII

X = CO_2Me

produced by treatment of the 1:1 adduct of the *trans* phosphine CXIV with the acetylenic ester with deuterium oxide.

Accurate integrations taken by means of signal averaged ^{1}H NMR spectra show clearly that the olefinic hydrogen atom in this compound is not replaced by deuterium although all the other non-aromatic, and non-ester protons are replaced by deuterium. This is confirmed by the mass spectrum which shows a molecular ion at *m/e* 376 corresponding to the replacement of four hydrogen atoms by deuterium. This is consistent with the proposed mechanism since the olefinic proton in the products XLVI and CLXXII is derived from the proton adjacent to the displaced Ph_2P group and is not particularly activated. On the other hand, the other protons in XLVI are derived either from the solvent or are adjacent to a phosphonium group and, under the basic conditions of the reaction, these protons should be exchangeable with the deuterium oxide solvent.

One other point regarding the ^{1}H NMR spectra of XLVI and CLXXII is that the original ^{1}H NMR assignment by Davies[22] of the poorly defined multiplet at τ2.6-3.3 to the olefinic proton in the compound XLVI appears to be incorrect since the multiplicity of this signal in the spectrum of CLXXII remains unchanged, whereas it should collapse to a doublet. This signal is, therefore, probably due to the aromatic ring protons while the olefinic proton signal is, probably buried under the main aromatic signal.

In the hydrolysis of the 1:1 adduct, the fate of the missing Ph_2P-group is uncertain. However, in one experiment in which the crude hydrolysis product had been exposed to acetone, a very small amount of a colourless compound was obtained. This compound showed no significant peaks in the mass spectrum above *m/e* 201 ($Ph_2P{=}O$) and the IR and ^1H NMR spectra and analyses are consistent with the structure CLXXIII which could be formed by the addition of $Ph_2P(O)H$ to acetone. The compound was unstable in solution and repeated ^1H NMR scans of the same sample showed that acetone is regenerated over a period of several hours. Unfortunately it proved impossible to duplicate this experiment with the limited quantities of the 1:1 adduct available. Such additions of phosphine derivatives to carbonyl functions are well known.[63]

Repeated attempts to form a hydrobromide or a perchlorate were unsuccessful as only uncrystallizable oils and gums were obtained.

The adduct reacts with acetone to give resinous products which could not be separated even by chromatography.

The Reaction of Tetraphenylbiphosphine With Dimethyl Acetylenedicarboxylate

This experiment was carried out for two reasons. First, the reactions of dimethyl acetylenedicarboxylate with bisphosphines containing both one and two carbon atoms between the phosphorus atoms and with both non-rigid and rigid bridges between these phosphorus atoms had been studied in detail and the case with no bridging carbon atoms would be of interest. Second, the P-P bond is easily cleaved[64] and a possible reaction path of the tetraphenylbiphosphine with dimethyl acetylenedicarboxylate could be as shown in the sequence CXV → CLXXV.

This could be a one step synthesis of the 1,4-diphosphorin system from the P-P bond by a method related to the cyclizations already discussed.

Treatment of the biphosphine with dimethyl acetylenedicarboxylate (both 1:1 and with an excess of the ester) in dry benzene under nitrogen gave a dark brown solution of what appeared to be mainly tarry and polymeric materials. However, very small quantities of a colourless solid were obtained. The mass spectrum showed a strong molecular ion peak at *m/e* 544 with a lesser peak at *m/e* 528. These correspond to the dioxide CLXXVI and monoxide CLXXVII respectively.

Elemental analyses are consistent with the dioxide CLXXVI but agree better with the monoxide CLXXVII. The ^{1}H NMR spectrum shows a broad aromatic signal and one major and one or two minor peaks in the methoxy region. The integration agreed approximately with the ratio of 20 aromatic protons to a total of six methoxy protons. Thus it seems likely that the adduct is a mixture of the mono and dioxide and this is supported by the IR spectrum which shows several peaks in the normal P=O stretching range around 1200-1150 cm^{-1} (see experimental section).

The origin of the oxygen atoms is not clear. Every effort was made to exclude water and air from the reaction while it was proceeding but no particular precautions were taken during the work-up. The product could, therefore, be derived from CLXXIV by atmospheric oxidation or from CLXXV by ylide hydrolysis.

