David G. Holah, Alan N. Hughes and Daniel Kleemola

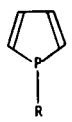
Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1

Received May 1, 1978

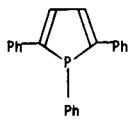
Reactions of the three phospholes 1-phenylphosphole, 3-methyl-1-phenylphosphole and 3,4-dimethyl-1-phenylphosphole with dimethyl acetylenedicarboxylate are reported. All three phospholes react extremely readily with the acetylenic ester to give ring-expanded bicyclic ylidic systems, although 1-phenylphosphole appears to react by a different pathway from the other two phospholes. These reactions show that simple phospholes in general, in contrast to heavily substituted phospholes, are quite good nucleophiles in organic reactions and the results of this study are consistent with a relatively easily perturbed aromatic structure for these phospholes.

J. Heterocyclic Chem., 15, 1319 (1978)

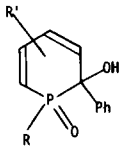
It now seems clear (1,2) that simple phospholes (*e.g.*, I) are somewhat unusual pyramidal but aromatic systems, although the degree of aromaticity and the extent to which aromatic character varies with the substitution pattern have not yet been established (2). The evidence for this aromatic character has been discussed extensively elsewhere (1-3) and, by and large, the sum of the chemical, spectroscopic and theoretical evidence is entirely consistent with such a conclusion. However, although extremely simple phospholes such as 1-methylphosphole



I



II

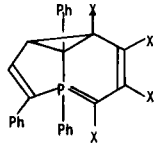


III

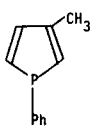
(I, R = Me) (4,5) and heavily substituted phospholes such as 1,2,5-triphenylphosphole (II) (6) are weak bases and poor donors, very recent work has shown that many simply substituted phospholes are surprisingly good σ donors towards a variety of transition metal chlorides (7,8), chlorocarbonyls (8) and metal (0) carbonyls (9-13). Whether this good donor character demonstrates a phosphorus lone-pair (in what is only a weakly aromatic system) which is truly readily available for chemical reactions in general or whether it simply demonstrates that the electronic structure of many simple phospholes is readily perturbed by transition metal ions or atoms (as is the case with λ^3-phosphorins (14)) is not yet clear.

Relatively few studies of the nucleophilic character of simple phospholes in organic reactions have been carried out. Among such investigations, quaternization studies (5) indicate that simple phospholes (particularly those without ring-carbon substitution) quaternize with methyl iodide rather less readily than do tertiary phosphines in general. In related investigations, Mathey has shown (15-17) that simple phospholes react fairly readily with benzoyl chloride and water *via* a 1-benzoylphospholium salt (not isolated) in a synthetically very valuable ring expansion reaction to give compounds of type III. A few other investigations of the nucleophilic and basic character of phospholes have been discussed elsewhere (3).

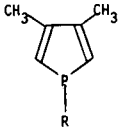
One synthetically very useful electrophile in reactions with tertiary phosphines in general is dimethyl acetylenedicarboxylate (DMADC). Reactions between the lone-pair electrons of phosphines and this ester are usually extremely rapid (even at -50°) and lead to a wide variety of structural types depending upon the structure of the phosphine and the reaction conditions (18). Only one such study has been carried out with a phosphole derivative and this showed (19) that, in contrast to triarylphosphines, no reaction occurs between 1,2,5-triphenylphosphole (II) and dimethyl acetylenedicarboxylate, even under reflux, in benzene. On the other hand, a very slow reaction occurs between the phosphole II and the acetylenic ester (in huge excess) at room temperature over a period of two days in the absence of solvent and the product of this reaction is (20) the unusual tricyclic ylide IV. The



IV



V



VI

X = CO_2CH_3

mechanism of the formation of IV is somewhat complex but essentially it involves initial attack of the phosphorus atom of II upon the triple bond of the ester, similar attack of the resulting zwitterion upon another molecule of the ester, cyclization of the new zwitterion upon the 3-position of the phosphole ring and then internal rearrangement of the resulting ylide.

Superficially, this reaction would suggest that phospholes are very poor nucleophiles in such reactions. However, in view of the fact that 1,2,5-triphenylphosphole is a poor donor in σ complex formation with transition metal systems (6) while other simple phospholes are obviously (6-13) quite good donors comparable in donor

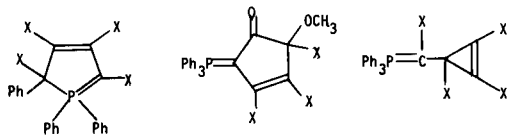
character with normal tertiary phosphines, this tentative conclusion might be incorrect. For this reason, we have undertaken a study of the reactions of the three simple phospholes 1-phenylphosphole (I, R = Ph), 3-methyl-1-phenylphosphole (V) and 3,4-dimethyl-1-phenylphosphole (VI, R = Ph) (all of which are good donors (6-13)) with dimethyl acetylenedicarboxylate. A further reason for this investigation was the extreme versatility of phosphine-acetylenic ester reactions (18). In particular, useful synthetic routes to relatively inaccessible bicyclic or tricyclic phosphorus heterocycles might be provided by such reactions. The results of these studies are summarized in the following discussion.

3,4-Dimethyl-1-phenylphosphole (VI, R = Ph) and 3-Methyl-1-phenylphosphole (V).

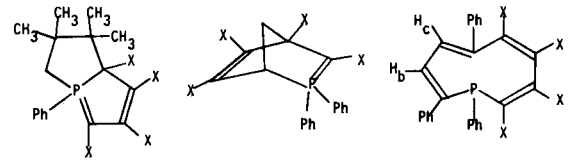
The investigation was begun with these phospholes because previous studies (5,8,21) had indicated that they could be expected to be more reactive than phospholes without ring-carbon substitution. For example, it has been shown (8,21) that 3,4-disubstitution (as in VI, R = Ph and VI, R = CH_2Ph) causes greater reactivity at the P atom in phosphole-metal complex formation. This greater reactivity is also reflected in an increased rate of quaternary salt formation (5). Furthermore, nmr studies (5,22), discussed elsewhere (3), have also indicated that the electronic structures of 3,4-disubstituted phospholes are somewhat different from those of other simple phospholes.

It was found that both of these phospholes react smoothly and rapidly with dimethyl acetylenedicarboxylate at room temperature in benzene to give mainly one product in each case, as orange crystals (39%) from VI (R = Ph) and a yellow powder (21%) from V. This is in contrast to the behaviour of the more heavily substituted phosphole II which, as mentioned earlier, will not react under these conditions but which gives the tricyclic ylide IV with the acetylenic ester in the absence of solvent over a long period. Elemental analyses in excellent agreement with 1:2 adducts of the phospholes with dimethyl acetylenedicarboxylate were obtained. The molecular formulas and molecular weights were confirmed by mass spectra which showed the molecular ion peaks at m/e 472 and m/e 458, respectively, for the two adducts. Minor products, obtained in very small quantity indeed in each case, appeared from mass spectra to be 1:2:1 adducts of the phospholes, the ester and water, but these adducts were not further investigated.

Before considering the natures of these particular adducts, it would be as well to consider the types of adduct (in particular, 1:2 adducts) produced in reactions of various phosphines with dimethyl acetylenedicarboxylate. For reactions of tertiary phosphines with the acetylenic ester, the range of known, characterizable structural types for 1:2 adducts obtained from triphenylphosphine includes VII (23), VIII (24) and IX (25); from 2,2,3,3-tetramethyl-1-phenylphosphetan the bicyclic system X has been obtained (26); diphenylvinylphosphine gives the bridged system XI (27) and, as already mentioned, 1,2,5-triphenylphosphole (II) gives the tricyclic ylide IV (20). In addition, thermal rearrangement of IV gives the ring expanded product XII (20) and various short-lived 1:2 adducts have been postulated as intermediates in the formation of the structures listed above.



