Cycloaddition and Related Reactions of Some Unsaturated Phosphines with Dimethyl Acetylenedicarboxylate

MAUREEN DAVIES, A. N. HUGHES, AND S. W. S. JAFRY
Department of Chemistry, Lakehead University, Thunder Bay, Ontario

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Diphenylvinylphosphine reacts with dimethyl acetylenedicarboxylate to give either an equilibrium mixture of two cyclic ylidic 1:1 adducts or a strained bicyclic ylidic 1:2 adduct depending upon the reaction conditions. The adducts have been characterized by trapping them as their hydrolysis or deuterolysis products or by their Wittig reactions. *trans*-1,2-Bis(diphenylphosphino)ethylene reacts with the ester to give a 1:1 zwitterionic adduct which exhibits some ylidic properties and hydrolyzes by a very unexpected mechanism. The *cis* isomer of this phosphine reacts with the ester to give the expected 1,4-diphosphorin which has been fully characterized.

La diphénylvinylphosphine réagit avec l'acétylène dicarboxylate de diméthyle pour conduire soit à un mélange à l'équilibre de deux composés d'addition 1:1 de type ylure cyclique soit à un composé d'addition 1:2 de type ylure bicyclique tendu, en fonction des conditions de la réaction. Ces composés d'addition ont été caractérisés en les piègeant en tant que produits issus de l'hydrolyse et deutériolyse ou encore par réaction de Wittig. Le bis-(diphénylphosphino)-1,2 éthylène *trans* réagit avec l'ester en donnant un composé d'addition 1:1 de type zwitterion qui possède quelques propriétés d'ylure et s'hydrolyse selon un mécanisme très inattendu. L'isomère *cis* de cette même phosphine réagit avec l'ester pour conduire à la diphosphorine-1,4 attendue qui a été complètement caractérisée. [Traduit par le journal]

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Until quite recently, cyclic phosphonium ylides (apart from the 1,1-disubstituted phosphorins) were relatively little known (1) and little work had been done on convenient and generally applicable syntheses of these systems. Since triphenylphosphine reacts readily with dimethyl acetylenedicarboxylate (2) and benzyne (3), it seemed likely that one possibly general route to cyclic phosphonium ylides of various ring sizes would be the cycloaddition of various unsaturated linkages such as suitable alkynes and arynes to vinylphosphines. Such additions would produce five-membered cyclic phosphonium ylides. Furthermore, by analogy with the insertions of dimethyl acetylenedicarboxylate into the P=C bonds of open-chain ylides (4), these initial products could possibly react further to give larger ylidic rings.

Such reactions would be essentially one-step processes involving relatively easily accessible starting materials. We therefore report here the results of our investigations regarding the reactions of diphenylvinylphosphine (**1**, R = H), *trans*-1,2-bis(diphenylphosphino)ethylene (**2**), *cis*-1,2-bis(diphenylphosphino)ethylene (**3**), and 3,4,5-triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene (**4**) with dimethyl acetylenedicarboxylate. A preliminary communication regarding the reactions of **1** (R = H) with the acetylenic ester has already appeared (5). In addition, certain exploratory experiments involving the generation of benzyne in the presence of **1** and **2** are briefly mentioned. It should also be noted that, during the early stages of this work, Savage and Trippett (6) reported the cycloaddition of acrylonitrile to diphenyl(1-phenylvinyl)phosphine (**1**, R = Ph) to give the ylide **5**.

As expected, diphenylvinylphosphine reacts readily with dimethyl acetylenedicarboxylate in ether or benzene although the nature of the product depends upon the mode of addition and the proportions of the reactants. Thus, dropwise addition of a benzene solution of the ester to an equimolar amount of the phosphine in benzene at room temperature under nitrogen leads immediately to the formation of a very dark solution. Evaporation of the solution yields a tarry material in which the principal product appears to be a dark blue polymeric material. Repeated ethereal extraction of the blue material and crystallization of the residual crude product from ethanol leads to the isolation (in about 23% yield) of colorless crystals, m.p. 130–132°, which analyze well for a mole-

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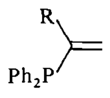

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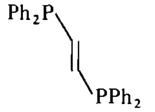

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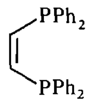

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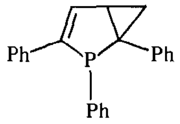

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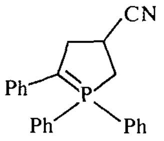

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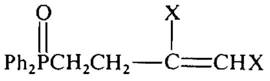
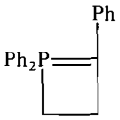


$$\mathrm{Ph_2\overset{\overset{O}{\|}}{P}CH_2CH_2{-}\overset{\overset{X}{|}}{C}{=}CHX}$$

7

$X = -CO_2Me$



11

cular formula of $C_{20}H_{21}O_5P$, *i.e.* a 1:1:1 adduct of the phosphine, the ester, and water. The mass spectrum shows a molecular ion at *m*/*e* 372 which is consistent with the proposed molecular formula. The same product is formed regardless of whether dried or undried solvents are used (although ether containing appreciable amounts of ethanol should be avoided) and this indicates that during the reaction (or during work-up if anhydrous solvents are used), hydrolysis of an initially formed 1:1 adduct of the ester with the phosphine occurs.

The expected initial product of the reaction is the cyclic ylide **6** (a 3*H*-phosphole derivative) and, since most phosphonium ylides are very sensitive to water, this might be expected to hydrolyze to give the phosphine oxide **7** by protonation followed by ring cleavage of the resulting cyclic phosphonium hydroxide by elimination of the most stable carbanion (7). In support of this, the base peak in the mass spectrum of the 1:1:1 adduct occurs at *m*/*e* 201 which is typical of compounds containing the $\mathrm{Ph_2\overset{\overset{O}{\|}}{P}—}$ grouping (6). Furthermore, the i.r. spectrum also shows a typical (8) P=O stretching frequency at 1193 cm^{-1} and a weak substituted C=C vibration at 1664 cm^{-1}. However the ^1H n.m.r. spectrum is inconsistent with structure **7** since, although it shows the presence of two methylene groups, the coupling pattern clearly shows that these two groups are not adjacent. The spectrum shows a ten proton aromatic complex multiplet at τ 2.0–2.6, an olefinic one proton quartet at τ 2.6–3.3, two ester methyl groups at τ 6.30 and 6.37, one methylene group as a doublet of doublets centered on τ 6.69 (with the indication that $J_{HH} = 8$ and $^2J_{PH} = 16$ Hz), and one methylene group as a very closely spaced doublet ($J =$ *ca.* 1.5 Hz) at τ 6.65 superimposed upon the other methylene signal. One interesting feature of this spectrum is that to some extent it is concentration dependent. For example, at concentrations approaching 50%, the ester peaks are shifted a few cycles upfield while the two methylene signals are shifted very slightly downfield.