Attempts to work-up the reaction mixture in a glove box to exclude all air and moisture gave only tarry materials and the reaction was, therefore, abandoned as being unsuitable for the convenient synthesis of phosphorus heterocycles containing two phosphorus atoms.

Conclusion

The bisphosphines 1,2-bis(diphenylphosphino)-ethane (CXI), bis(diphenylphosphino)methane (CXII) and *cis* 1,2-bis(diphenylphosphino)ethylene (CXIII) react readily and smoothly with dimethyl acetylenedicarboxylate to form cyclic phosphonium bis-ylides in high yield. Therefore, although much further work needs to be done, this type of reaction can be said to be general and of synthetic value.

Trans 1,2-bis(diphenylphosphino)ethylene (CXIV) also reacts readily with the acetylenic ester to give a 1:1 adduct which, from spectroscopic and chemical studies, seems to have largely zwitterionic character but undergoes some of the reactions of an ylidic structure. Hydrolysis of this adduct follows an unexpected course in which one of the diphenylphosphino groups is eliminated to give a product which is identical with that obtained from diphenylvinylphosphine, dimethyl acetylenedicarboxylate and water. A possible mechanism for this hydrolysis is supported by deuterolysis studies.

It would be useful to extend the work to reactions of bisphosphines and biphosphines with other unsaturated electrophiles such as propiolic esters and phenylpropiolic esters. One other electrophile which should be studied in this reaction is hexafluoro-2-butyne where resonance stabilization of ylidic or zwitterionic negative charge would not be possible in any adducts which may be formed. ^{31}P studies of dimethyl 1,1,4,4-tetraphenyl-1,4-diphosphorin-2,3-dicarboxylate should be undertaken in relation to the possible aromatic character of the system. Similar studies should also be carried out for the 1:1 adduct of *trans* 1,2-bis(diphenylphosphino)ethylene with the acetylenic ester to establish the chemical environment of the two phosphorus atoms.

Note Added in Proof

During the final proof reading, it was found that each of three structures inadvertently had been assigned two structure numbers in the diagrams. It was felt that correcting all structure numbers in the text and diagrams would probably introduce more errors than were corrected and it was therefore decided to allow the dual numbering to stand. This makes no difference to the arguments used in the text but, to avoid ambiguity, both of the assigned numbers for a given structure have been indicated on certain of the diagrams.

EXPERIMENTAL

INTRODUCTION

Solvents, where necessary, were dried as follows: diethylether was dried by heating under reflux with lithium aluminium hydride ($LiAlH_4$) while benzene and pentane were dried by heating under reflux with calcium hydride (CaH_2). All solvents were distilled just before use.

Nitrogen (high purity grade) was dried by passage first through concentrated sulphuric acid and then through sodium hydroxide pellets.

Perkin-Elmer 137 and Beckman IRI2 spectrophotometers were used for recording the IR spectra and the calibration of the instruments was checked against a standard polystyrene film. In all cases, a Nujol mull was prepared and demountable sodium chloride cells were used.

A Unicam SP800 spectrophotometer was used for recording UV spectra. Spectroscopic grade chloroform was used as the solvent and 1 cm fused silica cells were employed for all the UV measurements. The calibration of the instrument was checked using a holmium filter.

The ^{1}H NMR spectral measurements were made using a Varian model A60-A spectrometer. The samples were dissolved in deuterated chloroform ($CDCl_3$), trifluoroacetic acid (CF_3CO_2H) or deuterated trifluoroacetic acid (CF_3CO_2D) with tetramethylsilane (TMS) as the internal standard. ^{1}H NMR signal averaging measurement were carried out on a Varian Data Systems model 620 I unit. These measurements were made to improve integrator accuracy and to record the spectra of very dilute samples.

An Hitachi-Perkin Elmer RMU-7 double-focussing mass spectrometer, using (usually) a direct inlet system, was used to measure the mass spectra. For a few volatile solids, better results were obtained using the liquid sample inlet.

All melting points are uncorrected and were determined using a high temperature Electrothermal melting-point apparatus.

Elemental analyses were performed by Dr. Franz Pascher of Bonn and Dr. W.J. Buis of Utrecht.

The Reaction of 1,2-Bis(diphenylphosphino)ethane with Dimethyl Acetylenedicarboxylate.