VII VIII IX



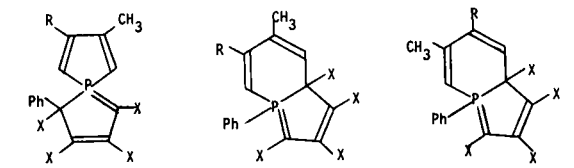
X XI XII

X = CO_2CH_3

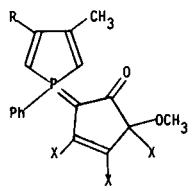
It can be seen that all but one of these products are α-carbonyl stabilized ylides.

Other products have been obtained from reactions of acyclic and cyclic tertiary phosphines with the acetylenic ester but these are not 1:2 addition products of the phosphine with the ester. They include 2:1 or 1:1 adducts (28) and 1:2 adducts less one oxygen atom (29). Again, these are ylidic systems and it seems that reactions of this type almost always produce ylides even though the stoichiometry of the products may vary according to the reaction conditions and the nature of the phosphine.

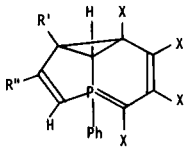
Bearing these observations in mind then, it seems highly probable that the products of the reactions of 3,4-dimethyl-1-phenylphosphole (VI) and 3-methyl-1-phenylphosphole (V) with dimethyl acetylenedicarboxylate (designated here as adduct A and adduct B, respectively) are ylides. By analogy with the various known phosphine and phosphole reactions which lead to IV, VII, VIII, IX and X and which have already been discussed, the most likely structure for each of these adducts is one of XIII, XIV, XV, XVI, XVII and XVIII. Indeed, it is difficult to visualize reaction pathways which could



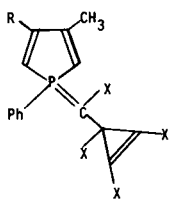
XIII XIV XV



XVI



XVII



XVIII

lead to other structural types unless those pathways are very complex.

A detailed spectroscopic analysis of the two products shows quite conclusively that adduct A has structure XIV (R = CH_3) while adduct B has the very closely related structure XIV (R = H). Thus, the infrared spectra of A (ν CO at 1750, 1737, 1703, 1670 and 1525 cm^{-1}) and B (ν CO at 1747, 1704, 1665 and 1530 cm^{-1}) are typical (20) of α-carbonyl stabilized ylides. For example, the tricyclic ylidic structure IV obtained from 1,2,5-triphenylphosphole (II) and the ester shows ν CO at 1740, 1710, 1660, 1650 and 1520 cm^{-1}. Furthermore, the uv spectra (in 95% ethanol) of the two adducts are virtually identical, A shows λ max (ε) at 223 (19320), 269 (8900, inflection), 277 and 289 (10000, inflections) and 331 (12780) nm, while B shows λ max (ε) at 223 (20150), 262 (9100, inflection), 269 and 275 (10000, inflections) and 332 (12750) nm, and are again typical (23) of α-carbonyl stabilized ylides. In this connection, it should be noted that the ylide VII shows (23) a very similar spectrum with λ max (ε) at 228 (28000), 268 (8200, inflection), 275 (6800, inflection) and 344 (19000) nm suggesting that the adducts A, B and VII contain basically the same chromophoric unit. As occurs with VII, the long wavelength ylidic bands around 330 nm in the spectra of A and B vanish upon protonation in concentrated hydrochloric acid.

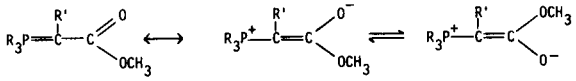
Relatively little information can be obtained from the mass spectra of the two adducts which show a fairly complex pattern with most of the peaks below m/e 400 of quite low intensity but, apart from confirming the molecular weights of A and B, the spectra do show that the phosphorus-phenyl grouping is intact in both adducts. Compounds containing the phosphorus-phenyl unit usually reflect this in the mass spectrum with a significant peak at m/e 108. In the mass spectrum of A, there is a weak peak at m/e 108 (*ca.* 3% of base peak at m/e 472) and the meaning of this is doubtful. However, there is a much stronger peak at m/e 109 (27% of base peak and much stronger than most peaks in the spectrum below m/e 400). This could be due to the fragment (Ph-P-H) formed by some hydrogen-transfer type of fragmentation and this is confirmed by a precise mass determination which shows that for A, this peak is indeed due to an ion of formula $C_6H_6P^+$ since the calculated mass is 109.0207 and that found is 109.0198. There can therefore be little doubt that the adduct A contains the phosphorus-phenyl unit and the similarity of the spectrum of the adduct B in this region suggests that the same is true for this compound. The mass spectra, then, rule out structures of type XIII for A and B.

There is one negative feature of the two mass spectra which is of interest and that is that there is no fragment ion in either of the two spectra corresponding to the molecular weight of the phosphole from which the adduct was prepared. This indicates that in the reaction of the ester with the phospholes to give 1:2 α-carbonyl stabilized ylides as already shown by the ir and uv evidence, the ester residues in the products A and B are almost certainly bound not only to the phosphorus atom but also to at least one of the carbon atoms of the original phosphole ring. The reason for this deduction is that in more normal ylides such as triphenylphosphonium ylides, simple fission of the ylidic link readily occurs on electron impact (24,30) and an ion corresponding to the parent phosphine is observed. This would appear to be evidence against structures such as XVI and XVIII (where electron impact could cause similar fragmentation leading to the formation of an aromatically stabilized phosphole molecular ion) but this evidence certainly cannot be regarded as conclusive. As will be seen shortly, however, there is other strong evidence which is also incompatible with either of these structural types.

Final confirmation of the proposed structures of the two adducts comes from the nmr spectra of product A and product B under various conditions. In deuteriochloroform at room temperature, the spectra of the two adducts are very similar. Thus, A shows five aromatic protons as a complex multiplet at τ 2.00-2.55, two olefinic protons as apparently two overlapping doublets (appearing as a triplet with a broadened central peak) at τ 3.50-4.00 with J = 20-22 Hz for each doublet (the resolution is such that one doublet of J = 45 Hz could straddle another doublet with J = *ca.*, 4 Hz but this is much less likely), four ester methoxy signals at τ 6.01, 6.38, 6.45 and 7.01 with the peak at τ 6.45 much shorter and broader than the other peaks, and two allylic methyl signals at τ 7.78 and 7.97. Similarly, adduct B shows in deuteriochloroform at room temperature, five aromatic protons as a broad-based peak at τ 2.43, three olefinic protons as a complex multiplet at τ 3.18-4.50, four ester methoxy groups as four singlets at τ 6.08, 6.41, 6.51 and 7.07, and three allylic methyl protons as a singlet at τ 7.87. Again, the methoxy signal at τ 6.51 is broader and shorter than the other methoxy signals. One other feature of the spectrum of adduct B is that in several samples, a small amount of

some aliphatic impurity appeared in the nmr spectrum as a complex multiplet of very weak peaks (total integration 1-2 protons) in the range τ 8.10-9.50. While this impurity could never be completely removed, careful chromatographic isolation of the adduct reduced the impurity to insignificant amounts.