This spectrum fits the isomeric structure **9** extremely well and this structure is also consistent with the i.r. and mass spectral data. Thus, the tentatively assigned values of J_{HH} and $^2J_{PH}$ for the methylene group (τ 6.69) adjacent to the phosphorus atom are in excellent agreement with those observed for related structures in the literature (see for example, values for $^2J_{PH}$ for compounds containing the $\mathrm{Ph_2\overset{\overset{O}{\|}}{P}CH_2—}$ grouping quoted in ref. 6). Furthermore, the locations of the two methylene groups in the spectrum are as expected for **9**. The methylene group adjacent to the terminal ester group (τ 6.65) presumably occurs as a poorly defined doublet ($J =$ *ca.* 1.5 Hz) because of long-range coupling with the phosphorus atom. Such long-range couplings are known to give rise to values of $^5J_{PH}$ of the order of 1 Hz (9). On the other hand, it is possible that this methylene group is coupled to the olefinic proton which could account for the broadening of the peaks in the olefinic quartet. The fact that the olefinic signal occurs as a quartet (in the approximate ratio 1:3:3:1) implies that J_{HH} and $^3J_{PH}$ have approximately the same value (7 Hz).

These tentative n.m.r. assignments have been confirmed by ^1H–^1H spin decoupling (field sweep) experiments. In this case, since the couplings in some instances are relatively large and the signal width is therefore considerable, selective decoupling techniques (10*a*) were found to give the best results. Irradiation of the low field doublet of the doublet of doublets of the methylene signal centered on τ 6.69 while scanning the olefinic signal causes the two high field peaks of the olefinic signal to collapse to an intense, sharp singlet centered on the more intense of the original peaks. Likewise, irradiation of the high field doublet of the methylene doublet of doublets causes the low field pair of peaks of the olefinic signal to collapse in a similar fashion. Conversely, irradiating the more intense of the two low field peaks of the olefinic signal while scanning the methylene signal at τ 6.69 causes the high field doublet of this signal to collapse to a singlet. Similar irradiation of the more intense of the two high field peaks of the olefinic signal leads to a collapse of the low field doublet of the methylene signal.

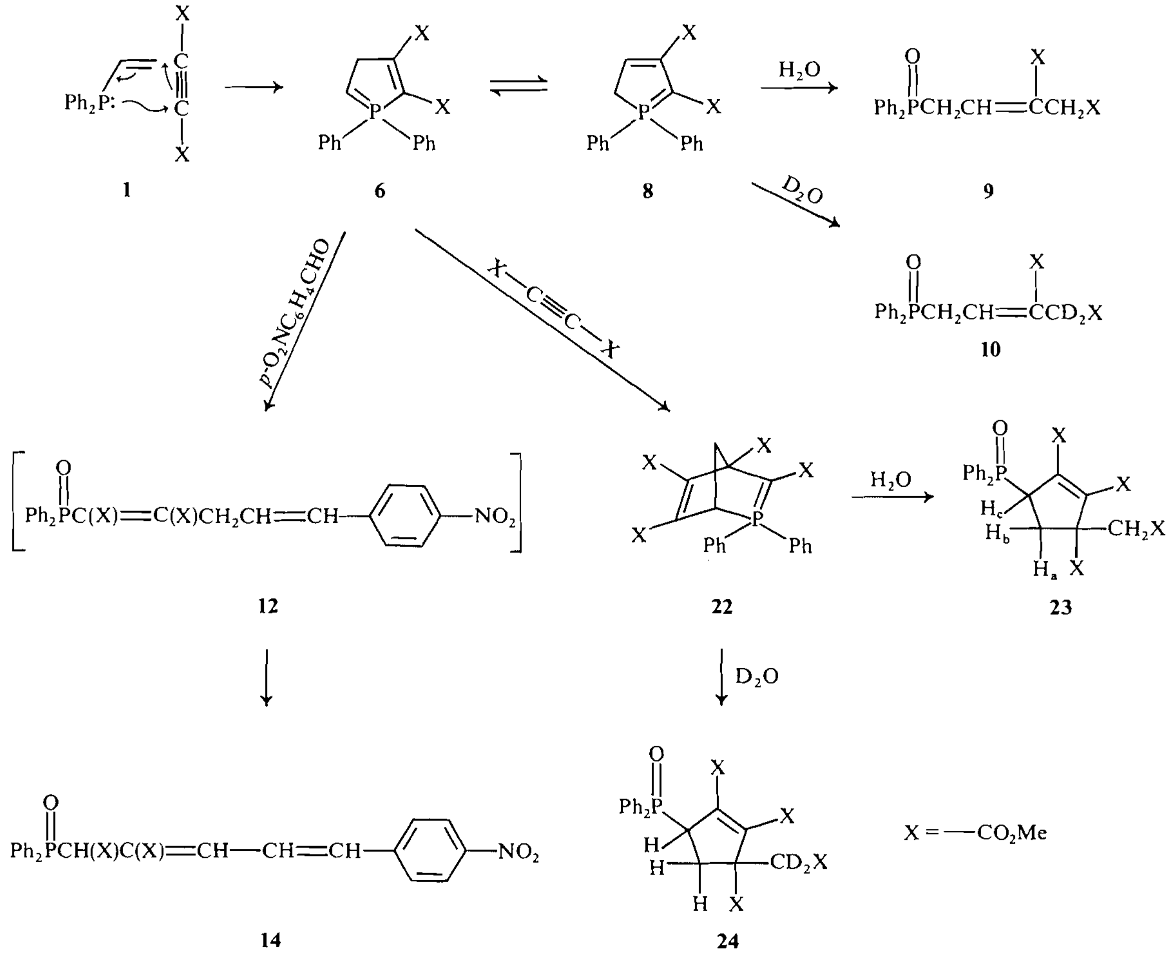
These results clearly show that the olefinic proton is coupled to the methylene protons at τ 6.69 ($J = 8$ Hz) and that the olefinic $^3J_{PH}$ coupling is 7 Hz (the small difference in these couplings accounts for the broadened peaks in the olefinic quartet). Furthermore, the $^2J_{PH}$ coupling of the methylene group adjacent to the phosphorus atom is 16 Hz and these selective decoupling experiments show (10*a*) that $^2J_{PH}$ and $^3J_{PH}$ are of opposite sign.

Very careful scanning of the spectrum in the decoupling mode shows that there is no coupling between the olefinic protons and the methylene group centered on τ 6.65 (assigned to the methylene group adjacent to the terminal ester group) and the narrow splitting of this signal (1.5 Hz) is therefore confirmed as being due to long-range P–H coupling.

Very strong support for structure **9** is also provided by the mass spectrum which shows weak peaks at *m/e* 299 (possibly $M^+ - CH_2CO_2Me$), 215 (possibly $Ph_2\overset{\overset{O}{\|}}{P}CH_2^+$) and 157 (possibly $M^+ - Ph_2\overset{\overset{O}{\|}}{P}CH_2$). These tentative assignments are confirmed by precise mass measurements (*m/e* 299: calcd., 299.0837; found, 299.0839; *m/e* 215: calcd., 215.0626; found, 215.0623; *m/e* 157: calcd., 157.0501; found, 157.0509). These peaks are very weak because cleavage would be preferred in a position allylic to the C=C link, *i.e.* adjacent to the phosphorus atom or the terminal ester group. These expected peaks are very strong in the mass spectrum of the 1:1:1 adduct. Finally, the spectrum shows a peak of medium intensity at *m/e* 340 corresponding to loss of methanol from the —CH_2CO_2Me grouping. The fragmentation is confirmed by a weak metastable peak at m^* 310.7. Such eliminations are common in esters of this type (11).

