The Reactions of 3-Butyl-1,2-diphenylphosphindole with Dimethyl Acetylenedicarboxylate

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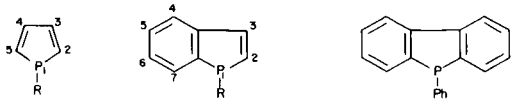
Unlike 1,2,5-triphenylphosphole, 3-butyl-1,2-diphenylphosphindole reacts smoothly with two molecules of dimethyl acetylenedicarboxylate to give the phosphindole oxide, a yellow adduct and a colourless adduct. The ease of the reaction is taken to indicate less lone pair interaction with the π-system in phosphindoles than in phospholes. The yellow adduct is shown to be a phosphindolium cyclopentadienylide, *i.e.* an adduct of the phosphindole and two molecules of the ester less one oxygen atom. The colourless adduct is shown to be a 1:2:1 adduct of the phosphindole, the ester and water and has a benzodihydrophosphonin structure. Mechanisms for the formation of both adducts are proposed. Adducts of this general type were previously unknown in organophosphorus chemistry.

In connection with our studies of the organic chemistry (1) of the potentially aromatic phosphole system (I) and also our investigations of the inorganic donor character of this system (2), we have had occasion to turn our attention to phospholes with additional fused rings. In particular, the phosphindole (benzo[*b*]phosphole) system (II) is of



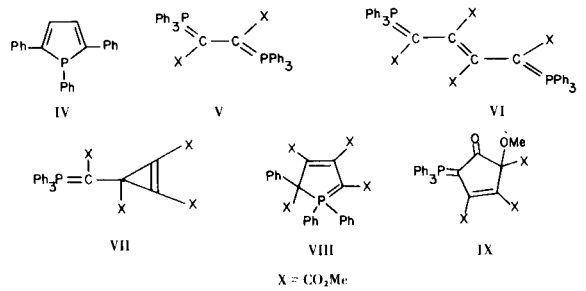
I II III

interest from both the organic reactivity and inorganic donor character viewpoints since, like the simple phospholes (I), the phosphorus atom non-bonding electron pair may interact to some extent with the π-cloud.

Despite prolonged study by a variety of techniques, the degree to which the phosphorus non-bonding electron pair is delocalized into the π system of simple phospholes in the planar transition state and the pyramidal ground state is still a matter for some controversy (3,4) but it is clear that any significant lone-pair interaction with the π cloud in the pyramidal ground state should be reflected to some extent in the reactivity at the phosphorus atom. A detailed discussion of this is outside the scope of this paper but the evidence for reduced reactivity at the phosphorus atom of simple phospholes of type (I) as compared with simple tertiary phosphines has been summarized elsewhere (2). It has also been suggested from pyramidal inversion studies (3a) that lone-pair delocalization should be much less in phosphindoles (II) and dibenzophospholes (*e.g.* III) although recent studies of rates of quaternization indicate (5) some delocalization in III.

Phosphindoles have received very little attention and, in the literature, there are only three papers which briefly mention the system. Two of these (6,7) briefly describe synthetic approaches to phosphindoles while the other one (3a) is concerned with pyramidal inversion studies and the question of aromaticity. We therefore decided to start our preliminary studies with an investigation of the reaction of phosphindoles with dimethyl acetylenedicarboxylate. The reasons for this were threefold. First, although simple tertiary phosphines such as triphenylphosphine react (8) extremely rapidly (even at -50°) with the electrophilic triple bond of dimethyl acetylenedicarboxylate through the phosphorus non-bonding electron pair, simple phospholes such as 1,2,5-triphenylphosphole (IV) do not react (9) under normal conditions with the ester even under reflux in benzene for several hours. This may possibly be taken as evidence for some non-bonding pair delocalization in simple phospholes and the reactivity of the phosphindole electron pair towards the acetylenic ester would therefore be of interest.

Second, the above mentioned reactions of ordinary tertiary phosphines can give a very wide variety of products

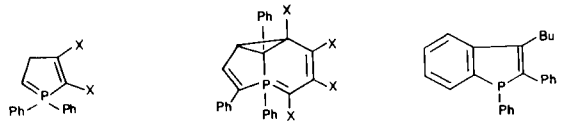


IV V VI

VII VIII IX

X = CO_2Me

which usually have a phosphonium ylide structure. For example triphenylphosphine reacts with the ester to give, depending upon the conditions, the ylides V (10), VI (11), VII (12), VIII (13) and IX (14) while vinylphosphines react similarly to give (15) cyclic ylides such as X by a 1,3-cycloaddition reaction. Thus, if the phosphindole system is reactive towards the ester, the products would be of interest in that they may throw further light upon how the structures of the products in reactions of this type depend upon reaction conditions and the electronic structure of the phosphine.