These spectra produce two important pieces of evidence. The first is that in both cases, the number of olefinic protons is precisely the same as in the original phospholes. This, of course, eliminates structures such as XVII. The second point is that the broadening and shortening of one of the methoxy signals in each spectrum is strongly suggestive of ester carbonyl stabilization of the ylidic negative charge. With adduct A, this deduction was confirmed by spectra at 50° and 10° which showed that the methoxy peak at τ 6.45 becomes much sharper and taller at the higher temperature while at the lower temperature, it becomes much shorter and broader. The only other change is that at 50°, the olefinic signals become slightly better resolved to give two doublets centered on τ 3.70 and 4.12 each with J = 24 Hz (or, less likely, J = 45 Hz straddling J = 4 Hz). This behaviour is typical (20) of α ester carbonyl stabilized ylides where restricted rotation about the ylidic carbon-carbonyl bond occurs as shown in XIXa and XIXb giving two preferred conformers in comparable concentrations. This results in a broadened methoxy signal (often two signals at low temperatures) which sharpens at higher temperatures when rotation about the carbon-carbonyl bond is rapid. Similar behaviour is observed with adduct B.



XIXa XIXb

Further confirmation of this deduction comes from the nmr spectrum of adduct A in DMSO-d_6. At room temperature, the spectrum shows much the same pattern as in deuteriochloroform except that the two olefinic protons appear as a doublet of two broadened peaks with J = 21 Hz. This would appear to eliminate the less likely alternative couplings mentioned above. As the temperature is raised to 150°, the four ester methoxy peaks all become very sharp and of equal height, while the olefinic signal becomes two doublets with all peaks of equal area, the lower field pair having J = 21 Hz and the higher field pair having J = 20 Hz. This behaviour (conformational preference) of the ester groups could not be shown by structures of type XVI where ylidic stabilization is through a ketonic carbonyl group.

The nmr spectrum of adduct A in trifluoroacetic acid also confirms the ylidic nature of the system since extra indistinct peaks occur in the range τ 4.0-5.3 (somewhat less than one proton) and major modifications occur in the methoxy region of the spectrum. This is again typical (20) of α ester carbonyl stabilized ylidic systems in acid solution where protonation may occur at the α carbon atom and also at the γ carbon atom in structures such as VII (23). The spectrum of adduct B in trifluoroacetic acid was too poorly resolved to give much information.

Further examination of the nmr spectral data for adduct A shows conclusively (subject to consideration of one minor point regarding XVIII to be discussed shortly) that the structure is XIV (R = CH_3). The methoxy peak pattern is very similar to that shown (23) by VII and virtually identical to that shown (26) by X, both of which contain the structural unit of the five-membered ylidic ring (as does XIV (R = CH_3)). The two low field doublets at τ 3.70 and 4.12 (J = 20-24 Hz depending upon the solvent) suggest that the two olefinic protons are not coupled to one another and are close to, if not adjacent to, the phosphorus atom in view of the large coupling constants. Superficially, this might suggest that the original phosphole ring is intact and that the two proton signals are due to protons on α ring carbon atoms in phospholium type structures since such proton signals fall in the region observed here. However, the two protons clearly have different chemical shifts which would be unlikely (but not impossible) for a phospholium system. Furthermore, the phosphorus-hydrogen couplings in such systems are usually (15,31,32) in the range $^2J_{P\text{-}H}$ = 31-33 Hz and this would be further evidence against a phospholium type of structure as found in XIII, XVI and XVIII.

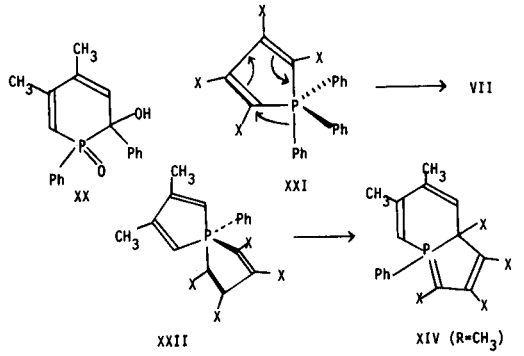
On the other hand, the fact that the $J_{P\text{-}H}$ couplings in the spectrum of the adduct A are equal would seem to be evidence against XIV (R = CH_3) but this is not the case. For example, in the structure XX, which contains a six-membered ring analogous to that in XIV (R = CH_3), the values of $J_{P\text{-}H}$ are virtually equal (17) at 14 and 15.5 Hz for the two ring protons although these values are somewhat lower than those observed for the adduct A under discussion (J = *ca.*, 20 Hz depending upon the solvent and temperature). It should be noted, however, that other structures closely related to XX show (17) $J_{P\text{-}H}$ values for both protons as high as 17 Hz. Furthermore, the proton signals are in almost the same locations in the spectrum of XX (τ 3.76 and 3.87) as in the spectrum of the adduct A (τ 3.74 and 4.12). In addition, the methyl proton signals of XX (τ 7.83 and 7.98) coincide almost exactly with those of the adduct A (τ 7.78 and 7.97). Similar deductions may be made for adduct B although the olefinic region of the spectrum is more complex and there is only one ring methyl group (at τ 7.87).

To summarize the information available at this point, the evidence accumulated is entirely consistent with the

structures XIV (R = CH_3) for adduct A and XIV (R = H) or XV (R = H) for adduct B. All other reasonable structures are eliminated for one or more reasons with the possible exception of XVIII (R = CH_3 or H) which, so far, has only two pieces of negative evidence (the mass spectrum and the values of J_{P-H}) against such structures. However, structures of this type can almost certainly be eliminated because stable structures of this type are unknown. Thus, in the reaction of triphenylphosphine (and other triarylphosphines) with dimethyl acetylenedicarboxylate (1:2) in ether at -50°, the analogous structure IX has been postulated (with good evidence) (25) as a transient intermediate which rearranges first to XXI and then to VII. Structure IX is not otherwise characterizable. Since there is no obvious extra stabilizing factor in XVIII (as compared with IX), it therefore seems highly unlikely that XVIII would be stable as a solid to well over 100° and stable indefinitely in solution if IX rearranges almost instantaneously at -50°.

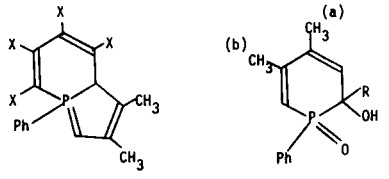
Two main points regarding the possible structures for the adducts A and B remain to be settled. First, are these structures reasonable on mechanistic grounds bearing in mind that they are bicyclic? Second, it is necessary to determine whether adduct B has structure XIV (R = H) or the closely related structure XV (R = H). In fact, both of these points are easily clarified.

The structures XIV and XV are bicyclic analogues of the well known (23,26) cyclic ylides VII and X. The formation of both structures is thought to proceed *via* transient structures of type IX and then type XX with rearrangement of a good leaving group from an apical position of the trigonal bipyramidal phosphorus atom to the carbon atom adjacent to the phosphorus atom as shown in the sequence XXI → VII. It should be noted here that the five-membered ring adopts an apical-equatorial arrangement since this gives lower angle strain than a diequatorial arrangement (26). If, as seems likely, the adducts under discussion are formed by similar mechanisms, the intermediate in the formation of XIV (R = CH_3) would be XXII in which, for angle strain reasons, *both* five-membered rings would occupy apical-equatorial arrangements with the phenyl group in an equatorial position. Migration from an apical position would therefore give XIV (R = CH_3) as shown or, as an alternative, a phosphonium ylide XXIII which is not α-carbonyl stabilized and which is not compatible with most of the spectroscopic evidence. Conversely, formation of XIII would require either migration of the equatorial phenyl group or some pseudorotational process in XXII which temporarily places the phenyl group in an energetically unfavourable apical position. Alternatively, the rearrangement may not involve an intermediate of type XXII although this seems unlikely in view of other related reactions leading to VII, X, and several related structures (23,26).