The i.r. spectrum also shows two ester carbonyl stretching frequencies at 1722 (α,β-unsaturated ester) and 1749 cm^{-1} (saturated ester) and this is in agreement with structure **9**.

Structure **9** could be derived either from **7** by proton migration (a process which seems unlikely) or from hydrolysis of the cyclic ylide **8** (a 2*H*-phosphole derivative) which is a tautomer of **6**. Moreover, in such a tautomeric equilibrium, **8** should be preferred over **6** since in **8** there is more delocalization of the ylidic carbon atom negative charge over the adjacent ester group. Deuterolysis experiments support the suggestion that **9** is derived from **8** by hydrolysis. Thus, when cycloaddition of the vinylphosphine **1** (R = H) and the acetylenic ester was carried out in rigorously dried ether followed by addition of a little D_2O to the reaction mixture, it was found that mainly double deuteration (to give **10**) and some triple deuteration occurs. For example, the mass spectrum shows that the strongest molecular ion peaks occur at *m/e* 374 (double deuteration) and 375 (triple deuteration). The n.m.r. spectrum shows that the narrow doublet due to the methylene group adjacent to the terminal ester group has almost disappeared from the spectrum although there is also a reduction (from 2 to about 1.4 protons) in the intensity of the other methylene signal. The ^1H n.m.r. spectrum therefore shows that deuteration occurs mainly at the site adjacent to the terminal ester group (although some deuteration occurs at the other methylene group) and this is



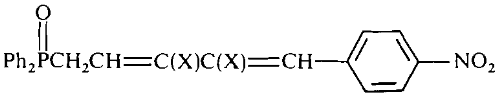
X = —CO$_2$Me

Scheme 1

consistent with the behavior expected of **8** on hydrolysis.

These observations then are fairly good evidence that the ylide **8** is formed from the initially formed ylide **6** by tautomerization. Furthermore, similar tautomeric equilibria have been observed in the case of the four-membered ylide **11** (6). Several attempts to trap **6** before tautomerization could occur were therefore made. Attempts to trap **6** in a Wittig reaction with acetone and with benzaldehyde were unsuccessful. The use of acetone gave only uncrystallizable materials and use of benzaldehyde gave the adduct **9** as the only isolable product. However, cycloaddition of the ester and phosphine in the presence of *p*-nitrobenzaldehyde leads to the formation of a 1:1:1 adduct of the ester, the phosphine, and the aldehyde for which elemental analyses are in excellent agreement with the formula $C_{27}H_{24}O_7NP$. The mass spectrum confirms the molecular weight as 505 and the base peak is again at *m*/*e* 201 indicating the presence of the $Ph_2\overset{\overset{O}{\|}}{P}$— grouping. Thus, a Wittig reaction has occurred and the intermediacy of a cyclic ylide is established.

The adduct expected from **6** would be **12** while that from **8** would be **13** but the ^1H n.m.r. spectrum shows that the adduct is neither of these since there are no signals due to methylene groups in the spectrum. The spectrum shows 17 aromatic/olefinic protons as a broad complex multiplet at τ 1.6–3.4, one methine proton as a



$Ph_2\overset{O}{\overset{\|}{P}}CH_2CH{=}C(X)C(X){=}CH{-}C_6H_4{-}NO_2$

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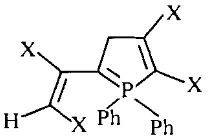

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$R_3P{=}C(X){-}C(X){=}CHR'$

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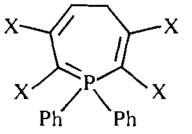

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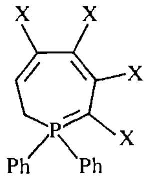

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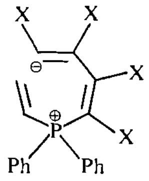

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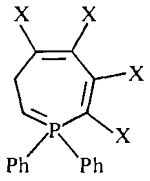

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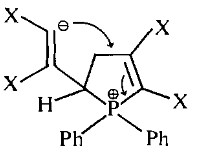

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$X = {-}CO_2Me$

doublet ($J = 15$ Hz) centered on τ 4.38, and two ester methyl group signals at τ 6.33 and 6.38. Of the various possible isomers obtainable by addition of *p*-nitrobenzaldehyde to **6** or **8**, only **14** agrees with all the physical data since it contains no methylene groups and the low field location and the splitting of the methine proton ($J = 15$ Hz) are consistent with its position adjacent to a phosphoryl grouping and two other electron-withdrawing groups. Clearly **14** cannot be derived directly from **6** or **8** and is presumably derived from **12** by a prototropic shift. Such a shift is not surprising since it increases the conjugation in the system and the conditions of the reaction (the ylide **6** would be a strong base) would favor migration of the mildly acidic protons of the methylene group in **12**. A similar prototropic shift in **13** could produce a methine proton adjacent to an ester group (though far removed from the phosphorus atom) but this would decrease the conjugation. Some further, though not conclusive evidence for structure **14** is given by the mass spectrum which shows a peak at *m/e* 273 probably corresponding to the fragment $[Ph_2\overset{O}{\overset{\|}{P}}CHCO_2Me]^+$ (precise mass found: 273.0673; calcd.: 273.0681). This could only be derived from **14** unless major rearrangements occur on electron impact. This peak is comparable in intensity with the molecular ion peak though much weaker than the base peak. In addition, the i.r. spectrum shows both saturated (1745 cm^{-1}) and α,β-unsaturated (1692 cm^{-1}) ester carbonyl stretching frequencies.

As already mentioned, the mode of reaction and proportions of the reactants in the reaction of the phosphine **1** (R = H) with the acetylenic ester can influence the nature of the product. If the phosphine (1 mol) in ether is added to an ethereal solution of the ester (2 mol) under the same reaction conditions as the 1:1 addition, a 1:2:1 adduct of the phosphine, the ester and water is obtained in about 10% yield. Analyses are in excellent agreement with a molecular formula of $C_{26}H_{27}O_9P$ and the mass spectrum shows a molecular ion at *m/e* 514 together with the base peak at *m/e* 201 ($PH_2\overset{O}{\overset{\|}{P}}{-}$). On the basis of the arguments used in the case of the 1:1:1 adduct of diphenylvinylphosphine with the ester and water, it is virtually certain that the 1:2:1 adduct is derived from hydrolysis of an ylidic 1:2 adduct of the phosphine and the ester.