Dimethyl acetylenedicarboxylate (2.8 g, 100% excess) was dissolved in benzene (40 ml) and to this solution was added a solution of 1,2-bis(diphenylphosphino)ethane (3.98 g) in benzene (20 ml) slowly at room temperature under a slow stream of dry, oxygen-free nitrogen with constant stirring. A yellow coloration developed at once and, during the addition, a powdery bright yellow precipitate appeared. When the addition was complete, a thick, bright yellow precipate was obtained.

The precipitate was carefully filtered under a stream of nitrogen, washed with benzene and then with ether. It was then heated under reduced pressure (*ca.* 1 Torr) for several hours at 50°C to remove residual solvent. The crude bright yellow ylide dimethyl 1,1,4,4-tetraphenyl-1,4-diphosphacyclohexa-1,3-diene-2,3-dicarboxylate (CXVIII) was obtained in 81.6% yield (4.41 g). A small amount (1.278 g) of the crude adduct was recrystallized from hot benzene and the recrystallized product was again heated for several hours at 50°C under reduced pressure (8×10^{-6} Torr) to remove trapped solvent. The pure adduct was obtained as bright yellow crystals, m.p. 140-150° (decomp.), in 64.5% yield (0.81 g) (Found: C, 69.46; H, 5.88; P, 12.8; $C_{32}H_{30}O_4P_2$ requires: C, 71.11; H, 5.55; P, 11.48%). As outlined in the discussion, the analyses are poor because of varying amounts of occluded benzene.

The IR spectrum shows ν_{max} at 1594, 1585 (ylidic $\geq$C=O stretching), 1445, 1330, 1280 1270, 1180, 1115, 1100, 910, 860, 820, 760, 745, 720, 715, and 650 $cm.^{-1}$

The UV spectrum in chloroform shows λ_{max} at 375 mμ. The ^1H NMR spectrum in deuterated chloroform shows 20 aromatic protons at τ2-2.85, between two and six benzene protons (close to six on very freshly prepared samples) as a very sharp singlet at τ2.68 and ten methoxy protons as a very broad and poorly defined signal between τ6.1 and τ8.0. The ^1H NMR spectrum of the ylide (CXVIII) in deuterated chloroform with a few drops of CF_3CO_2H added shows 20 aromatic protons at τ2.0 - 2.6, between 2 and 6 benzene protons (according to the age of the sample) at τ2.68 and ten methylene and methoxy protons at τ6.1-7.3 with the methoxy protons as a sharp singlet at τ6.57. The two apparently missing methine protons appear in the spectrum as a broad hump at τ4.67

when the ^{1}H NMR spectrum of the ylide is recorded in pure trifluoroacetic acid (with TMS added).

The spectrum in CF_3CO_2D is virtually identical with that recorded in CF_3CO_2H except that the methine protons, as expected, are not observed.

The mass spectrum shows a weak molecular ion peak at *m/e* = 540.

Hydrolysis of Dimethyl 1,1,4,4-Tetraphenyl-1,4-diphosphacyclohexa-1,3-diene-2,3-dicarboxylate (CXVIII).

The ylide CXVIII (0.8 g) was mixed with water (3 g) and stirred at 70°C for 5 hours. The resulting colourless solution was extracted with chloroform. The chloroform layer, containing the dioxide (CXIX), was separated and dried over anhydrous magnesium sulphate and the solution was filtered and then evaporated to dryness under reduced pressure. The crude dioxide was obtained as a colourless solid (0.42 g, 66%) which was further recrystallized from acetone to give colourless crystals, m.p. 275°C (m.p. of a authentic sample was 276-277°C).

The IR spectrum shows ν_{max} at 1440 (P-Ph) 1350, 1330, 1190 (strong, P=O), 1130, 1120, 1100, 1080, 1045, 1000, 935, 870, 770, 755, 745, 735, 715, and 700 cm.$^{-1}$

The mass spectrum shows a strong molecular ion peak at *m/e* 430.

Preparation of the Bisperchlorate of Dimethyl 1,1,4,4-Tetraphenyl-1,4-diphosphacyclohexa-1,3-diene-2,3-dicarboxylate (CXVIII)

The ylide CXVIII (1 g) was dissolved in warm methanol (3 ml) and cooled to room temperature. To this solution was added dropwise, perchloric acid (1 ml) and a colourless solution was obtained. By careful heating, the volume was reduced to half and the solution was left for crystallization. After a few hours, colourless crystals were obtained. These were filtered and then washed with a little cold methanol. The crystals were then pumped for several hours at room temperature under reduced pressure (*ca.* 1 Torr). The pure perchlorate was obtained in 38% yield (0.52 g).
(Found: C, 51.75; H, 4.15; Cl, 9.63; P, 8.11. $C_{32}H_{32}O_{12}Cl_2P_2$ requires: C, 51.82; H, 4.31; Cl, 9.58; P, 8.36%).