On mechanistic grounds then, XIV (R = CH_3) is the favoured structure for adduct A and similar arguments would give XIV (R = H) or XV (R = H) as the structure of adduct B.

That adduct B, in fact, has structure XIV (R = H) is also made clear by the nmr evidence. Thus, in the spectrum of XX, the lower field methyl signal (at τ 7.83) has been assigned to the methyl group *para* to the phosphorus atom and it is possible that similar assignments can be made for adducts A and B. In support of this, examination of the nmr spectra (17) of ten compounds of type XXIV (closely related to XX and the probable structures of adducts A and B) shows that the signal of



the methyl group (a) *always* falls in the range τ 7.90-7.83 (with the majority at τ 7.90-7.86) while the signal of the methyl group (b) falls in the range τ 8.03-7.96 even though the nature of the R group varies widely. The methyl group of adduct B appears in the nmr spectrum at τ 7.87 which puts it in the range of the methyl group (a) and well outside that of (b). It seems fairly clear then that adduct B has structure XIV (R = H) although XV (R = H) remains a slight possibility.

The phospholes 3,4-dimethyl-1-phenylphosphole (VI, R = Ph) and 3-methyl-1-phenylphosphole (V) therefore react with dimethyl acetylenedicarboxylate much more readily than does 1,2,5-triphenylphosphole (TPP) to give products of an entirely different structural type and by an entirely different mechanism. That is to say, neither of the two phospholes under discussion here acts as a vinylphosphonium salt in the later stages of the reaction as does TPP. While it might be argued that in the 3,4-dimethyl phosphole, the 3- and 4-methyl groups could sterically hinder 1,3-cyclization of the type which occurs with TPP, this clearly is not the case for 3-methyl-1-phenylphosphole. This suggests that 1,2,5-triphenylphos-

phole is a non-typical phosphole in these reactions as has been shown for other reactions by Mathey (15-17) in his ring expansion studies, by Hughes and Srivanavit in their studies of iodomethylphospholium salt hydrolyses (33) and by several studies of phosphole coordination chemistry (7,8). Since many early studies on phosphole chemistry were carried out with the readily accessible TPP system, the deductions from these studies should be treated with caution.

1-Phenylphosphole (I, R = Ph).

As with the other two phospholes discussed above, 1-phenylphosphole reacts readily with dimethyl acetylenedicarboxylate but this time, the reaction yields three products. Unfortunately, yields were very low and purification was extremely difficult. It has therefore proved impossible to establish the structures of these products beyond all reasonable doubt although it is highly probable that the structures assigned tentatively to two of the products are correct. Two of the products were obtained every time the reaction was carried out and they proved to be a yellow 1:2 adduct of the phosphole with the ester and what appears to be (on the basis of a molecular weight determination by mass spectrometry) a colourless hydrolysis product of the yellow adduct or an isomeric adduct. It should be mentioned here also that hydrolysis products of 1:2 adducts were sometimes isolated in very small quantities from the phosphole-acetylenic ester reactions described earlier but determination of the structures of these hydrolysis products, including the above compound, was not attempted because they were obtained usually in very small yield and because hydrolyses of bicyclic and tricyclic ylides in general and of IV in particular is the subject of a separate investigation (34). The third product of the reaction (colorless) was much more difficult to obtain but was again found to be a 1:2 adduct of the phosphole with the ester. Its formation is extremely sensitive to small changes in reaction conditions and purification procedures.

Dealing first with the yellow 1:2 product, isolated by chromatography, certain positive information was easily obtained. For example, the C and H analyses were in good agreement with a 1:2 adduct although a P analysis (taken on a less pure sample prepared later) was in less good agreement. However, the 1:2 nature of the adduct was confirmed by a strong molecular ion peak in the mass spectrum at m/e 444. Very small impurity peaks at higher mass (*e.g.*, m/e 462) were also observed and the compound was clearly not completely pure. The mass spectrum also showed strong peaks at m/e 108 and 109 showing that the phosphorus-phenyl unit remains intact and this rules out structures of types VII and XIII. That the adduct is again a carbonyl stabilized ylide is shown by the ir spectrum which shows ν CO at 1745, 1702, 1662, 1640 and 1525 cm^{-1} which, as noted earlier, is typical of such systems.

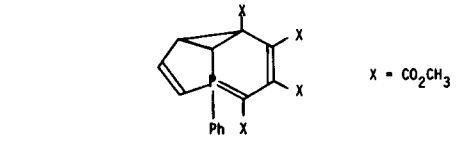
The uv spectrum would appear to rule out structures of type XIV obtained from the other two phospholes discussed here since, although the spectrum is broadly speaking what we would expect from a carbonyl stabilized ylide, it is completely different in general appearance from the spectra of the adducts XIV (R = CH_3 or H) which are virtually identical in appearance, locations of maxima and extinction coefficients. The spectrum of the yellow adduct under discussion shows λ max (ϵ) at 225 (18130), 248 (13630) and 332 (9820) nm. Furthermore, the peak at 248 nm is very broad and has a very long tail-off to the long wavelength side. Since the spectra of XIV (R = CH_3 or H) are so similar, it is difficult to see how the removal of one more methyl group could cause such profound changes in the appearance of the spectrum. It therefore appears that 1-phenylphosphole reacts by a different route than do the analogous 3,4-dimethyl and 3-methyl phospholes.

The nmr spectrum obtained for the adduct was rather poorly defined and had to be recorded on very freshly prepared solutions because of what appeared to be hydrolytic decomposition. However, the spectrum gives considerable positive information. The spectrum shows an aromatic proton signal as a rather broad based peak centred on τ 2.43 (*i.e.*, a phenyl group which is probably attached to a positively charged phosphorus atom), a very broad complex multiplet in the range τ 2.70-4.60 probably due to olefinic protons, and a broad based and poorly resolved complex multiplet with four principal peaks (at τ 6.06, 6.39, 6.48 and 6.98) in the range τ 5.50-7.10 primarily due to ester methyl groups. There are also very weak, broad signals at the high field end of the spectrum in the range τ 8.40-9.37. The compound is clearly an ester stabilized ylide since the four principal peaks in the ester methyl region show the same temperature dependence as those of XIV (R = CH_3 or H) already discussed. That is to say, the peak height and resolution of the peak at τ 6.48 is very sensitive to temperature changes and this behaviour is compatible with rotational isomerism about an ylidic carbon-ester group bond. This then rules out structures related to XVI.