There are several possible modes of reaction. For example, Michael addition of the ylide **6** to a second mole of the ester could occur to give the ylide **15** although this type of addition is not possible for the ylide **8**. This type of mechanism was suggested by Trippett (12) for the addition of cyanomethylenetriphenylphosphorane ($Ph_3P{=}CHCN$) to dimethyl acetylenedicarboxylate and would presumably be due to the highly acidic nature of the methine proton in the initially formed zwitterion. On the other hand, Bestmann and Rothe (4) have found that addition of alkylidenephosphoranes to the ester leads (in every case studied by his group), to insertion of the ester into the $R_3P{=}CHR'$ link to give compounds of type **16**. This would suggest that **6** or **8** could react further with the ester to give the seven-membered ylides **17** or **18** respectively (or, possibly, tautomers of these). Another possible mode of reaction is the generation of the zwitterion **19** followed by cyclization to give **20**. A similar reaction path occurs in the reaction of 1,2,5-triphenylphosphole with an excess of the ester (13). Finally, the initially formed ylide **6** could react further with the ester to give **21** which could cyclize by attack at the β-position of a vinylphosphonium grouping to give the strained bicyclic ylide **22** in much the same way as **6** itself is formed.

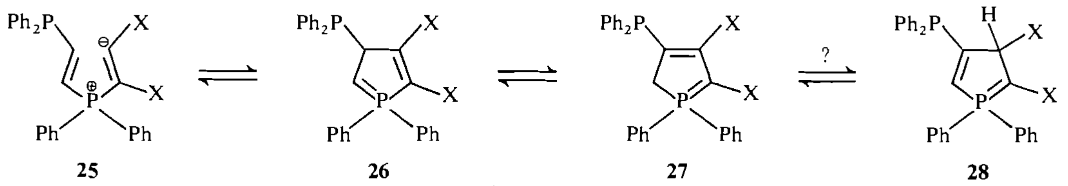
Examination of the ^1H n.m.r. spectrum of the 1:2:1 adduct shows quite conclusively that it is **23** which is derived from hydrolysis of the bicyclic ylide **22**. Thus, hydrolysis of the other possible intermediates **15**, **17**, **18**, or **20** (or possible tautomers) would lead to a product containing olefinic protons whereas careful integration of the ^1H n.m.r. spectrum of the 1:2:1 adduct shows clearly that the adduct contains no olefinic protons.

The spectrum of the 1:2:1 adduct shows ten aromatic protons as a complex multiplet at τ 1.9–2.7, one methine proton as eight unevenly spaced, poorly defined, and partly overlapping peaks of similar intensity centered on τ 5.72, four ester methyl groups at τ 6.29, 6.32, 6.38, and 6.82, two methylene protons as an *apparent* doublet at τ 6.72 and 6.81, and two other methylene protons as a poorly defined multiplet of at least 12 maxima at τ 6.80–7.70. Since the two ring methylene protons in **23** would be non-equivalent, they would have somewhat different chemical shifts and may couple with each other, the neighboring methine proton, and the phosphorus atom to give up to 16 peaks of which at least 12 are observed. Similarly, the methine proton should appear at a much lower field location as two doublets of doublets through coupling with the phosphorus atom and the non-equivalent ring methylene protons. The side-chain methylene group presumably occurs as an apparent doublet (the inner peaks of a closely spaced AB signal of which the outer peaks are buried under the ester signals and the other methylene signals) in the spectrum because its proximity to an asymmetric center renders the two protons non-equivalent as is the case with the diastereotopic protons of 1,2-dichloropropane (14*a*). The signal separation of the two inner peaks of the AB pattern in such cases normally falls in the range 2–15 Hz (*e.g.* 14*b*). It is unlikely that the splitting of this signal is due to long-range coupling with the phosphorus atom since the value of $J = 5.5$ Hz is rather high compared with other measured values of $^5J_{PH}$ (9).

Again, double resonance and mass spectral studies confirm the proposed structure **23** for the 1:2:1 adduct. Careful scanning of the n.m.r. spectrum in the decoupling mode shows that fairly strong irradiation (*i.e.* full decoupling) at τ 7.00 while scanning the region of the eight peak one-proton signal centered on τ 5.72 causes the latter signal to collapse to a doublet of doublets with one coupling constant of 7 Hz and the other of 12 Hz. Similarly, irradiation at τ 7.32 again causes the one-proton eight peak signal to collapse to a doublet of doublets in which one coupling constant is 4.5 Hz while the other is 12.5 Hz. Designating the proton at τ 7.32 as H_a, the proton at τ 7.00 as H_b, and the proton at τ 5.72 as H_c, it is clear that $J_{H_aH_c} = 4.5$, $J_{H_bH_c} = 7$, and $J_{PH_c} = 12.5$ Hz. Thus, the P–H coupling constant is of the right order of magnitude for $^2J_{PH}$ while the couplings of H_c with H_a and H_b are consistent with the proposed structure **23**.

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

One fact which did emerge from these de-



SCHEME 2

coupling experiments is that the weak outer peaks of the closely spaced methylene AB signal centered on τ 6.77 appear to be at τ 6.50 and τ 7.02 since irradiations of H_c while scanning H_a or H_b show that these peaks remain unchanged while considerable changes occur in the remaining peaks. Further support for this assignment comes from the fact that the intensity ratio (5.5:1) of the two fairly clearly seen low field peaks of the AB pattern (τ 6.50 and τ 6.72) is as predicted by theory (10*b*).

Mass spectral studies offer further confirmation for the structure **23**. For example, the loss of methanol characteristic of the —CH_2CO_2Me grouping (11) is shown by a peak at *m*/*e* 482 and the one-step fragmentation is confirmed by a metastable peak at *m** 452. Furthermore, the expected loss of the allylic —CH_2CO_2Me group is shown by a weak peak (25% of the molecular ion peak and 3% of the base peak) at *m*/*e* 441. Again, this fragmentation is confirmed by a weak metastable peak at *m** 378.3. Unfortunately, precise mass measurements for these peaks were not possible because suitable reference peaks were not available. Similarly, a weak peak at *m*/*e* 240 suggests the loss of both of the allylic $Ph_2\overset{\overset{O}{\|}}{P}$— and —$CH_2CO_2Me$ groups and this is confirmed by precise mass studies (calcd.: 240.0634; found: 240.0636). Presumably this peak is weak because the charge would tend to stay with the $Ph_2\overset{\overset{O}{\|}}{P}$— grouping and the fact that the base peak in the spectrum at *m*/*e* 201 is due to this grouping offers some support for this suggestion.

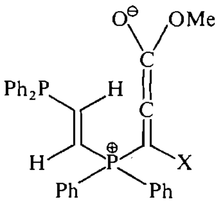
As with the 1:1:1 adduct, deuterolysis experiments on the 1:2 adduct offer further confirmation of these n.m.r. assignments since generation of this adduct in rigorously dried solvents followed by treatment of the solution with a little D_2O leads to the formation of **24**. The ^1H n.m.r. spectrum is virtually identical with that of **23** except that the AB pattern due to the side-chain methylene group has vanished from the spectrum. The only other change is a very small reduction in the signal strength of the other methylene multiplet. The heavy deuteration in the side-chain of **24** is strong evidence for the intermediacy of **22**. Reactions of **1** (R = H) with the ester are summarized in Scheme 1.