The IR spectrum shows ν_{max} at 1740 (normal $>C=O$ stretching), 1580, 1445 (P-Ph), 1270, 1105-1055 (broad typical perchlorate vibration), 1000, 915, 865, 830, 815, 770, 740, and 680 cm.$^{-1}$

The Reaction of Bis(diphenylphosphino)methane with Dimethyl Acetylenedicarboxylate

A solution of bis(diphenylphosphino)methane (3.07 g) in diethylether (50 ml) was added slowly to an ether solution of dimethyl acetylenedicarboxylate (1.14 g in 10 ml) under a slow stream of dry nitrogen at room temperature with constant stirring. A cream-coloured precipitate was obtained which was filtered, washed with ether and pumped under reduced pressure (*ca.* 1 Torr) at 60°C for 3 hours.

Dimethyl 1,1,3,3-Tetraphenyl-5*H*-1,3-diphosph(V)ole-4,5-dicarboxylate was obtained as a powdery cream-coloured solid (2.85 g, 67%), m.p. 150° (decomp.). The crude product was recrystallized from benzene. (Found: C, 70.36, H, 5.18; P, 12.05. $C_{31}H_{28}O_4P_2$ requires: C, 70.7; H, 5.3, and P, 11.8%).

The IR spectrum shows ν_{max} at 1740 (normal $>$C=O stretching), 1605 ($>$C=O group attached to ylidic carbon atom), 1440 (P-Ph), 1330, 1290, 1155, 1105, 1100, 1095, 940, 900, 860, 780, 750, 700, and 670 $cm.^{-1}$ The UV spectrum in $CHCl_3$ shows λ_{max} at 300 mμ.

The ^1H NMR spectrum in deuterated chloroform shows 20 aromatic protons as a complex multiplet at τ1.6-3.0, one methine proton as a multiplet of at least five peaks centred on τ5.0, six methoxy protons as three peaks of unequal area at τ6.51, 6.68 and 6.86, and one other proton as a multiplet at τ8.75 at room temperature.

The ^{1}H NMR spectrum of the ylide CXLIV in $CDCl_3$ at 0°C shows almost the same pattern except that the methine and ylidic proton signals at τ5 and τ8.75 are much better defined as quintets and septets respectively and the methoxy signal at τ6.86 is considerably broadened. At -20°C the only difference noticed is in the splitting of the methoxy signal at τ6.86 into a very closely spaced doublet. The ^{1}H NMR in $CDCl_3$ with a few drops of CF_3CO_2H added shows a considerably modified spectrum and the ^{1}H NMR spectrum in pure CF_3CO_2H (with TMS) is much more consistent with the protonated structure CXLVIII. In this case the spectrum shows 20 aromatic protons as a very broad hump at τ1.6-2.7, 6 methoxy protons as a sharp singlet at τ6.25 and between three and four protons as two very broad humps centred on τ4.34 and τ4.9 respectively with the first of these signals integrating for approximately 2 protons, while the second is somewhat less intense.

In CF_3CO_2D solution, as expected, only the aromatic and methoxy protons are observed.

The mass spectrum shows a molecular ion peak at *m/e* 526.

Formation of the Perchlorate of Dimethyl 1,1,3,3-Tetraphenyl-5*H*-1,3-diphosph(V)ole-4,5-dicarboxylate (CXLIV)

To the ylide CXLIV (0.1 g) was added perchloric acid (0.5 ml, 75%) dropwise with constant stirring under a stream of nitrogen. A viscous colourless liquid was obtained to which was added warm methanol (0.5 ml). The solution was then left for crystallization. After four days, colourless crystals were formed and these were filtered and washed with pentane followed by a little ether. The crystals were pumped under reduced pressure (*ca.* 1 Torr) at 50°C for 4 hours to give the pure monoperchlorate CL (30 mg, 25%).