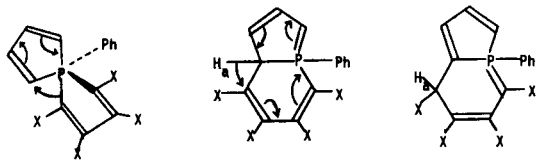
Numerous attempts were made to obtain better and clearer nmr spectra but it proved impossible to obtain really pure samples of the adduct in sufficient quantity. The main problem comes with the integration of the poorly resolved and sometimes overlapping signals since slightly different results are obtained with different samples (presumably of different degrees of purity) and with slightly different conditions in deuteriochloroform solution. If one considers the individual signals, in most of the spectra, the ratios of the areas of the aromatic:olefinic:ester methyl region:other high field protons, are 5:a little over

2:12:a little less than 1. This is about one too few protons for a 1:2 adduct. If one takes into consideration that the olefinic and aromatic proton signals overlap and are difficult to integrate separately, the integrations become aromatic + olefinic:ester methyl region:other high field protons = 8:13:a little less than 1. This is about one too many protons for a 1:2 adduct. What is clear is that there are no longer four olefinic protons as would be expected if the four protons on the original phosphole ring remained on double bonds, *i.e.*, at least one of the ring carbon atoms of the phosphole has been attacked in such a way as to give a carbon atom which is either saturated or bears no hydrogen atom. This would appear to rule out structures related to XVIII.

The only remaining structural type of the kind discussed earlier for the products of the other phospholes in these reactions is that of XVII and one might be tempted to assign this type of structure (in this case XXV) to the yellow ylidic 1:2 adduct of 1-phenylphosphole with dimethyl acetylenedicarboxylate. However, this structure also does not fit the admittedly poor spectrum very well.



XXV



XXVI XXVII XXVIII

If we consider the first of the integrations mentioned above, there are two problems. First, although there would be two olefinic protons as required, there would be a maximum of one cyclopropyl proton at high field and structure XXV requires two. Furthermore, this particular proton signal occurs at much too high a field in the spectrum for cyclopropyl protons of this type. Thus, in the spectrum of IV, the similar cyclopropyl proton occurs in the ester methyl region at τ 6.43. If one assumes that the other cyclopropyl proton required for structure XXV is hidden under the ester methyl signals, the remaining integrations become very poor and much too high for a 1:2 adduct. In our opinion, the high field peaks at τ 8.40-9.37 are due to traces of the solvents used in the chromatographic separation of the adduct (diethyl ether and petroleum ether) and also other impurities and some evidence for this is given by the fact that different samples show slightly different integrations in this range although the signal intensities could never be reduced to zero even by prolonged pumping of the adduct.

Assuming that these high field peaks (approximately one proton in total) are indeed due to impurities as seems highly likely, the second set of integrations mentioned above now becomes quite reasonable since the number of protons would agree with a 1:2 adduct. Considering this set of integrations, eight aromatic and olefinic protons are clearly incompatible with structure XXV as well as all the other possible structures considered so far. The question therefore arises as to whether there is another possible reaction pathway not yet considered for these reactions. In fact, there is one other pathway considered and rejected by Tebby, *et al.* (20), in the determination of the structure of the tricyclic ylide IV. In this reaction, an intermediate 1:2 adduct of type XXVI would be formed similar to the structure XXII proposed as an intermediate in the formation of XIV (R = CH_3) (a similar intermediate is presumably formed in the reaction leading to XIV (R = H)). This could rearrange by apical migration of a suitable leaving group as does XXII but, this time, the migrating group would be a carbon atom bearing an ester group as shown in the sequence XXVI → XXVII. However, XXVII is not a carbonyl stabilized ylide and rearrangement to the lower energy system XXVIII might occur as shown and as suggested by Tebby (20) in related systems. Tautomeric rearrangements of this type in cyclic ylides are well established (27).

The structure XXVIII would be a carbonyl stabilized ylide compatible with the ir evidence and the temperature dependence of the nmr spectrum. Furthermore, the uv spectrum would probably differ somewhat in general appearance from those of XIV (R = CH_3 or H) and also of IV (20) as is observed. Finally, the nmr spectrum would show eight aromatic and olefinic protons as is apparently observed. Of course, the proton H_a in structure XXVIII still has to be assigned in the nmr spectrum of the adduct. This proton would be both allylic and adjacent to an electron-withdrawing ester group. Protons of this type resonate (27) in the methoxy region of the spectrum and we would therefore expect the signal to be masked at least in part by the ester methyl group signals in the spectrum. This would give 13 protons in this region as is apparently observed if the second set of integrations mentioned earlier is correct and it should be noted again that the signals in this region of the spectrum are more complex than in the spectra of XIV (R = CH_3 or H).

The weight of the evidence therefore favours XXVIII as the structure of the yellow 1:2 adduct obtained from 1-phenylphosphole and dimethyl acetylenedicarboxylate although the less than satisfactory analyses, nmr spectra and nmr integrations make this assignment only tentative at this stage. Clearly, this proposed reaction pathway is not followed by the other two phospholes in reactions with the acetylenic ester since the nmr spectra show no evidence for such a mechanism.

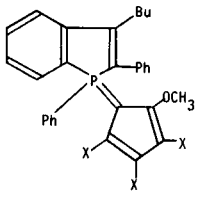
Considering finally the colourless 1:2 adduct of 1-

phenylphosphole with the ester obtained only occasionally and always in very low yield, a more definite, though not conclusive, structural assignment may be made. Only 90 mg. of the compound was obtained and the structure assignment therefore rests mainly on a very detailed spectroscopic analysis together with an excellent C, H analysis. No phosphorus analysis was obtained because all of the available sample was used up in spectroscopic studies. However, the mass spectrum did confirm the molecular weight as 444.

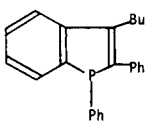
The ir spectrum shows quite clearly that, unlike the isomeric yellow 1:2 adduct, the colourless 1:2 adduct is not a carbonyl stabilized ylide since no carbonyl peak occurs in the 1530 cm^{-1} region and all carbonyl absorption occurs as a broad band centred on 1740 cm^{-1} with maxima at 1760, 1736 and 1725 cm^{-1}. There is also a weak peak at 1625 cm^{-1} which is probably due to a carbonyl conjugated carbon-carbon double bond. The spectrum between 1300 and 650 cm^{-1} is very complex and offers little information except that there is no trace of any phosphine oxide P=O peaks in the 1200 cm^{-1} region.

The most information is given by the nmr spectra of the adduct under various conditions. The room temperature nmr spectrum in deuteriochloroform is very well defined and shows five aromatic protons as a complex multiplet between τ 2.20 and 2.76, 3 olefinic protons as a series of at least 12 peaks of various areas in the range τ 2.84-4.00, 1 tertiary or olefinic proton as a doublet of doublets with the two coupling constants having values of J = 8 Hz and J = 2 Hz, and three very sharp methoxy signals at τ 6.17 (3 protons), 6.24 (6 protons) and 7.06 (3 protons). There is no significant change in the methoxy region of the spectrum over the temperature range -40° to 32° and this confirms that the compound is not an ester carbonyl stabilized ylide.

The information above suggests that the product is either an ylide which is not α carbonyl stabilized or is not an ylide at all. Products of either type from reactions of tertiary phosphines with dimethyl acetylenedicarboxylate are rare and, in fact, only one stable product of each type is known. Thus, the ylide XXIX is formed from 3-butyl-1,2-diphenylphosphindole (XXX) and two molecules of the ester (29) while the nine-membered ring XII is formed by thermal rearrangement (boiling chloroform)



XXIX



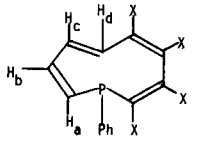
XXX

X = CO_2CH_3

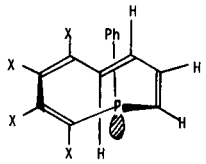
of the tricyclic ylide IV (19,20). Clearly, the adduct under consideration cannot have a structure similar to that of XXIX which is a 1:2 adduct less one oxygen atom. Furthermore, the mass spectrum does not show a peak corresponding to the molecular ion of the original phosphole from which it was derived as occurs with the adduct XXIX. The ylide XXIX is stabilized by the cyclopentadienyl grouping. An ylide not stabilized by an electron withdrawing group is out of the question since such ylides are well known to be extremely air and water sensitive.