X XI XII

X = CO_2Me

Third, although 1,2,5-triphenylphosphole (IV) does not react with the ester under normal conditions, it will react (9) with a very large excess of the undiluted ester at room temperature over a period of several days to give (9) a 1:2 adduct of the phosphole with the ester which has been assigned (16) the complex structure XI. This structure is believed to be formed by cycloaddition of two molecules of the ester to the vinylphosphine fragment of the phosphole followed by a further intramolecular reaction. Thus, on the limited evidence available, phospholes react extremely slowly and give somewhat different products from tertiary phosphines and the unusual nature of the products makes similar studies of the phosphindole system desirable.

The phosphindole chosen for these studies was 3-butyl-1,2-diphenylphosphindole (XII) since the literature (6,7) indicated that this was the only one which could be synthesized in sufficient (though still small) quantity for such studies.

Unlike 1,2,5-triphenylphosphole (IV), 3-butyl-1,2-diphenylphosphindole (XII) reacts smoothly with dimethyl acetylenedicarboxylate in dry benzene under argon at room temperature over a period of two days to give three products. This ease of reaction alone supports the suggestion (3a) that lone pair delocalization is less in phosphindoles than in phospholes. One of these products was identified as the oxide of the starting phosphindole while the other two were isolated in low yield (*ca.* 10% each) as yellow crystals (m.p. 194°) and colourless crystals (m.p. 188°) respectively.

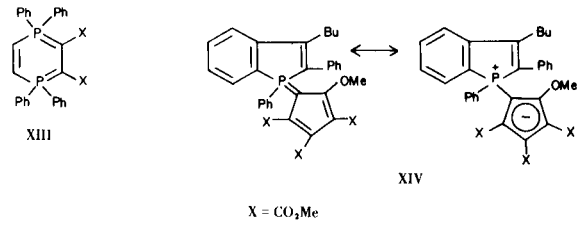
At first sight, the yellow adduct appeared to be a 1:2 adduct of the phosphindole with the ester since the nmr spectrum (to be discussed in detail later) showed 14 aromatic protons as a complex multiplet at τ 1.80-3.00, four methoxy singlets at τ 6.10, 6.25, 6.70 and 6.95, two methylene protons as a broad, poorly defined distorted triplet centered on τ 7.33, four methylene protons as a multiplet at τ 8.23-8.9 and three methyl protons as a poorly defined distorted triplet at τ 9.18. However, repeated analyses on several different samples gave results consistently 1.5-2% too high in carbon for a 1:2 adduct. The mass spectrum showed the molecular weight of the adduct to be 610 and *not* 626 as would be expected from a 1:2 adduct (17). This molecular weight was confirmed by a low voltage (15 eV) spectrum which showed the peak at m/e 610 as the only peak in the spectrum. This means that in the addition of the phosphindole to the ester, either an oxygen atom or a methane molecule is lost. That it is oxygen which is lost is shown by the nmr spectrum which shows all four of the expected methoxy signals and all of the protons of the butyl group. In short, no hydrogen atoms are lost in the reaction. The analytical figures obtained are in excellent agreement with a molecular formula of $C_{36}H_{35}O_7P$ which confirms the loss of an oxygen atom. The addition has therefore followed an entirely different course from all other reported phosphine/phosphole-dimethyl acetylenedicarboxylate reactions.

The infrared spectrum (Nujol) of the yellow adduct shows two strong carbonyl absorptions. The first of these occurs as a sharp peak at 1740 cm^{-1} and is clearly a normal ester peak while the other is a very broad, rounded absorption with maxima at 1685 and 1670 cm^{-1} and with a shoulder at 1655 cm^{-1}. This displacement to lower than usual frequency is indicative of a carbonyl group adjacent to an ylidic carbon atom where delocalization of the ylidic negative charge over the carbonyl group to give the resonance stabilized unit $R_3\overset{+}{P}-\underset{|}{C}\cdots\overset{-}{\underset{|}{C}}\cdots O$ can occur. However, the adduct cannot be a conventional α carbonyl stabilized ylide of the type produced in most other reactions of phosphines with the acetylenic ester since these normally (13) show carbonyl stretching frequencies in the range 1530-1500 cm^{-1} and this region is blank in the spectrum of the adduct in both Nujol and potassium bromide disc. For example, the carbonyl stabilized ylide VIII shows (13) carbonyl absorptions at 1740, 1700, 1670 and 1530 cm^{-1}, IX shows (14) similar absorptions at 1760, 1740, 1675 and 1530 cm^{-1} and the more complex structure XI shows (16) carbonyl absorptions at 1740, 1710, 1660, 1650 and 1520 cm^{-1}. It follows that if the

adduct is an ylide, it is not of the conventional carbonyl stabilized type and some other stabilizing unit must be present.