(Found: C, 56.78; H, 4.70; Cl, 5.63 P, 10.07. $C_{31}H_{29}O_8ClP_2$ requires: C, 59.37; H, 4.62, Cl, 5.68; P, 9.89%).

The IR spectrum shows ν_{max} at 1740 (normal $>$C=O stretching), 1580, 1445(P-Ph) 1270, 1105-1055 (broad typical perchlorate peak), 1000, 915, 865, 830, 815, 700, 740, and 680 cm^{-1}

Hydrolysis of Dimethyl 1,1,3,3-Tetraphenyl-5*H*-1,3-diphosph(V)ole-4,5-dicarboxylate (CXLVI)

The crude ylide CXLIV (0.1 g) was mixed with aqueous sodium hydroxide solution (6 ml, 25%)

and stirred at 80° for 2 hours when the pale yellow colour was discharged. The reaction mixture was extracted with chloroform (50 ml) and the chloroform layer was separated and washed several times with water to remove excess of base. The neutral organic layer was separated, dried over anhydrous magnesium sulphate, filtered and than evaporated to dryness to give the crude monoxide CLIII as a white solid (60 mg, 74%).

The crude oxide was further recrystallized from hot acetone (10 ml) when white cotton-like crystals were obtained. These crystals were filtered and pumped under reduced pressure at 60° to give the pure oxide CLIII (20 ml, 33%), m.p. 186° (lit.[65] m.p. 185°).

The IR spectrum shows ν_{max} at 1440 (P-Ph), 1180 (P=O), 1130, 785, 770, 750, 740, 720, and 650 $cm.^{-1}$

The mass spectrum shows a molecular ion peak at *m/e* 400.

The Reaction of *Cis* 1,2-Bis(diphenylphosphino)-ethylene with Dimethyl Acetylenedicarboxylate

Cis 1,2-Bis(diphenylphosphino)ethylene (4.75 g) was dissolved in benzene (500 ml) and to this was added dropwise a solution of dimethyl acetylenedicarboxylate (1.744 g) in benzene (100 ml) under a dry nitrogen stream with constant stirring while maintaining the temperature of the reaction flask around 8°C.

After the addition was over, a buff precipitate was formed which was filtered, washed with benzene and then pumped under reduced pressure (*ca.* 1 Torr) at 50°C for 4 hours. The dry ylide CLVIII was obtained as a buff powder (4.76 g, 73%).

The ylide CLVIII is highly water sensitive and it was therefore not possible to recrystallize it since it hydrolyzed rapidly even in quite rigorously dried solvents.

(Found: C, 69.45; H, 5.41; P, 11.06. $C_{32}H_{28}O_4P_2$ requires: C, 71.37; H, 5.24; P. 11.52

The IR spectrum shows ν_{max} at 1640, 1600 (ylidic $>$C=O stretching), 1440 (P-Ph), 1340, 1310, 1260, 1160, 1120, 740, 710, 695, and 670 $cm.^{-1}$

The ^1H NMR spectrum in $CDCl_3$ at room temperature shows 22 aromatic and olefinic protons as a broad complex multiplet at τ1.9-2.9 and six methoxy protons as a very broad unresolved hump at τ6.2-7.1. The ^1H NMR spectrum becomes much clearer in the methoxy region at lower temperature. The broad hump at 42°C becomes at 20°C two very broad signals at τ6.47 and τ7.1 respectively, with one or two other smaller peaks in the same region. At 0°C these two peaks are much sharper at τ6.37 and τ7.1. respectively, with one or two small peaks as before. At -40°C the two peaks become well defined and occur at τ6.32 and τ7.1.

Addition of a few drops of CF_3CO_2H to the sample in $CDCl_3$ modified the spectrum to show 22 aromatic and olefinic protons at τ1.8-2.8 and six methoxy protons at τ6.44. There was no sign of the expected methine protons. However, the ^{1}H NMR spectrum of the ylide CLVIII in pure CF_3CO_2H (with TMS added) shows 22 aromatic and olefinic protons as a multiplet at τ1.6-2.5 while the six methoxy protons occur as a singlet at τ6.27. The methine protons of CLIX occur as a broad hump at τ4.6-5.0.

The mass spectrum shows a molecular ion peak at *m/e* 538.