The possibility therefore remains that the structure of the adduct is XXXI which would be analogous to XII and would presumably be formed in a similar manner. A detailed analysis of the nmr spectrum shows that this is almost certainly the case.

The main aromatic proton resonance occurs at τ 2.62 which is at markedly higher field than is observed for the cyclic ylidic adducts XIV (R = CH_3) (τ 2.41) and XIV (R = H) (τ 2.36) already discussed. This indicates that the phosphorus atom in the adduct under discussion is less positively charged than in the ylidic systems and this



XXXI



XXXII

X = CO_2CH_3

would be consistent with a tertiary phosphine structure. The limited quantities available did not allow chemical conversion to the phosphine oxide as can be done with XII (19,20). That the phosphorus-phenyl grouping has remained intact during the reaction is shown by peaks at m/e 108 and 109 in the mass spectrum as discussed earlier.

Comparison of the nmr spectrum of the adduct under discussion with that of the adduct XII shows marked similarities between the two spectra. Thus, the four methoxy signals in the spectrum of XII occur at τ 6.16, 6.23, 6.30 and 7.09 (20) while those of the colourless 1:2 adduct occur at τ 6.17, 6.24 (two methoxy groups) and 7.06, *i.e.*, the methoxy signals in the two spectra are in virtually identical locations. Next, the proton marked as H_c in structure XII occurs (because of shielding due to conformational effects in the nine-membered ring discussed extensively elsewhere (20)) as a doublet at τ 5.12 (J = 9 Hz). This proton is therefore coupled with H_b, which occurs as a triplet with $J_{H\text{-}H} = J_{P\text{-}H} = 9$ Hz at τ 3.62, but not with the phosphorus atom. If the 1:2 adduct prepared from 1-phenylphosphole and the ester has structure XXXI as suggested, conformational and shielding effects

should be much the same as in XII and the protons H_c and H_b should appear in much the same locations although the signals would be more complex because of the additional protons present.

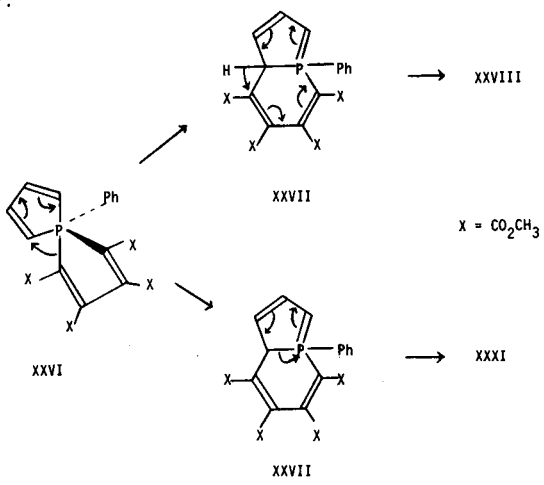
Examination of the olefinic region of the nmr spectrum of the 1:2 adduct shows the presence of a high field, probably olefinic, proton as a doublet of doublets centred on τ 5.48 with the coupling constants of value 8 Hz and 2 Hz, respectively. This proton therefore agrees well in both location and one coupling constant (8 Hz compared with 9 Hz) with H_c in structure XII and may be attributable to H_c in XXXI. The other coupling constant could be due to ^{31}P-^{1}H coupling or, more likely, $J_{H_c-H_d}$ if the postulated structure XXXI is correct. That it is due to $J_{H_c-H_d}$ is shown by two observations. First, at the upper end of the main complex olefinic signal in the range τ 3.15-4.00, there is a very well defined single proton doublet at τ 3.91 with J = 2 Hz. That this is H_d coupled with H_c was confirmed by double resonance experiments. Thus, irradiation of the proton at τ 3.91 while scanning the proton at τ 5.48 caused major changes in the appearance of the signal of the latter proton. Similarly, irradiation of the proton at τ 5.48 while scanning the proton at τ 3.91 causes the latter signal to collapse to a broad based singlet.

Double irradiation also allowed the location of the other proton coupled with H_c (J_{H-H} = 8 Hz). This proton signal is obviously complex and must be somewhere in the range τ 2.84-3.83. If the structure XXXI is the correct one, the signal would be complex because of coupling with H_a, H_c and ^{31}P. Double irradiation at τ 3.30 while scanning the proton signal (H_c) at τ 5.48 causes the latter signal to collapse to a broad hump. Irradiation of H_c while scanning at τ 3.30 similarly causes major changes in the appearance of the spectrum at this location. The proton tentatively designated as H_b therefore resonates at or very close to τ 3.30 and this is very close to the signal of proton H_b in structure XII (τ 3.62). The remaining signal of H_a therefore overlaps with that of H_b but is centered on the high field side of H_b.

The evidence is therefore strong that the colourless 1:2 adduct has structure XXXI and that the compound probably has the same conformational arrangement (as discussed in reference 20) as the analogous structure XII, *i.e.*, probably as shown in XXXII. Another point, of perhaps minor significance, which suggests that the structures of XII and the adduct are related is the presence in the ir spectra of both compounds of a weak conjugated C=C bond absorption at 1642 cm^{-1} for XII and at 1625 cm^{-1} for the colourless adduct.

As mentioned earlier, it proved very difficult to prepare this compound again in sufficient quantity for final and conclusive determination of the structure but there is one further observation of possible significance. Structure XII is derived from the tricyclic ylide structure IV by thermal rearrangement (19,20). Not surprisingly, both XII and IV have identical mass spectra (20). However, the mass spectra of the yellow ylidic adduct tentatively assigned structure XXVIII and the colourless 1:2 non-ylidic adduct of probable structure XXXI are considerably different and this would be a further argument against the alternative structure XXV for the yellow adduct though not necessarily an argument in favour of XXVIII.

On a concluding note, one might think that the phosphacyclononatetraene (phosphonin) XXXI would be formed from XXV (just as XII is derived from IV) even though XXV could not be isolated. While this is quite possibly the case, it is also possible that both XXVIII and XXXI are derived from the common intermediates XXVI and the hypothetical non-stabilized ylide XXVII as shown below:



Further work on this problem would be worthwhile.

Conclusions.

While not all structures discussed in this paper on phosphole-acetylenic ester reactions have been established beyond all possible doubt, certain general observations may be made.

First, it is clear that simple phospholes are reasonably good nucleophiles in reactions with dimethyl acetylenedicarboxylate and, for the most part, the products are ester carbonyl stabilized bicyclic ylides. This is relatively unexpected behaviour in view of the extremely low basicity determined (4) for 1-methylphosphole, the poor donor (6) and nucleophilic (19) character of 1,2,5-triphenylphosphole and the negligible donor character (21) of 1-benzylphosphole discussed elsewhere (3). It would appear that very simple 1-alkylphospholes (*e.g.*, 1-methylphosphole) and heavily substituted phospholes (*e.g.*, 1,2,5-triphenylphosphole) are atypical of phospholes in general as was suggested by Mathey's hydrolytic ring expansions of simple phospholes with benzoyl chloride (15-17) and several other reactions of 1,2,5-triphenylphosphole mentioned earlier in this paper.