Attempts to trap the ylide **22** in a Wittig reaction with acetone, benzaldehyde, and *p*-nitrobenzaldehyde were unsuccessful. However, this is not surprising since the ylidic link in **22** would be highly hindered. Attempts to prepare perchlorate salts of **6**, **8**, and **22** were also unsuccessful but this too is not unexpected since recent work on related cyclic ylides (15) has shown that these salts are highly soluble in water and ethanol and are extremely difficult to crystallize even when the ylides themselves are available in considerable quantity.

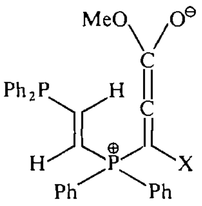
The experiments already described for the phosphine **1** were extended to other α,β-unsaturated phosphines and, in the case of *trans*-1,2-bis(diphenylphosphino)ethylene (**2**), some quite surprising results were obtained.

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 **2**, 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.

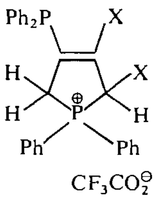
The most likely mode of reaction is cycloaddition of the type shown in the sequence $\mathbf{2}\rightarrow\mathbf{25}\rightleftharpoons\mathbf{26}\rightleftharpoons\mathbf{27}\rightleftharpoons\mathbf{28}$ (Scheme 2). This would be very similar to the 1:1 reaction between diphenylvinylphosphine and dimethyl acetylenedicarboxylate already described where similar



29



30



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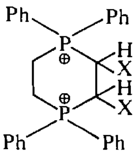

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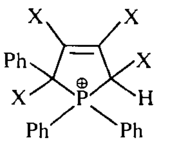

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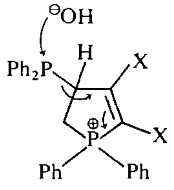

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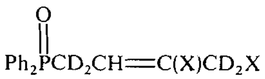
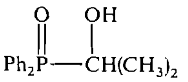


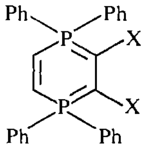
$Ph_2\overset{\overset{O}{\|}}{P}CD_2CH{=}C(X)CD_2X$

35

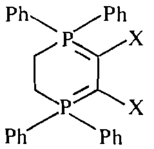


$Ph_2\overset{\overset{O}{\|}}{P}{-}\overset{\overset{OH}{|}}{C}H(CH_3)_2$

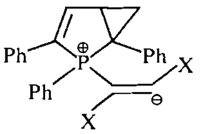
36



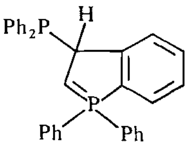
37



38



39



40

X = —CO_2Me

tautomeric equilibria have been observed. Furthermore, Savage and Trippett (6) have suggested equilibria of this type in the reaction of **1** (R = Ph) with acrylonitrile.

The i.r. spectrum shows two distinct carbonyl frequencies. One of these is at 1712 cm^{-1} and is clearly due to a normal unsaturated 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 (16). Superficially, this would suggest that the adduct is either **27** or **28** with **27** the more likely by analogy with the reaction of diphenylvinylphosphine and dimethyl acetylenedicarboxylate.

However, the ^1H n.m.r. spectrum of the adduct at −2 °C is definitely not consistent with **27** and probably not consistent with **26** or **28**. The spectrum shows 21 aromatic/olefinic protons as a complex multiplet at τ 2.18–3.32, one apparently olefinic proton as two poorly defined doublets of doublets centered on τ 3.60 and 4.00, respectively, and six methoxy protons as three peaks of unequal area at τ 6.13 (3 protons), 6.23, and 6.56. At −50 °C, the spectrum is much the same apart from small downfield shifts and better definition of the two doublets of doublets except that the three proton methoxy signal which occurs at τ 6.13 in the spectrum at −2 °C appears as a very closely spaced doublet with peaks of unequal intensity at τ 6.01 and 6.03. There is no evidence in the spectrum for a proton on an ylidic carbon atom which would be expected to resonate in the range τ 8–11 (9). At 42 °C, the spectrum is unstable because of sample decomposition but the spectrum of a very freshly prepared sample is much the same as the spectrum at −2 °C except that the olefinic proton signals are very poorly defined.

The ^1H n.m.r. spectrum in the methoxy region is consistent with the i.r. spectrum in that it indicates that one of the ester groups is adjacent to a carbanionic center and shows conformational preference as has been observed (16) for certain cyclic phosphonium ylides. However, this would also apply to **25** where the only nonaromatic protons are olefinic and where one ester group is adjacent to a carbanionic center. Major contributors to the resonance hybrid of **25** would be **29** and its rotational isomer **30**.

The multiplicity of the olefinic proton signal is of interest. Presumably the two fairly widely separated doublets of doublets (25 Hz) could be the result of the conformational preference of the methoxycarbonyl group as in **29** and **30** and its effect upon the proton β to the phosphonium center. One might perhaps expect this proton to appear under the aromatic signal but it has been shown that in some related structures such as **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 (17) between τ 3.0 and 3.5. Further, the close proximity of the carbanion negative charge to this proton would be expected to shield it to some extent. In theory, ignoring different conformational arrangements of the ester groups in **25**, eight peaks 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 (17, 18) that the protons on the bridging carbon atoms of bisphosphines show less than the normal expected multiplicity. In the opinion of the authors, the eight peaks observed are probably due to rotational isomerism of the ester groups although the difference in chemical shift of the two doublets of doublets (25 Hz) is within the normal J_{PH} coupling range for similar (17) bridged phosphines. This suggestion is reinforced by the observation that the olefinic signals become much more poorly defined as the temperature is increased. Furthermore, one ester methyl group appears as a three proton singlet at -2 °C while the other (presumably the one adjacent to the carbanion by analogy with the behavior of similar systems (16)) appears as two peaks (corresponding possibly to two conformational arrangements) at τ 6.23 and 6.56.

Thus, of the possible structures considered so far, only **25** (best represented as **29** or **30**) is fully consistent with both the ^1H n.m.r. and i.r. spectra, although the reasons why this tautomer should be preferred over the other possible tautomers in the equilibrium are obscure. Unfortunately, because of the extreme sensitivity of the adduct to trace amounts of water and oxygen and an apparent thermal sensitivity, it was not possible to carry out double resonance studies.