Hydrolysis of Dimethyl 1,1,4,4-Tetraphenyl-1,4-diphosphorin-2,3-dicarboxylate (CLVIII)

The ylide CLVIII (200 mg) was mixed with an excess of 1:1 aqueous ethanol and stirred for five hours at room temperature. During this time, the dark brown solution became almost colourless. The solution was allowed to stand at room temperature for two days and a white precipitate slowly settled down. This was filtered, washed with acetone and pumped under reduced pressure (*ca.* 1 Torr) to give the dioxide CLX (110 mg, 68%). The dioxide was further recrystallized from a 1:1 mixture of ethanol and acetone to give colourless crystals, m.p. 244°C (lit.[45] m.p. 244°-245°C).

The IR spectrum shows ν_{max} at 1440 (P-Ph) 1230, 1200 (P=O), 1185, 1175, 1120, 1100, 1030, 1000, 930, 780, 765, 750, 730, 710, 700, and 670 $cm.^{-1}$

The mass spectrum shows the molecular ion peak at *m/e* 428.

Preparation of the Bisperchlorate of the Ylide Dimethyl 1,1,4,4-Tetraphenyl-1,4-diphosphorin-2,3-dicarboxylate (CLVIII)

To the solid ylide CLVIII (200 mg) was added, with constant stirring and under a nitrogen stream, perchloric acid (1 ml) dropwise at room temperature. After about ten minutes the solid initially buff mass became colourless. The mixture was stirred for another 30 minutes and then methanol (3 ml) was added. The mixture was warmed briefly to dissolve the solid and the solution then left for crstallization. After two days, fine white crystals appeared and these were filtered, washed with a little methanol, then with pentane and finally with ether. The crystals were pumped under reduced pressure (*ca.* 1 Torr) at 50°C to remove residual solvent from the bisperchlorate which was obtained in 28% yield (76 mg).

(Found: C, 51.34; H, 4.03; Cl, 9.96; P, 8.01.

$C_{32}H_{30}Cl_2O_{12}P_2$ requires: C, 51.96; H, 4.06; Cl, 9.67; P, 8.38%).

The IR spectrum shows ν_{max} at 1770, 1760, 1740 (normal $>$C=O stretching), 1590, 1440, 1340, 1290, 1240, 1230, 1200, 1170, 1120-1065 (broad typical perchlorate peak), 1000, 900, 850, 800, 760, 740, 700, 690, 670, and 630cm.$^{-1}$

The Reaction of *Trans* 1,2-Bis(diphenylphosphino)-ethylene with Dimethyl Acetylenedicarboxylate

The *trans* phosphine (2.4 g) was dissolved in dry benzene (20 ml) and cooled to about 10°C. To this solution was added dry pentane (40 ml) slowly with constant stirring when the solution became slightly turbid. At this stage a few drops of benzene were added to remove the turbidity.

A mixture of dimethyl acetylenedicarboxylate (0.852 g) and benzene (10 ml) was then added slowly, under a stream of dry nitrogen with constant stirring to the *trans* phosphine solution while keeping the temperature of the reaction mixture around 8°C. When the addition was complete, a light yellow precipitate (2.10 g, 69%) of a 1:1 adduct was obtained. This was filtered under nitrogen and washed several times with dry benzene followed by pentane. The precipitate was then pumped under reduced pressure (*ca.* 2 Torr) and at 55°C for several hours.

Recrystallization of the adduct could not be achieved because of its high sensitivity towards water and air. (Found: C, 71.10; H, 5.44; P, 11.18. $C_{32}H_{28}O_4P_2$ requires: C, 71.4; H, 5.2; P, 11.5%). The compound decomposed over a wide temperature range on heating.

The IR spectrum shows ν_{max} at 1712 (normal $>$C=O stretching), 1601 (stretching of the C=0 group adjacent to a carbanionic centre), 1445, (P-Ph), 1350, 1240, 1170, 1130, 1120, 1104, 1060, 950, 860, 820, 810, 765, 758, 750, 740, 720, 704, 700, and 670 $cm.^{-1}$

The ^1H NMR shows a ratio of 20 aromatic protons as a complex multiplet at τ2.8-3.32 one apparently olefinic proton as two poorly defined quartets centred on $\tau 3.63$ and $\tau 4.04$ respectively and six methoxy protons as three peaks of unequal area at $\tau 6.15$, $\tau 6.28$ and $\tau 6.59$. At -50°C, the spectrum is much the same. The ^{1}H NMR spectrum of the adduct in trifluoroacetic acid at room temperature shows a ratio of approximately 20 aromatic protons at $\tau 1.6-2.8$ to approximately one proton as a diffuse multiplet at $\tau 4.3-5.1$ to approximately six methoxy and two methylene or methine protons as a complex multiplet between $\tau 5.6$ and $\tau 6.65$. The ^{1}H NMR spectrum in CF_3CO_2D is similar except that the multiplet at $\tau 4.3-5.1$ is absent.