Second, the results obtained here are in agreement with those of similar very recent studies regarding the inorganic donor character of the phsopholes under study in this paper towards nickel (II) chloride and other transition metal halides (7,8) which again show these phospholes to be quite good donors behaving broadly like normal tertiary phosphines. Thus, although simple phospholes might well be aromatic species in the pyramidal ground state, the degree of aromaticity would appear to be relatively low in cases where the phospholes behave like tertiary phosphines. In this connection, it is interesting to note that although a recent paper by Epiotis and Cherry (2), mentioned in the introduction to this paper, shows fairly conclusively that phospholes are aromatic (in the sense of a low ground state enthalpy arising from a Hückel type of lone-pair delocalization), the degree of aromatic character was not estimated. These results then, like those obtained with the metal halide-simple phosphole systems mentioned above, indicate that for some simple phospholes at least, the degree of lone-pair delocalization in the pyramidal ground state is small.

Next, although the phospholes 3,4-dimethyl-1-phenylphosphole, 3-methylphosphole and 1-phenylphosphole react like 1,2,5-triphenylphosphole to give cyclic ylides, the type of ylide obtained is entirely different. Thus, whereas with 1,2,5-triphenylphosphole dimethyl acetylenedicarboxylate cyclizes on to the phosphorus atom and the β ring carbon to give IV under fairly drastic conditions, this does not occur with the simple phospholes which ring expand under very mild conditions *via* a 1,2-shift in a trigonal bipyramidal intermediate such as XXII to give structures like XIV (R = CH_3 or H) and, possibly, XXVIII. Only 1-phenylphosphole shows any evidence of cyclization in the manner of 1,2,5-triphenylphosphole (to give XXXI) and this, if it occurs, is clearly a relatively minor pathway. Again, heavily substituted phospholes appear to show atypical behaviour.

Finally, some of these reactions may be synthetically useful since bicyclic systems of phosphorus and carbon, particularly those with phosphorus at a ring junction, are rare.

EXPERIMENTAL

The ir spectra were recorded on a Beckman IR 12 spectrophotometer for samples mulled in Nujol using sodium chloride demountable cells. The uv spectra were obtained using a Unicam SP 800A recording spectrophotometer with 1 cm fused silica cells. Ethanol (95%) or concentrated hydrochloric acid was used as solvent and the calibration of the spectrophotometer was checked against a holmium filter.

The ^1H nmr measurements were made with a Varian Associates model A60-A spectrometer equipped for variable temperature studies. Deuteriochloroform, dimethylsulfoxide (DMSO) and trifluoroacetic acid were used as nmr solvents with tetramethylsilane as internal reference. The spin decoupling studies were carried out using a V-6058A field sweep decoupling unit and the signal averaging using a Varian Data Systems model 620i unit.

Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-7 double focussing mass spectrometer using a direct heated inlet system. Precise masses were determined using the peak matching technique.

Column chromatography was carried out using neutral alumina as the adsorbent while benzene for the reactions was dried by distillation from calcium hydride. Nitrogen (certified pure) was dried by passage through concentrated sulfuric acid followed by passage through sodium hydroxide pellets.

Phosphorus analyses were carried out by Dr. Franz Pascher of Bonn. All other analyses were carried out in these laboratories using a Perkin-Elmer Model 240 Elemental Analyzer.

Melting points are uncorrected.

Syntheses.

Simple phospholes were prepared by the method described by Mathey (22,31). Briefly, equimolar amounts of phenyldibromophosphine and the appropriate butadiene derivative were mixed together and stored in the body of a refrigerator for several days, the length of time depending upon the diene used. When the reaction was complete, heating the adduct under reflux with two moles of diazabicyclo[5.4.0]undec-5-ene (DBU) in a benzene-dichloromethane mixture effected dehydrobromination giving the crude phosphole in solution. This solution was washed with water, dried, taken down to low bulk and the phosphole extracted with hexane. Further purification and isolation of the phosphole was carried out as described by Mathey and the pure phosphole was used for further experiments as soon as possible after preparation to avoid any deterioration. 1,2,5-Triphenylphosphole (II) was also prepared by literature (35) methods.

Reaction of 3,4-Dimethyl-1-phenylphosphole (VI, R = Ph) with Dimethyl Acetylenedicarboxylate.

With ice-bath cooling and vigorous stirring under dry, oxygen-free nitrogen, a solution of dimethyl acetylenedicarboxylate (3.28 g., 0.0321 mole) in dry benzene (75 ml.) was treated dropwise with a solution of 3,4-dimethyl-1-phenylphosphole (2.16 g., 0.0115 mole) in dry benzene (50 ml.). Reaction was immediate and the resulting dark red mixture was heated under reflux for 30 minutes under a slow stream of nitrogen. The mixture was concentrated by evaporation under nitrogen and chromatographed on neutral alumina using benzene as eluent. Further elution with benzene/diethyl ether mixtures of steadily increasing diethyl ether content resulted in a broad orange band moving slowly down the column. This orange band was finally eluted with pure diethyl ether. Concentration of the ether fractions resulted in slow crystallization (several days) of orange globular clusters of crystals (2.13 g., 39.2% yield) of XIV (R = CH_3), m.p. 205-207°; ir (Nujol): ν CO 1740, 1710, 1660, 1650, and 1520 cm^{-1}; uv: λ max 223 (ϵ 19320), inflection 269 (ϵ 8900), inflection 277 (ϵ 10000), inflection 289 (ϵ 10000) and 331 nm (ϵ 12780); nmr (deuteriochloroform): τ 2.00-2.55 (m, 5H, aromatic), 3.50-4.40 (m, 2H, olefinic), 6.01 (s, 3H, OMe), 6.38 (s, 3H, OMe), 6.45 (s, 3H, OMe), 7.01 (s, 3H, OMe), 7.75 (s, 3H, Me), 7.97 (s, 3H, Me); ms: m/e 472 (M^+).

Anal. Calcd. for $C_{24}H_{25}O_8P$: C, 61.02; H, 5.30; P, 6.57. Found: C, 61.04; H, 5.60; P, 6.62.

Reaction of 3-Methyl-1-phenylphosphole (V) with Dimethyl Acetylenedicarboxylate.

Under similar conditions to those outlined above, a solution of dimethyl acetylenedicarboxylate (2.90 g., 0.0205 mole) in benzene

(50 ml.) was treated dropwise with a solution of 3-methyl-1-phenylphosphole (1.73 g., 0.0100 mole) in dry benzene (50 ml.). Reaction was again immediate and the resulting dark brown mixture was heated under reflux for 30 minutes under a slow stream of nitrogen. The concentrated mixture was chromatographed on neutral alumina using benzene as eluent. Further elution with benzene/diethyl ether was carried out as described above and this resulted in a bright yellow band moving slowly down the column. Final elution from the column was again achieved with pure diethyl ether. Concentration of the ether fractions followed by addition of low-boiling petroleum ether resulted in the precipitation of a yellow powder (0.964 g., 21.0% yield) identified as the ylide XIV (R = H), m.p. 157-159°; ir: ν CO 1747, 1704, 1665 and 1530 cm^{-1}; uv: λ max 223 (ϵ 20150), inflection 262 (ϵ 9100), inflection 269 (ϵ 10000), inflection 275 (ϵ 10000), 332 nm (ϵ 12750); nmr (deuteriochloroform): τ 2.43 (m, 5H, aromatic), 3.18-4.50 (m, 3H, olefinic), 6.08 (s, 3H, OMe), 6.41 (s, 3H, OMe), 6.51 (s, 3H, OMe), 7.07 (s, 3H, OMe), 7.87 (s, 3H, Me); ms: m/e 458 (M^+).