The nmr spectra of the adduct under various conditions are highly informative. First, the spectrum at room temperature shows by the methylene triplet at τ 7.33 that the butyl group is still allylic as in the starting material. Also, variable temperature studies in deuterated chloroform show no significant change in the methoxy signals over the range +30° to -46°. This confirms, as deduced from the ir spectrum, that the compound is not an ylide stabilized by an ester group on the ylidic carbon atom. Such compounds show (13) splitting in the methoxy signals at low temperatures as a result of slow interconversion of two preferred conformers by restricted rotation about the ylide-carbonyl carbon-carbon bond as, in the case of, for example, the compound VIII (13). Addition of a little trifluoroacetic acid to the adduct in deuterated chloroform causes little change in the nmr spectrum other than small shifts to lower field and this shows that if the adduct is an ylide, it is relatively resistant to protonation. The solution, however, does become colourless upon addition of the acid.

However, the spectrum of the adduct in pure trifluoroacetic acid shows major differences from that in deuterated chloroform. The expected 14 aromatic protons occur as a complex multiplet at τ 1.60-2.90 and the allylic butyl group shows the two allylic methylene protons as a broad hump with some fine structure centred on τ 7.08 with the remaining butyl protons at high field in much the same location as in the deuterated chloroform spectra. The biggest change in the spectrum is in the methoxy region which shows five unequal and broadened methoxy resonances at τ 5.75, 5.87, 6.03, 6.62 and 6.86 with several smaller resonances in the same region. Careful integration using signal averaged spectra shows that the methoxy and allylic methylene region in the range τ 5.10-7.47 integrates (several samples) for 14.6-15.1 protons rather than the expected 14 protons. It is therefore clear that protonation of the adduct occurs in trifluoroacetic acid and the complexity of the methoxy region in the nmr spectrum in acid solution suggests that protonation may occur at any one of several sites leading to a complex mixture of isomers. This behaviour in trifluoroacetic acid is similar to that of VIII although in the case of VIII, protonation occurs (13) largely (though not exclusively) at one site to give a somewhat simpler spectrum. It is interesting to note that with the ylidic adduct XIII, where the ylidic negative charges are apparently at least partly delocalized over the six-membered ring rather than the ester groups, similar behaviour is observed in trifluoroacetic acid (15). In this case however, the additional protons (derived from protonation by trifluoroacetic acid) appear as a very broad hump



XIII XIV

X = CO_2Me

at τ 4.60-5.00 with the broadening due to rapid exchange with the solvent.

That the yellow adduct is indeed an ylide is strongly supported by ultraviolet absorption studies. The ultraviolet spectrum of the adduct in ethanol shows a broad rounded peak at 294 nm ($\epsilon \sim 6500$) and a second absorption as an inflexion at 344 nm ($\epsilon \sim 1500$). Addition of two drops of trifluoroacetic acid to the solution in the eell caused no detectable change in the spectrum. Similar behaviour was observed with the nmr spectrum in deuterated chloroform. The spectrum in pure trifluoroacetic acid shows neither of the peaks at 294 nm or 344 nm but instead, an entirely new absorption appears at 325 nm ($\epsilon \sim 16000$). This indicates that a completely different species is present in acid solution. Neutralization with sodium bicarbonate of a solution in trifluoroacetic acid followed by dissolution in ethanol leads to the reappearance of the original absorptions at 294 and 344 nm, *i.e.* the changes which occur in acid are reversible. This is typical phosphonium ylide behaviour (13).

Returning to the mass spectrum of the yellow adduct, the molecular ion peak occurs at *m/e* 610 (70% of base peak) with major fragments at *m/e* 595 (M-CH_3, base peak) and *m/e* 579 (50% of base peak) corresponding to M-OCH_3. The remainder of the spectrum is relatively featureless until *m/e* 342 (10% of base peak) which corresponds to the molecular weight of the phosphindole XII and suggests that possibly this unit is intact in the yellow adduct. Another peak (10% of base peak) occurs at *m/e* 268 and this corresponds to two molecules of the acetylenic ester less one oxygen atom. A weak peak (*ca.* 4% of base peak) also occurs at *m/e* 358 corresponding to the phosphindole oxide which may be formed either by oxygen scavenging in the instrument by the phosphindole or by a rearrangement fragmentation process. All other peaks in the spectrum, except the usual low mass peaks, are very weak.

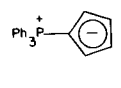
This evidence then suggests that the basic phosphindole structure is intact in the yellow adduct and that the remainder of the structure is attached to the phosphindole skeleton only at the phosphorus atom. This in itself suggests an ylide structure since, apart from complex zwitteronic structures incompatible with the uv and other evidence, the only reasonable alternative is a five-covalent phosphorus structure and it has been established (16) that most five-covalent phosphole type structures are unstable. Furthermore, it is unlikely that any changes induced in a

five-covalent phosphorus structure by trifluoroacetic acid would be reversible.

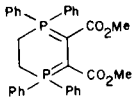
Very little of the material was available for chemical studies but oxidation of a small amount of the yellow adduct with hydrogen peroxide in hot ethanol (a slow process requiring several hours) yielded 3-butyl-1,2-diphenylphosphindole 1-oxide as the only isolable product. This confirms that in the adduct, the phosphindole unit is intact and therefore the only point of attachment of the remainder of the structure is the phosphorus atom.