The ^1H n.m.r. 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 20 aromatic protons at τ 1.6–2.8 to approximately one proton as a diffuse multiplet at τ 4.3–5.1 to approximately six methoxy and two methylene or methine protons as a complex multiplet between τ 5.60 and 6.65. One interesting feature of this last region is that each of the two methoxy signals (centered on τ 6.98 and 6.42 respectively) is split into two closely spaced and unequal peaks. Clearly, these methoxy signals cannot be due to rotational isomerism relative to a carbanionic center 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 n.m.r. spectrum in CF_3CO_2D is similar except that the multiplet at τ 4.3–5.1 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 20 aromatic protons as a multiplet at τ 1.5–2.8, one methine proton as a doublet ($J = 13$ Hz) at τ 4.49, two methoxy groups as singlets at τ 5.95 and 6.45, respectively, and two methylene protons as a multiplet partly hidden under the methoxy protons in the range τ 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

31 (derived from **27**) agrees in every respect with the ^1H n.m.r. spectrum of the solution of the adduct in CF_3CO_2H which has been allowed to stand for several days. Thus the methine proton at τ 4.49 is virtually identical in location and splitting with the similar protons in **32** (15) and **33** (16), while the multiplicity of the methylene protons is very like that of the similar protons in **32**.

To summarize, the i.r. and ^1H n.m.r. evidence indicates that the 1:1 adduct of **2** with dimethyl acetylenedicarboxylate is an equilibrium of the structures **25**, **26**, **27**, and possibly **28** in which the zwitterionic form **25** greatly predominates over the other forms. However, in the presence of acid, the ylidic contributors to the equilibrium are protonated more readily than the zwitterionic form. This may also be true in the reactions of diphenyl(1-phenylvinyl)phosphine with acrylonitrile (6) and of diphenylvinylphosphine with dimethyl acetylenedicarboxylate where the initial 1:1 adduct could not be 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.

If the adduct has appreciable ylidic character, it should hydrolyze in the manner of an ylide to give (7) a phosphine oxide. However, when the adduct was dissolved in aqueous ethanol and warmed with stirring for several hours, the oxide **9** was formed which is identical with the hydrolysis product obtained from the 1:1 adduct of diphenylvinylphosphine with dimethyl acetylenedicarboxylate, *i.e.* one of the diphenylphosphino groups has been lost. The m.p. and the i.r., ^1H n.m.r., and mass spectra of this product are identical with those of an authentic sample.

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 **26**, 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 **34**.

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. On the other hand, it is well known (19) that in phosphonium compounds, nucleophilic attack may sometimes take place at the atom β to the phosphorus atom as in the sequence $R_3\overset{+}{P}-X-Y \;\; \ddot{N}u \rightarrow R_3P{=}X$.

In the structure **34** the diphenylphosphino group is not β to the phosphonium group but is vinylogously β to this group and attack of hydroxide ion on **34** as shown to give **8** and then **9** by hydrolysis could conceivably occur. 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 center.

Deuterolysis experiments using hot D_2O (99.7%) for several hours give some support to this mechanism since the compound **35**, together with some trideuterated material, is produced by treatment of the 1:1 adduct of **2** with the acetylenic ester with deuterium oxide.

Accurate integrations taken by means of signal averaged ^1H n.m.r. spectra show clearly that the olefinic hydrogen atom in this compound is not replaced by deuterium since the aromatic/olefinic : ester methyl integration is exactly 11:6. Furthermore, the n.m.r. spectrum shows that the methylene protons adjacent to the terminal ester group have been completely replaced by deuterium whereas traces (much less than one proton on integration) of the other methylene protons remain. This is confirmed by the mass spectrum which shows a molecular ion at *m/e* 376 together with a smaller peak at *m/e* 375 corresponding to the replacement of a maximum of four hydrogen atoms by deuterium. This is consistent with the proposed mechanism since the olefinic proton in the products **9** and **35** 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 **9** 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 which is present in great excess.

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 product of hydrolysis had been exposed to acetone, a very small amount of a colorless compound (m.p. 143°) was obtained. This compound showed no significant peaks in the mass spectrum above *m/e* 201 ($Ph_2P{=}O$) and the i.r. and ^1H n.m.r. spectra and analyses are consistent with the known (20) compound **36** (m.p. 137–139°) which can be formed by the addition of $Ph_2P(O)H$ to acetone. The compound is unstable in solution and repeated ^1H n.m.r. scans of the same sample showed that acetone is regenerated over a period of several hours. These observations tend to support attack of $\bar{O}H$ upon the exocyclic Ph_2P-group in **34** on hydrolysis of **25**.

The adduct **25** apparently does not enter into Wittig reactions.

The reactions with dimethyl acetylenedicarboxylate described for the *trans*-bisphosphine **2** were extended to the *cis*-bisphosphine **3** in order to see if addition of the type observed for **1** and **2** would occur or if the second phosphorus atom would attack on the unsaturated ester grouping in the initial zwitterionic intermediate to give the 1,1,4,4-tetraphenyl-1,4-diphosphorin **37**. Additions of this type have been observed (21) in the 1:2 addition of the ester to triphenylphosphine. During the later stages of this investigation, Tebby and co-workers (22) published a brief account of essentially the same work in which he described the cycloaddition of **3** and the acetylenic ester to give **37**.

There are only minor differences between our findings and those of Tebby. Thus, Tebby characterized the adduct mainly from the mass spectrum and the i.r. spectrum (which shows that both ester groups are attached to ylidic carbon atoms) and the behavior of the adduct **37** on hydrolysis which leads to the dioxide of **3**. No analytical data were reported although we were able to obtain reasonable analyses. Tebby was unable to carry out ^1H n.m.r. studies on the adduct because of its sensitivity to hydrolysis but, using freshly prepared samples of the adduct, we have been able to obtain reproducible ^1H n.m.r. measurements which confirm the bis-ylide nature of the adduct. The spectrum shows 22 aromatic and olefinic protons as a broad complex multiplet at τ 1.9–2.9 and six methoxy protons as a very broad unresolved hump at τ 6.2–7.1. The unresolved nature of the methoxy region is probably due to the presence of several interconvertible rotational isomers since the ester groups are adjacent to ylidic carbon atoms. Some support for this is given by the fact that the spectrum in the methoxy region at room temperature is almost identical in appearance to that of the cyclic bis-ylide **38** (23). Also, at −40° (where interconversion should be slow) the methoxy region is resolved into two reasonably sharp peaks of unequal area at τ 6.32 and 7.10 with the peak at τ 6.32 almost twice the area of the other peak. Furthermore both peaks show signs of splitting into doublets with unequal splitting of the two signals.

The adduct **37** also forms a crystalline bisperchlorate confirming its bis-ylide nature and ^1H n.m.r. studies of **37** in trifluoroacetic acid solution also confirm the proposed structure. The spectrum shows 22 aromatic/olefinic protons at τ 1.6–2.5 and six methoxy protons as a singlet at τ 6.27. The two methine protons appear as a broad hump at τ 4.6–5.0 with the broadening presumably due to exchange with the solvent.

One interesting point regarding the i.r. spectrum of **37** is that the main carbonyl absorption is at 1640 cm^{-1} with lesser peaks on either side. This is at a considerably higher location than for the apparently similar ester groups in **38** ($\nu = 1585\ cm^{-1}$). This may indicate that perhaps the carbanionic negative charges in **37** are delocalized into the ring to give something approaching an aromatic system whereas in **38** the delocalization is over the ester groups.