Anal. Calcd. for $C_{23}H_{23}O_8P$: C, 60.26; H, 5.02; P, 6.77. Found: C, 60.29; H, 5.48; P, 6.29.

Reaction of 1-Phenylphosphole (I, R = Ph) with Dimethyl Acetylenedicarboxylate.

Dimethyl acetylenedicarboxylate (2.32 g., 0.0163 mole) in benzene (50 ml.) was treated with the phosphole (1.42 g., 0.0080 mole) in benzene (50 ml.) under the same conditions already outlined for the other phospholes. The resulting dark brown mixture was concentrated to low bulk and chromatographed on alumina using benzene as the eluent. Further elution with benzene/diethyl ether mixtures as described earlier resulted in a very pale yellow band moving down the column. This band was finally eluted with pure ether. Concentration of the ether fractions resulted in slow crystallization (overnight) of colourless needles (0.098 g., 2.7% yield) of what is almost certainly the nine-membered ring compound XXXI, m.p. 140-143°; ir (Nujol): ν CO 1760, 1736 and 1725 cm^{-1}; nmr (deuteriochloroform): τ 2.20-2.76 (m, 5H, aromatic), 3.00-4.00 (m, 3H, olefinic), 5.35-5.60 (m, 1H, olefinic), 6.17 (s, 3H, OMe), 6.24 (s, 6H, OMe), 7.06 (s, 3H, OMe); ms m/e 444 (M^+).

Anal. Calcd. for $C_{22}H_{21}O_8P$: C, 59.46; H, 4.73; P, 6.98. Found: C, 59.69; H, 4.85; P, insufficient sample.

A second darker yellow band was eluted more slowly from the same alumina column with diethyl ether. Concentration of these later fractions and addition of low-boiling petroleum ether resulted in the precipitation of a yellow powder (0.208 g., 5.86% yield) which was tentatively identified as the ylide XXVIII, m.p. 118-120°; ir (Nujol): ν CO 1745, 1702, 1662, 1640 and 1525 cm^{-1}; uv: λ max 225 (ϵ 18130), 248 (ϵ 13630) and 332 nm (ϵ 9820); nmr (deuteriochloroform): τ 2.43 (m, 5H, aromatic), 2.70-4.60 (m, 3H, olefinic), 5.50-7.10 (m, 13H, 12 ester methoxy + 1 tertiary C-H); ms: m/e 444 (M^+).

Anal. Calcd. for $C_{22}H_{21}O_8P$: C, 59.46; H, 4.73; P, 6.98. Found: C, 60.40; H, 4.91; P, 5.98 (P on a later sample).

Repeated attempts to purify the material to obtain better analyses proved fruitless and the assignment of structure must therefore remain tentative as outlined in the discussion.

In all of the phosphole-acetylenic ester reactions described above, if elution of the column was continued, 1:2:1 adducts of the appropriate phosphole, the ester and water were obtained in very small quantities and were characterized only by mass spectra. For the reasons outlined in the discussion, these adducts were not further investigated.

Acknowledgment.

We thank the National Research Council of Canada for generous financial support of this work.

REFERENCES AND NOTES

(1) W. Schäfer, A. Schweig and F. Mathey, *J. Am. Chem. Soc.*, **98**, 407 (1976).

(2) N. D. Epiotis and W. Cherry, *ibid.*, **98**, 4365 (1976).

(3) A. N. Hughes and D. Kleemola, *J. Heterocyclic Chem.*, **13**, 1 (1976).

(4) L. D. Quin and J. G. Bryson, *J. Am. Chem. Soc.*, **89**, 5984 (1967).

(5) L. D. Quin, S. G. Borleske and J. F. Engel, *J. Org. Chem.*, **38**, 1858 (1973).

(6) D. G. Holah, A. N. Hughes and K. Wright, *Coord. Chem. Rev.*, **15**, 239 (1975).

(7) D. G. Holah, A. N. Hughes, B. C. Hui and P. K. Tse, *J. Heterocyclic Chem.*, **15**, 89 (1978).

(8) D. G. Holah, A.N. Hughes, B. C. Hui and P. K. Tse, *ibid.*, submitted for publication.

(9) F. Mathey, *J. Organomet. Chem.*, **93**, 377 (1975).

(10) F. Mathey, *Tetrahedron Letters*, 4155 (1976).

(11) J. M. Rosalky, B. Metz, F. Mathey and R. Weiss, *Inorg. Chem.*, **16**, 3307 (1977).

(12) F. Mathey and G. Muller, *J. Organomet. Chem.*, **136**, 241 (1977).

(13) F. Mathey, *ibid.*, **139**, 77 (1977).

(14) M. Fraser, D. G. Holah, A. N. Hughes and B. C. Hui, *J. Heterocyclic Chem.*, **9**, 1457 (1972).

(15) F. Mathey, *Tetrahedron*, **28**, 4171 (1972).

(16) F. Mathey, *ibid.*, **29**, 707 (1973).

(17) F. Mathey, D. Thavard and B. Bartet, *Can. J. Chem.*, **53**, 855 (1975).

(18) For a review of early studies in this area, see M. A. Shaw and R. S. Ward, *Top. Phosphorus Chem.*, **7**, 1 (1972).

(19) A. N. Hughes and S. Uaboonkul, *Tetrahedron*, **24**, 3437 (1968).

(20) N. E. Waite and J. C. Tebby, *J. Chem. Soc. C*, 386 (1970).

(21) L. D. Quin, J. G. Bryson and J. F. Engel, *Phosphorus*, **2**, 205 (1973).

(22) F. Mathey and R. Mankowski-Favelier, *Org. Magn. Reson.*, **4**, 171 (1972).

(23) N. E. Waite, J. C. Tebby, R. S. Ward and D. H. Williams, *J. Chem. Soc. C*, 1100 (1969).

(24) N. E. Waite, J. C. Tebby, M. A. Shaw, R. S. Ward and D. H. Williams, *ibid.*, 1620 (1971).

(25) N. E. Waite, D. W. Allen and J. C. Tebby, *Phosphorus*, **1**, 139 (1971).

(26) J. R. Corfield, M. J. P. Harger, J. R. Shutt and S. Trippett, *J. Chem. Soc. C*, 1855 (1970).

(27) M. Davies, A. N. Hughes and S. W. S. Jafry, *Can. J. Chem.*, **50**, 3625 (1972).

(28) M. A. Shaw, J. C. Tebby, J. Ronayne and D. H. Williams, *J. Chem. Soc. C*, 944 (1967).

(29) A. N. Hughes, K. Amornraksa, S. Phisithkul and V. Reutrakul, *J. Heterocyclic Chem.*, **13**, 65 (1976).

(30) R. G. Cooks, R. S. Ward, D. H. Williams, M. A. Shaw and J. C. Tebby, *Tetrahedron*, **24**, 3289 (1968).

(31) F. Mathey, R. Mankowski-Favelier and R. Maillet, *Bull.*

Soc. Chim. France, 4433 (1970).

(32) L. D. Quin, S. G. Borleske and J. F. Engel, *J. Org. Chem.*, 38, 1954 (1973).

(33) A. N. Hughes and C. Srivanavit, *Can. J. Chem.*, 49, 879 (1971).

(34) A. N. Hughes, K. Amornraksa and S. Phisithkul, unpublished results.

(35) I. G. M. Campbell, R. C. Cookson, M. B. Hocking and A. N. Hughes, *J. Chem. Soc.*, 2184 (1965).