To summarize the evidence then, one atom of oxygen is lost in the addition of two molecules of the ester to the phosphindole. Nmr and uv spectral evidence and chemical evidence suggest strongly a phosphonium ylide structure. Nmr and ir spectral evidence shows that this ylide is not significantly α-carbonyl stabilized and the mass spectrum and chemical evidence shows that the phosphindole skeleton is intact. Furthermore, the slowness of the oxidation with hydrogen peroxide and the difficulty of protonation indicates that the ylide is exceptionally stable.

In our opinion, the only structure which fits all of these criteria (bearing in mind the possible mechanism of formation to be discussed a little later in this paper) is the phosphindolium cyclopentadienylide XIV. It can be seen that although XIV is formally an ylidic structure, the ylidic negative charge is stabilized by being incorporated into a 6π electron aromatic cyclopentadienylide ring. Such a structure would be exceptionally stable (as is the case (18) with XV which is prepared by conventional methods) and there would be little delocalization of the negative



XV

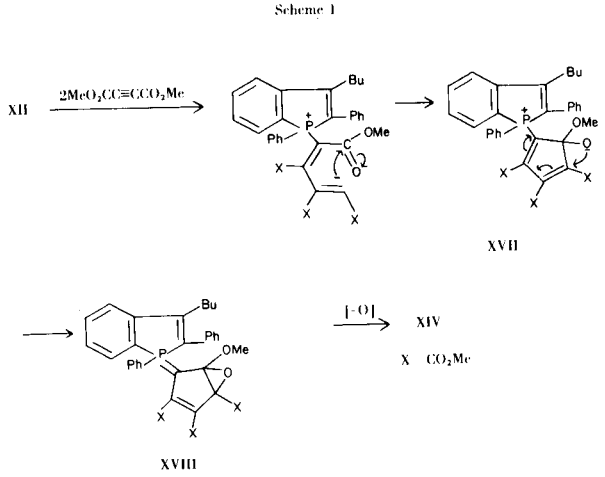


XVI

charge into the ester groups thereby accounting for the relatively small decrease in the stretching frequency of the ester carbonyl groups to ~ 1670 cm^{-1}. In this connection, it is significant that in the ir spectrum of XIII, where the ylidic negative charges may form part of an aromatic sextet, the ester carbonyl stretching frequency is at 1640 cm^{-1} (15) whereas in the similar structure XVI where no such delocalization is possible, the ylidic carbonyl stretching frequency occurs (19) at the more conventional location of 1585 cm^{-1}. The structure XIV also explains the nmr spectrum of the adduct in trifluoroacetic acid where protonation clearly occurs at more than one, and probably several, sites. In XIV, protonation could occur at any one of the five carbon atoms of the aromatic cyclopentadienylide rather than just adjacent to the phosphorus atom as would be usual for conventional ylides. It would have been desirable to form either a perchlorate salt or a tetrafluoroborate salt of the adduct assigned structure XIV but insufficient meterial was available for this and, furthermore, it has been shown (20) that such salts of quite high molecular weight ylides are highly soluble in the normal polar crystallizing solvents and are extremely difficult to crystallize even when relatively large quantities of the ylide are available.

The mechanism of formation of the adduct is possibly similar to that proposed (21) for IX except for the last stage and is outlined in Scheme 1.

Scheme 1



Why oxirane formation rather than methoxy migration (which occurs in the formation of IX) should take place is obscure. Another problem is deoxygenation of XVIII to give XIV. However, this could occur by one of two possible mechanisms. First, it could take place during the isolation of the adduct which involves both column and preparative layer chromatography on silica with the driving force being provided by the activity of the silica and the formation of an aromatic cyclopentadienylide ring. Second, deoxygenation of oxiranes and desulfurization of thiiranes by phosphines is known to occur quite readily (22) and the postulated intermediate adduct XVIII would be generated in the presence of unreacted phosphindole (which, indeed, is recovered from the mixture of products) which could act as a normal tertiary phosphine. It is perhaps significant that one of the products of the reaction is the phosphindole oxide. If the second of these mechanisms occurs it would have to involve biphilic (22) attack (*i.e.* direct attack of phosphorus on oxygen) rather than the more usual nucleophilic attack of phosphorus upon carbon followed by a four centre elimination of the phosphindole oxide because of the rigid stereochemistry of XVIII. Again, the driving force could be provided by the formation of a cyclopentadienylide ring and also perhaps by the electron withdrawing groups attached to the oxirane ring.

Turning now to the third product of the reaction, the colourless adduct of m.p. 188°, a probable structure assign-

ment may be made on the basis of the following evidence.

The microanalytical results are in excellent agreement with a molecular formula of $C_{36}H_{37}O_9P$ and this formula is confirmed by the mass spectrum which shows a molecular ion peak at *m/e* 644. This molecular formula corresponds to an adduct of one molecule of the phosphindole, two molecules of dimethyl acetylenedicarboxylate and one molecule of water. It is a reasonable assumption then that the adduct is derived from hydrolysis of an unisolated intermediate ylidic 1:2 adduct of the phosphindole with the ester. Such hydrolyses even of ester stabilized ylides are common (15).