When the trifluoroacetic acid solution of the 1:1 adduct was left for several days, the ^{1}H NMR spectrum then showed twenty aromatic protons as a multiplet at $\tau 1.5-2.8$, one methine proton as a doublet at $\tau 4.49$, two methoxy groups as singlets at $\tau 5.95$ and $\tau 6.45$ respectively and two methylene protons as a multiplet hidden under the methoxy protons in the range $\tau 5.6-6.3$.

The mass spectrum showed a strong molecular ion peak at *m/e* 538.

Hydrolysis of the 1:1 Adduct of *Trans* 1,2-Bis(diphenylphosphino)ethylene and Dimethyl Acetylenedicarboxylate

The 1:1 adduct (1.85 g), obtained by treating *trans* 1,2-bis(diphenylphosphino)-ethylene with dimethyl acetylenedicarboxylate, was dissolved in aqueous ethanol (30 ml, 1:1 mixture) and heated under reflux for 24 hours. A white precipitate was obtained which was filtered and washed with a little benzene followed by pentane. The oxide was then pumped under reduced pressure (*ca.* 1 Torr) and at 60°C, The crude oxide XLVI (0.80 g) was obtained in 63% yield, (m.p. 132°, lit.[22] m.p. 132°). The crude product was further recrystallized from benzene and obtained as fine cotton-like crystals. (Found: C, 64.85; H, 5.83; P, 8.78. $C_{20}H_{21}O_5P$ requires: C, 64.51; H, 5.64; P, 8.33%).

The IR spectrum shows ν_{max} at 1740, 1720 ($>$C=0 stretching), 1448, 1445 (P-Ph), 1380, 1340, 1310, 1230, 1220, 1190 (P=0), 1100, 1010, 822, 780, 770, 755, 748, 728, 710, and 700 cm^{-1}.

The ^1H NMR spectrum of the hydrolysis product shows a pattern identical to that obtained by Davies[22] for the spectrum of $Ph_2P(0)CH_2CH=CXCH_2X$ ($X=CO_2Me$).

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

Deuterolysis of the 1:1 Adduct of *Trans* 1,2-Bis(diphenylphosphino)ethylene and Dimethyl Acetylenedicarboxylate

This experiment was carried out as in the previous experiment except that pure D_2O was used as the deuterolyzing agent. The oxide CLXXII (m.p. 136°) was obtained in 70% yield. The IR spectrum was almost identical to that of the hydrolysis product XLVI.

The ^1H NMR was also found to be very similar to that of XLVI except that the aliphatic protons had vanished from the spectrum.

The mass spectrum shows a molecular ion peak at *m/e* 376 which confirms that tetradeuteration occurred.

The Reaction of Tetraphenylbiphosphine With Dimethyl Acetylenedicarboxylate

To a solution of the tetraphenylbiphosphine (0.67 g) in benzene (5 ml) was added slowly an ethereal solution of dimethyl acetylenedicarboxylate

(0.26 g in 10 ml) with constant stirring inside a dry box flushed with dry nitrogen and at room temperature. A dark brown solution was obtained. To this brown solution was added petroleum ether (50 ml, 65-110°) and a tarry material was obtained. The sticky mass was dissolved in a little dry acetone and a small amount of white crystals settled down. These were washed and pumped under low pressure (*ca.* 1 Torr) at 60°C. The yield of CLXXVI (10%) was very poor and the m.p. was found to be 205°. (Found: C, 68.35; H, 6.25; P, 11.15. $C_{30}H_{26}O_6P_2$ requires: C, 66.17; H, 4.69; P, 11.39%).

The IR spectrum shows ν_{max} at 1730, 1250, 1200, 1120, 1002, 895, 850, 760, 730, 695 and 670 $cm.^{-1}$

The mass spectrum indicates a molecular weight of 544 while the ^1H NMR spectrum shows a ratio 20 aromatic protons to a total of six methoxy protons. The sample is clearly impure.

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