The cyclic phosphine **4** is a highly hindered version of **1** and reactions of **4** with dimethyl acetylenedicarboxylate were carried out in an attempt to achieve cycloadditions of the type observed for **1**. The highly strained and hindered ylides which would be produced by such cyclizations would be of considerable interest. However, attempts to carry out the cycloaddition under a wide variety of conditions using rigorously dried ethereal and non-ethereal solvents and even no solvent other than an excess of the ester, gave only the oxide of **4**. The change in appearance of the various reaction mixtures clearly indicates that a reaction occurs rapidly but it seems likely that the probable initially formed zwitterion **39** is too hindered to cyclize or react further and hydrolyzes on work-up in the manner observed for similar zwitterions (24) to give the corresponding phosphine oxide.

Finally, as a continuation of the work described in this paper, some preliminary experiments involving the generation of benzyne in the presence of the phosphines **1** and **2** have been carried out and, in some cases, some very unusual results have been obtained. Thus, treatment of **1** with *o*-benzenediazonium carboxylate unexpectedly gives the bisphosphine $Ph_2PCH_2CH_2PPh_2$ in moderate yield while **2** reacts with *N*-nitrosoacetanilide in the presence of potassium acetate to give the expected ylide **40** in very low yield which has been trapped as its hydrolysis product. These reactions are under further investigation and will be reported fully in a later paper.

Experimental

The i.r. spectra were recorded in Nujol mulls using a Beckman IR12 spectrophotometer while n.m.r. measurements were made with a Varian Associates model A60-A spectrometer equipped with a V-6058A spin decoupler using deuteriochloroform or trifluoroacetic acid solutions with tetramethylsilane as internal reference. Signal averaging was carried out using a Varian Data Systems model 620i unit. Mass spectra were determined using an Hitachi–Perkin–Elmer model RMU-7 double focusing mass spectrometer fitted with a direct heated inlet system. Melting points are uncorrected and were recorded using a Mel-Temp high-temperature m.p. apparatus.

Ether was dried by distillation from sodium or lithium aluminum hydride while tetrahydrofuran and benzene were dried by distillation from calcium hydride. Dimethyl acetylenedicarboxylate was freshly distilled under reduced pressure (*ca.* 1 Torr) immediately before use.

3,4,5-Triphenyl-4-phosphabicyclo[3.1.0]hex-2-ene (**4**) was prepared by the method of Hughes and Srivanavit (25).

Addition of Dimethyl Acetylenedicarboxylate to Diphenylvinylphosphine

Dimethyl acetylenedicarboxylate (8.0 g) in benzene (50 ml) was added dropwise with magnetic stirring to diphenylvinylphosphine (12.1 g) in benzene (300 ml) under nitrogen at room temperature. The solution was heated under reflux for a few minutes during which time it turned a dark blue and a tarry precipitate appeared. One or two drops of water were then added and the mixture was again heated under reflux for a few minutes. The mixture was then evaporated under reduced pressure to about 50 ml. Ether (*ca.* 300 ml) was added to the gummy mixture and this dissolved much of the blue material. Repeated washing with small portions (*ca.* 30 ml) of ether left the crude adduct as a greyish crystalline material (7.1 g, m.p. 119–123°). The crystalline material was recrystallized from ethanol to give colorless needles (4.8 g, 23%) of the 1:1:1 adduct **9**, m.p. 130–132°.

Anal. Calcd. for $C_{20}H_{21}O_5P$: C, 64.51; H, 5.64; P, 8.33. Found: C, 64.74; H, 5.81; P, 8.78.

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

Addition of Dimethyl Acetylenedicarboxylate to Diphenylvinylphosphine in the Presence of D_2O

Ether (dried by distillation from $LiAlH_4$) was shaken with D_2O and again dried with $LiAlH_4$. Dimethyl acetylenedicarboxylate (1.34 g) in ether dried as above (50 ml) was added dropwise at room temperature to diphenylvinylphosphine (2.05 g) again in ether dried as above (50 ml) under nitrogen. When the addition was complete, D_2O (5 ml) was added to the reaction mixture which was then filtered to give a dark blue solid. This solid was recrystallized twice from benzene to give colorless needles of the deuterated adduct **10** (0.07 g), m.p. 132–133°.

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

Dimethyl acetylenedicarboxylate (3.53 g) in dry ether (80 ml, freshly distilled from $LiAlH_4$) was added dropwise over a period of 50 min to a mixture of diphenylvinylphosphine (5.0 g) and *p*-nitrobenzaldehyde (3.21 g) in dry ether (600 ml) under nitrogen at room temperature. The solution became dark green during the addition and was allowed to stand overnight in an atmosphere of dry nitrogen. The mixture was then filtered, the filtrate was evaporated to low bulk, and the mixture was chromatographed on neutral alumina using benzene followed by acetone as eluents. The acetone fractions were collected and evaporated to low bulk to give a crude sample of the adduct **14** (1.145 g, 10%), m.p. 190–194° (dec.). Further purification was effected by dissolution of the solid in chloroform followed by reprecipitation with ether. The pure adduct **14** was obtained as fine yellow crystals, m.p. 194–199° (dec.).

Anal. Calcd. for $C_{27}H_{24}O_7NP$: C, 64.16; H, 4.79; N, 2.77; P, 6.13. Found: C, 63.69; H, 4.98; N, 2.98; P, 6.14.

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

Addition of Diphenylvinylphosphine to Dimethyl Acetylenedicarboxylate

Diphenylvinylphosphine (8.8 g) in ether (50 ml) was added dropwise with stirring to freshly distilled dimethyl acetylenedicarboxylate (12.4 g) in ether (1500 ml) at room temperature under nitrogen. After the addition was complete, the dark colored mixture was filtered and the crude adduct **23** obtained as a greyish precipitate (2.3 g, 11%). This product was recrystallized from hot benzene to give the pure adduct **23** as colorless granular crystals, m.p. 198–201°.

Anal. Calcd. for $C_{26}H_{27}O_9P$: C, 60.70; H, 5.29; P, 6.02. Found: C, 60.70; H, 5.29; P, 6.63.

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

Deuterolysis of the 1:2 adduct **22** was carried out as described for the 1:1 adduct to give **24**, m.p. 206–213°.

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

The *trans*-phosphine (2.4 g) was dissolved in dry benzene (25 ml) and cooled to about 10 °C. To this solution was added dry pentane (35 ml) slowly with constant stirring until 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°. 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° for several hours.

Recrystallization of the adduct could not be achieved because of its high sensitivity towards water and air.

Anal. Calcd. for $C_{32}H_{28}O_4P_2$: C, 71.4; H, 5.2; P, 11.5. Found: C, 71.1; H, 5.4; P, 11.2.

The compound decomposed over a wide temperature range on heating.

The i.r. spectrum shows ν_{max} at 1712 (normal unsaturated ester C═O stretching), 1601 (stretching of the C═O group adjacent to a carbanionic center), 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}.