The infrared spectrum (Nujol) shows that all of the ester groups are conventional (*i.e.* non-ylidic) with carbonyl absorptions at 1755, 1745 and 1730 cm^{-1}. A sharp peak of medium intensity at 1630 cm^{-1} indicates the presence of a conjugated carbon-carbon double bond or a tri- or tetrasubstituted double bond. A peak at 1210 cm^{-1} is assignable (23) to a P=O linkage. This too lends support to the idea that the adduct is the hydrolysis product of an intermediate unisolated phosphonium ylide. That the colourless adduct is probably not derived from hydrolysis of the yellow adduct XIV is shown by the fact that boiling the latter in aqueous ethanol for several days leads only to recovery of unchanged XIV.

As with the yellow adduct XIV, nmr studies provide a great deal of information. The spectrum in deuterated chloroform at room temperature shows fourteen aromatic protons as a complex multiplet at τ 1.60-3.20, one proton as a triplet (J = 11 Hz) centred on τ 4.89, another proton as an overlapping doublet of doublets centred on τ 5.84 with the two coupling constants having values of 11 Hz and 6 Hz, four methoxy groups as three peaks at τ 6.38 (six protons), 6.56 (three protons) and 6.67 (three protons), two allylic methylene protons as a broadened distorted triplet centred on τ 7.06, four methylene protons as a very broad signal in the range τ 8.00-9.00 and three methyl protons as a broadened distorted triplet centred on τ 9.21. Clearly, the butyl group is still present and occupies an allylic position as before.

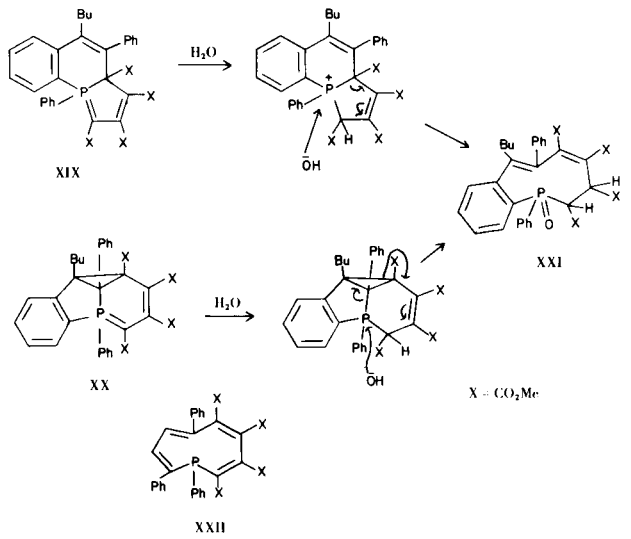
The two individual protons at low field are clearly close to the phosphorus atom and the coupling constants indicate that the protons are coupled to each other ($J_{H\text{-}H}$ = 11 Hz) and to the phosphorus atom ($J_{P\text{-}H}$ = 11 Hz and 6 Hz respectively). The low field locations indicate that both protons are tertiary and adjacent to electron withdrawing groups, the tentatively assigned values of $J_{P\text{-}H}$ are consistent (15) with typical values of $^2J_{P\text{-}H}$ and $^3J_{P\text{-}H}$ and the value of $J_{H\text{-}H}$ is consistent with either a geminal or vicinal arrangement of the two hydrogen atoms. On this evidence then, the adduct would appear to contain the unit O=P-CH-CH- although the unit O=P-CH_2- (where the protons are non-equivalent) cannot yet be excluded.

Selective ^1H-^1H decoupling (field sweep) experiments with the nmr spectrum show unambiguously that the unit O=P-CH-CH- is present. Thus, irradiation with the decoupling field midway between the lower two peaks of the low field triplet at τ 4.89 (designated as proton A) while scanning the other single proton signal causes the upper doublet of the upfield doublet of doublets (designated as proton B) at τ 5.84 to collapse. Similarly, decoupling irradiation between the upper two peaks of the signal due to proton A causes the lower doublet of the proton B signal to collapse. This shows that $J_{P\text{-}H_A}$ and $J_{P\text{-}H_B}$ are of opposite sign (24) and that the two protons are on adjacent carbon atoms. This confirms the tentatively assigned coupling constants. That the two protons are on adjacent carbon atoms is confirmed by similarly irradiating the proton B signal while scanning the proton A signal. As before, irradiation of the high field portion of the proton B signal causes the low field portion of the proton A signal to collapse.

This information gives a powerful clue to the structure of the colourless adduct. As mentioned earlier, it is virtually certain that the adduct is formed by hydrolysis of an intermediate unisolated ylide and the presence of a P=O linkage as shown in the ir spectrum strongly supports this idea. The structures of possible intermediate ylides should therefore be considered with a view to determining which of them could hydrolyze in such a manner as to give the O=P-CH-CH- unit. Phosphonium ylides normally hydrolyze in two main steps (25). In the first of these steps, the ylidic carbon atom is protonated by water to give a phosphonium hydroxide, *i.e.* this proton would normally appear adjacent to the phosphorus atom. In the second step, the phosphorus atom in the phosphonium salt so formed is attacked by hydroxide ion to give briefly a trigonal bipyramidal phosphorane from which the most stable carbanion leaves (usually from the apical position) and is protonated to give a phosphine oxide. Thus, in the hypothetical intermediate ylide in the reaction under consideration, the carbanion in the second stage of the hydrolysis must leave in such a manner as to place the second proton adjacent to the first. This would probably require rearrangement of the leaving carbanion before protonation of this carbanion occurs.

Considering the known phosphine/phosphole reactions with dimethyl acetylenedicarboxylate which lead to 1:2 ylidic adducts *without* loss of oxygen, *i.e.* the reactions which lead to the ylides VII, VIII, IX and XI - there are apparently two analogous phosphindole derived ylides which could give the O=P-CH-CH- structural unit on hydrolysis. These are the structures XIX (analogous to VIII) and XX (analogous to XI), both of which could possibly hydrolyze as shown in Scheme 2 to give the same benzodihydrophosphonin XXI. In either case, the second

Scheme 2



proton would be placed on the electronically rearranged leaving carbanion to give the maximum conjugation to the resulting product. Of the two possible reactions, we prefer XX → XXI since the similar structure XI is known to rearrange thermally under anhydrous inert atmosphere conditions to give the nine-membered ring phosphine XXII (9,16). Furthermore, since the phosphindole system is a benzophosphole, it might be expected to react more like 1,2,5-triphenylphosphole (which gives XI) rather than an ordinary tertiary phosphine (which gives VIII).

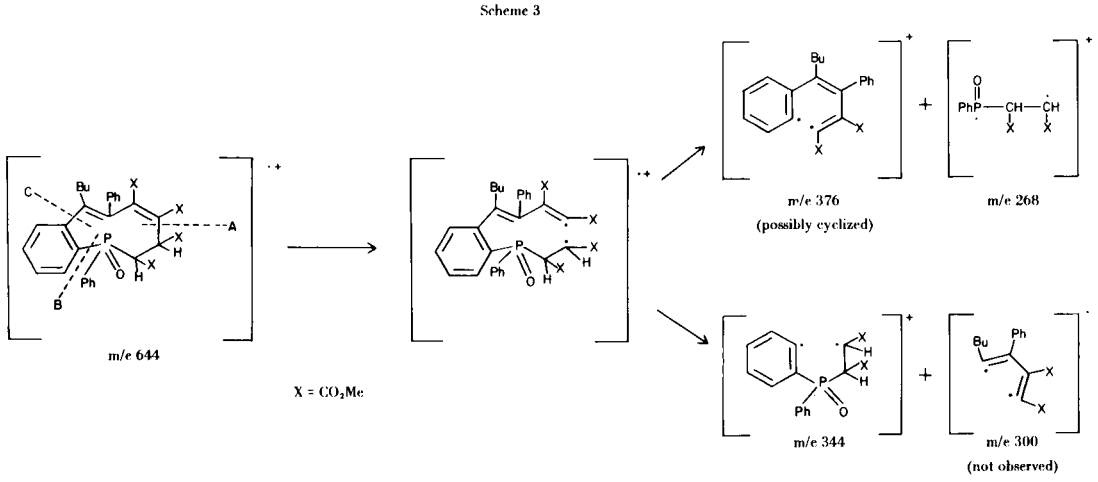
The structural evidence for the colourless adduct and mechanistic precedents then favour XXI although this evidence is as yet by no means conclusive. This structure, however, is also strongly supported by the mass spectrum. This shows a molecular ion peak at *m/e* 644 (5% of base peak at *m/e* 31), a peak at *m/e* 585 (20% of base peak) corresponding to M-CO_2Me and peaks at *m/e* 376 (25%), 344 (10%), 343 (20%), 301 (5%) and 268 (20%). Apart from this, the spectrum is almost featureless. The above peaks are in agreement with the kind of fragmentation which would be expected for XXI and which is outlined in Scheme 3.

For example, initial cleavage of the ring should occur at one of the single bonds. This apparently occurs at point A (Scheme 3) and this would be not unexpected since this bond is β to two ester groups and the resulting radical ion is very well resonance stabilized although similar cleavage could also occur across the -CHX-CHX- link. Thereafter, further cleavage could occur either at point B to give fragments at *m/e* 376 and 268 or at point C to give fragments at *m/e* 344 and 300. In practice, no significant peak occurs at *m/e* 300. However, there is a peak at *m/e* 343 and another at 301 possibly indicating some hydrogen transfer between the two fragments in the lower route of Scheme 3.