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

The 1:1 adduct (1.85 g), obtained in the above experiment, was dissolved in aqueous ethanol (30 ml, 1:1 mixture) and heated under reflux for 24 h. A white precipitate was obtained which was filtered and washed with a little benzene followed by pentane. The product was then pumped under reduced pressure (*ca.* 1 Torr) and at 60°. The crude oxide **9** (0.80 g, m.p. 132°) was obtained in 63% yield. The crude product was further recrystallized from benzene and obtained as fine cotton-like crystals.

Anal. Calcd. for $C_{20}H_{21}O_5P$: C, 64.5; H, 5.6; P, 8.3. Found: C, 64.9; H, 5.8; P, 8.8.

Deuterolysis was carried out as above except that pure D_2O was used as the deuterolyzing agent. The oxide **35** (m.p. 136°) was obtained in 70% yield. The i.r. spectrum was almost identical to that of the hydrolysis product **9**.

The ^1H n.m.r. was also found to be very similar to that of **9** except that the aliphatic protons had almost vanished from the spectrum while the mass spectrum shows a molecular ion peak at *m/e* 376 (with a small peak at *m/e* 375) which confirms that mainly tetradeuteration occurred.

The Reaction of cis-1,2-Bis(diphenylphosphino)ethylene (3) with Dimethyl Acetylenedicarboxylate

cis-1,2-Bis(diphenylphosphino)ethylene (**3**) (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°.

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° for 4 h. The dry ylide **37** was obtained as a buff powder (4.76 g, 73%).

The ylide **37** is highly water sensitive and it was therefore not possible to recrystallize it since it hydrolyzed rapidly even in quite rigorously dried solvents. Furthermore, the ylide has no definite m.p. and decomposes slowly above 140°.

Anal. Calcd. for $C_{32}H_{28}O_4P_2$: C, 71.4; H, 5.2; P, 11.5. Found: C, 69.5; H, 5.4; P, 11.1.

The i.r. 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}.

Hydrolysis of Dimethyl 1,1,4,4-Tetraphenyl-1,4-diphosphorin-2,3-dicarboxylate (37)

The ylide **37** (200 mg) was mixed with an excess of 1:1 aqueous ethanol and stirred for 5 h at room temperature. During this time, the dark brown solution became almost colorless. The solution was allowed to stand at room temperature for 2 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 of **3** (110 mg, 68%). The dioxide was further recrystallized from a 1:1 mixture of ethanol and acetone to give colorless crystals, m.p. 244° (lit. (26) m.p. 244–245°).

The i.r. spectrum shows ν_{max} at 1440 (P—Ph) 1230, 1200, 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 Dimethyl 1,1,4,4-Tetraphenyl-1,4-diphosphorin-2,3-dicarboxylate (37)

To the solid ylide **37** (200 mg) was added, with constant stirring and under a nitrogen stream, perchloric acid (1 ml, 74%) dropwise at room temperature. After about 10 min the solid mass, initially buff, became colorless. The mixture was stirred for another 30 min and then methanol (3 ml) was added. The mixture was warmed briefly to dissolve the solid and the solution then left for crystallization. After 2 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° to remove residual solvent from the bisperchlorate which was obtained in 28% yield (76 mg). The salt decomposed slowly above 200°.

Anal. Calcd. for $C_{32}H_{30}Cl_2O_{12}P_2$: C, 52.0; H, 4.1; Cl, 9.7; P, 8.4. Found: C, 51.3; H, 4.0; Cl, 10.0; P, 8.0.

The i.r. 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 630 cm^{-1}.

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1. For a review on cyclic phosphonium ylides see M. DAVIES and A. N. HUGHES. J. Heterocycl. Chem. 9, 1 (1972).
2. A. W. JOHNSON and J. C. TEBBY. J. Chem. Soc. 2126 (1961); and several later papers.

3. G. WITTIG and E. BENZ. Chem. Ber. **92**, 1999 (1959); E. ZBIRAL. Tetrahedron Lett. 1649 (1964).
4. H. J. BESTMANN and O. ROTHE. Angew. Chem. Int. Ed. **3**, 512 (1964).
5. A. N. HUGHES and M. DAVIES. Chem. and Ind. 138 (1969).
6. M. P. SAVAGE and S. TRIPPETT. J. Chem. Soc. C, 591 (1968).
7. A. WILLIAM JOHNSON. Ylid chemistry. Academic Press, New York, N.Y. 1966. p. 88.
8. D. E. C. CORBRIDGE. Top. in Phosphorus Chem. **6**, 235 (1969).
9. J. C. TEBBY. *In* Organophosphorus chemistry. Vol. 1. *Edited by* S. Trippett. The Chemical Society, London. 1970. p. 301.
10. (*a*) E. D. BECKER. High Resolution NMR. Academic Press. New York, N.Y. 1969. p. 192; (*b*) p. 138.
11. H. C. HILL. Introduction to mass spectrometry. Heyden, London. 1966. p. 65.
12. S. TRIPPETT. J. Chem. Soc. 4733 (1962).
13. N. E. WAITE and J. C. TEBBY. J. Chem. Soc. C, 386 (1970); A. N. HUGHES and S. UABOONKUL. Tetrahedron, **24**, 3437 (1968).
14. VARIAN. High resolution N.M.R. spectra catalog. Vol. 1. 1962. (*a*) Spectrum no. 30. (*b*) Spectra nos. 30, 74, 182, 277.
15. S. W. S. JAFRY. M.Sc. Thesis. Lakehead University, Thunder Bay, Ontario, 1971.
16. N. E. WAITE, J. C. TEBBY, R. S. WARD, and D. H. WILLIAMS. J. Chem. Soc. C, 1100 (1969).
17. J. J. BROPHY and M. J. GALLAGHER. Aust. J. Chem. **20**, 503 (1967).
18. A. J. CARTY and R. K. HARRIS. Chem. Commun. 234 (1967).
19. A. J. KIRBY and S. G. WARREN. The organic chemistry of phosphorus. Elsevier, Amsterdam. 1967. p. 207.
20. J. L. WILANS. U.S. Patent 3126416 (1964); Chem. Abstr. **61**, 1894*d* (1964).
21. M. A. SHAW, J. C. TEBBY, R. S. WARD, and D. H. WILLIAMS. J. Chem. Soc. C, 2442 (1967).
22. M. A. SHAW, J. C. TEBBY, R. S. WARD, and D. H. WILLIAMS. J. Chem. Soc. C, 504 (1970).
23. A. N. HUGHES and S. W. S. JAFRY. J. Heterocycl. Chem. **6**, 991 (1969).
24. M. A. SHAW, J. C. TEBBY, R. S. WARD, and D. H. WILLIAMS. J. Chem. Soc. C, 2975 (1968); E. M. RICHARDS, J. C. TEBBY, R. S. WARD, and D. H. WILLIAMS. J. Chem. Soc. C, 1542 (1969).
25. A. N. HUGHES and C. SRIVANAVIT. Can. J. Chem. **49**, 874 (1971).
26. A. M. AGUIAR and D. DAIGLE. J. Am. Chem. Soc. **86**, 2299 (1964).