There can be little doubt then that the structure of the colourless adduct is XXI but further chemical studies on this adduct were not possible because of the very small amount of material available. However, it was felt that some further study on the two possible modes of hydrolysis of the hypothetical intermediates XIX and XX as outlined in Scheme 2 would be desirable. The behaviour of the two analogous and readily available structures VIII and XI in hot aqueous ethanol was therefore investigated in order to determine whether hydrolysis of either would occur and whether the unit O=P-CH-CH- (and a nine-membered ring in the case of XI) would be generated by such an hydrolysis. The ylide VIII proved to be inert towards hot aqueous alcohol over a period of several hours but the adduct XI hydrolyzed readily under these conditions although traces of starting material were present for long periods after hydrolysis commenced.

Chromatographic examination showed the presence of

Scheme 3



several components in the crude reaction product and column chromatography on silica in chloroform followed by preparative thin layer chromatography on silica in chloroform/ether (4:1) gave two main solid fractions which are extremely soluble in the solvents used and from which the last traces of chloroform (as shown by mass spectrometry) cannot be removed even after pumping at 80° and at 10^{-6} Torr for several hours. Both fractions show in their mass spectra the expected (original adduct + water) strong molecular ion peaks at *m/e* 614 with no peaks of higher mass in the spectra but the fragmentation patterns are complex indicating that both fractions are mixtures. It is perhaps significant that both spectra show peaks at M-32 corresponding to loss of methanol. This indicates the possible presence of the unit $CHCO_2CH_3$ as would be expected. The ir spectra show that both fractions are, as expected, phosphine oxides with P=O stretching bands at 1180 cm^{-1}. However, microanalytical data are poor as both fractions analyze 1-3% low in carbon for the original adduct XI plus one water molecule over several analyses. This again suggests that the fractions were mixtures although the traces of chloroform already mentioned could have been responsible for this.

The nmr spectra of the two fractions are more informative since both show something like the expected pattern in the methoxy region at τ 5.00-7.00 with the main methoxy resonances together with several smaller peaks obviously due to tertiary protons coupled with the phosphorus and possibly each other. The tertiary proton peaks are partly obscured by the methoxy signals but in both cases, more than the expected number (eight) of tertiary proton peaks appear and integrations are poor again indicating that the two fractions are mixtures.

These two fractions have so far defied attempts at further purification and further studies on the hydrolysis of XI are therefore being carried out as a separate investigation. However, this preliminary study of the hydrolysis of XI showed that the proposed scheme for the formation of XXI from the hypothetical intermediate XX is at least feasible. In the light of all this spectroscopic and chemical evidence it therefore seems highly probable that the colourless adduct of the phosphindole, two molecules of ester and one molecule of water indeed has the proposed structure XXI.

EXPERIMENTAL

The ir spectra were recorded in Nujol mulls or potassium bromide discs using Beckman IR 12 and Perkin Elmer 237 spectrometers while nmr measurements were made with Varian Associates model A60-A and A60-D spectrometers euqipped with a V-6058A spin decoupler. Deuterated chloroform and trifluoroacetic acid were used as nmr solvents with tetramethylsilane as internal reference while the nmr signal averaging experiments were carried out in 100% deuterated chloroform or trifluoroacetic acid using a Varian Data Systems model 620i attachment. Mass spectra were determined using an Hitachi-Perkin Elmer model RMU-7 mass spectrometer fitted with a direct heated inlet system. The uv measurements were made with a Unicam SP 800A ultraviolet spectrophotometer using absolute ethanol or trifluoroacetic acid as solvent. Melting points are uncorrected. Solvents were dried by standard methods and dimethyl acetylenedicarboxylate was freshly distilled under reduced pressure before use.

3-Butyl-1,2-diphenylphosphindole (XII) and 3-Butyl-1,2-diphenylphosphindole 1-Oxide.

The phosphindole was prepared by a modification of the methods of Rausch *et al.*, (6) and Mislow *et al.*, (3a) in the following manner. Diphenylacetylene (8.9 g., 50 mmoles) in dry THF (50 ml.) was cooled in an ice bath and was treated under argon with a hexane solution of *n*-butyllithium (62.5 ml., *ca.* 1.6*M*). The dark red reaction mixture was then stirred at room temperature for 16 hours after which dichlorophenylphosphine (6.8 ml., 50 mmoles) in dry THF (25 ml.) was added. The mixture was heated under reflux for 6 hours and then stirred at room temperature for a further 12 hours. Water (25 ml.) was added and the organic solvent was removed under reduced pressure. The crude mixture was extracted with dichloromethane, the resulting solution was washed with water (50 ml.) and then dried (sodium sulfate). Removal of dichloromethane gave a dark viscous oil which, on Kugelrohr distillation (110°/2.5 Torr), gave a yellow oil. This was chromatographed on silica gel with light petroleum to give first 1-butyl-*trans*-1,2-diphenylethylene (from hydrolysis of the anion obtained by addition of *n*-butyllithium to diphenylacetylene) and then 3-butyl-1,2-diphenylphosphindole (3.9 g., 23%) as very pale yellow crystals m.p. 90-92°, lit. (6) m.p. 90-91°.

The corresponding 3-butyl-1,2-diphenylphosphindole 1-oxide was prepared by treatment of the phosphindole (1.026 g., 3 mmoles) in ethanol with hydrogen peroxide solution (100 vol., 2 ml.). The excess of peroxide was destroyed with 10% ferrous sulfate solution, the mixture was extracted with chloroform (3 x 30 ml.) and the combined chloroform extracts dried (sodium sulfate). The extracts were then evaporated to give a yellow oil which was chromatographed in chloroform on silica in the usual manner to give 3-butyl-1,2-diphenylphosphindole 1-oxide (0.954 g., 89%), m. p. 152-154°. Although this compound has been reported before (6), no m. p. was given. The ir spectrum shows a strong P=O band at 1200 cm^{-1} and the mass spectrum shows the molecular ion peak at *m/e* 358.

Reduction of 3-Butyl-1,2-diphenylphosphindole 1-Oxide.

The following procedure was used to regenerate 3-butyl-1,2-diphenylphosphindole from its oxide formed in a variety of trial reactions and as a by-product in the reaction of the phosphindole with dimethyl acetylenedicarboxylate. 3-Butyl-1,2-diphenylphosphindole 1-oxide (2 g., 5.8 mmoles) in dry benzene (100 ml.) was treated with a large excess (8 ml.) of trichlorosilane and the mixture was heated under reflux for 20 hours under a slow stream of dry argon. With ice-bath cooling and vigorous stirring under argon, the reaction mixture was treated dropwise with water until evolution of hydrogen chloride ceased. The mixture was filtered under inert atmosphere and the benzene layer was separated and washed with water (2 x 25 ml.). The solution was dried (sodium sulfate) and evaporated to dryness. The resulting viscous oil gave, on standing in the refrigerator over-night, crystals of the phosphindole XII (1.2 g., 63%), m. p. 90-92°.

Reaction of 3-Butyl-1,2-diphenylphosphindole with Dimethyl Acetylenedicarboxylate.

Dimethyl acetylenedicarboxylate (0.8 ml., 6.5 mmoles) was added dropwise under argon with stirring over 10 minutes to a solution of 3-butyl-1,2-diphenylphosphindole (1.026 g., 3 mmoles) in dry benzene (10 ml.). The resulting reddish brown mixture was stirred for 1.5 hours and was then allowed to stand at room temperature for 2 days. The concentrated mixture was chromatographed on silica and elution with light petroleum/diethyl ether (4:1) gave small amounts of unreacted dimethyl acetylenedicarboxylate. Further elution with diethyl ether gave 3-butyl-1,2-diphenylphosphindole 1-oxide (0.25 g., 23%) and a yellow oil. This oil was rechromatographed by preparative thin layer chromatography using chloroform/diethyl ether (7:3) as eluent to give two products.

The first of these, assigned the phosphindolium cyclopentadienylide structure XIV, was obtained as a yellow oil which was uncrystallizable from the common organic solvents but which solidified on pumping to give a yellow powder (0.18 g., 10%), m. p. 192-194°; ir (nujol) ν max: 1740, 1685, 1670, 1655 (sh) cm^{-1}; uv λ max: 294 nm (ϵ, 6500), infl. 344 nm (ϵ, 1500); nmr (deuteriochloroform): τ 1.80-3.00 (m, 14H, aromatic), 6.10 (s, 3H, OMe), 6.25 (s, 3H, OMe), 6.70 (s, 3H, OMe), 6.95 (s, 3H, OMe), 7.33 (m, 2H, allylic CH_2), 8.23-8.9 (m, 4H, $2CH_2$), 9.18 (distorted t, 3H, CH_3); ms: *m/e* 610 (M^+).

Anal. Calcd. for $C_{36}H_{35}O_7P$: C, 70.82; H, 5.74; P, 5.08. Found: C, 71.00; H, 6.03; P, 5.02.

The second product, assigned the benzodihydrophosphonin structure XXI, was obtained as colourless crystals (0.18 g., 10%), m. p. 188°; ir (nujol) ν max: 1755, 1745, 1730, 1630, 1210 (P=O) cm^{-1}; nmr (deuteriochloroform): τ 1.60-3.20 (m, 14H, aromatic), 4.89 (t, J = 11 Hz, 1H), 5.84 (2d, J = 11 Hz and 6 Hz), 6.38 (s, 6H, OMe), 6.56 (s, 3H, OMe), 6.67 (s, 3H, OMe), 7.06 (m, 2H, allylic CH_2), 8.00-9.00 (m, 4H, $2CH_2$), 9.21 (distorted t, 2H, CH_3); ms: *m/e* 644 (M^+).

Anal. Calcd. for $C_{36}H_{37}O_9P$: C, 67.08; H, 5.75; P, 4.81. Found: C, 66.87; H, 6.29; P, 4.77.

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