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Structure and reactivity studies of simple phosphol

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STRUCTURE AND REACTIVITY STUDIES
OF SIMPLE PHOSPHOLES

BY

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ABSTRACT

Newer techniques of phosphole synthesis, particularly those which lead to simple phospholes substituted with active functional groups, are briefly surveyed. A detailed account of chemical, physico-chemical, spectroscopic and theoretical studies related to the phosphole aromaticity problem is given and the present conflicting position is discussed.

Dielectric relaxation measurements, based on the reorientation of a dipole in an alternating electromagnetic field, were obtained for seven phospholes and phosphole derivatives in an attempt to determine phosphole pyramidal inversion barriers. Two phospholes gave results consistent with a pyramidal inversion process. Thus, what appears to be a pyramidal inversion barrier for 1-butyl-3,4-dimethylphosphole was found to be 30.5 kcal./mole while this barrier for 3,4-dimethyl-1-phenylphosphole was tentatively assigned a value of 17.3 kcal./mole.

Reactions of phospholes with dimethyl acetylenedicarboxylate were investigated with a view to determining the effect of the substitution pattern of the phosphole upon reactivity at the P atom. The results obtained in the reactions show the phospholes to behave broadly like tertiary phosphines, which would indicate only a small degree of lone-pair delocalization or an easily perturbed electronic structure in the pyramidal ground state.

3,4-Dimethyl-1-phenylphosphole and 3-methyl-1-phenylphosphole react with dimethyl acetylenedicarboxylate to give ester carbonyl stabilized bicyclic ylidic 1:2 adducts of the same type. On the other hand, 1-phenylphosphole reacts with dimethyl acetylenedicarboxylate to give three products, an ester carbonyl stabilized bicyclic ylidic 1:2 adduct of a different type from that obtained with the other phospholes, a hydrolysis product of this or a related adduct, and a non-ylidic 1:2 adduct which is almost certainly a phosphonin derivative.

A new and possibly general route to the hitherto relatively inaccessible phosphindole system, using the extreme readiness of simple phosphole sulfides to undergo dimerization, is described. Thus, 3,6-dimethyl-1-phenylphosphindole sulfide is prepared in good yield in two steps from 3-methyl-1-phenylphosphole.

ACKNOWLEDGEMENTS

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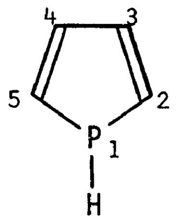
INTRODUCTION

Since the last reviews of phosphole (I) chemistry appeared (1,2), several major developments have taken place in the field. For example, greatly improved synthetic methods have been developed making phospholes with a wide variety of substitution patterns available for study, although phosphole itself remains unknown. Thus, Quin *et al*. (3,4,5) have reported three synthetic approaches to *P*-alkyl- and *C*-alkylphospholes which, in their final stages, rely on dehydrobromination of species such as the dibromophospholane II and the *P*-bromo-3-phospholenium salt III obtained by a variety of reaction paths. Also, Mathey (6,7,8) has reported an elegant one-step synthesis of phospholes by addition of phenyldibromophosphine to conjugated dienes followed by treatment with DBU. Related syntheses of 1-alkoxy- and 1-aryloxyphosphole oxides (*e.g*. IV) by dehydrobromination of 2-bromo-3-phospholene oxides such as V have also been reported (9).



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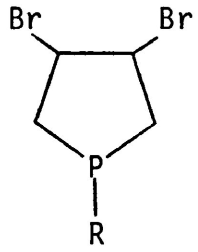

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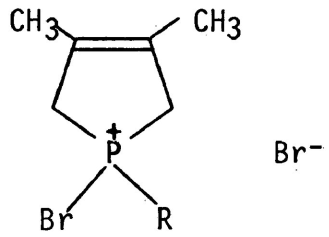

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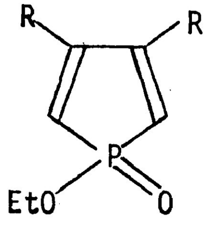
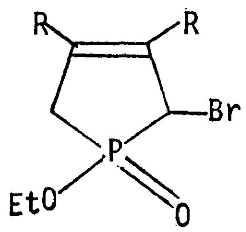
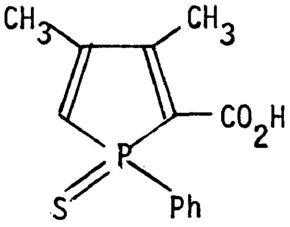


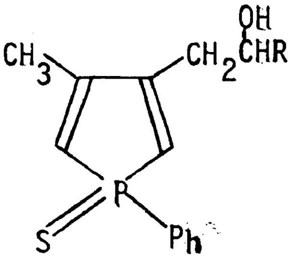


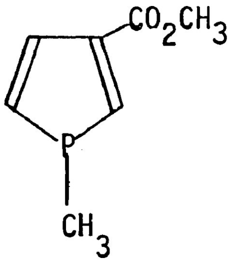
IV

V

Of particular importance are the recent syntheses (4, 5, 10, 11) of the first phosphole derivatives containing active functional groups on the ring. Examples of such phosphole derivatives are VI, VII, and VIII. These were prepared by treating anions such as IX with carbon dioxide, aldehydes or ketones (10, 11) or by treating phospholenium salts such as X with DBU (4, 5).







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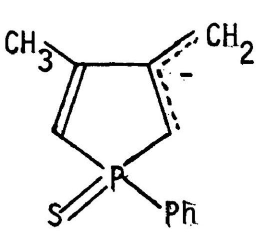
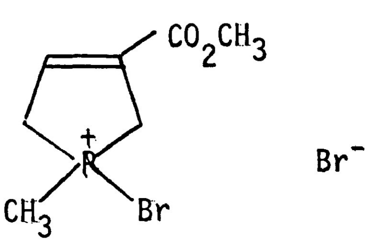
VII

VIII

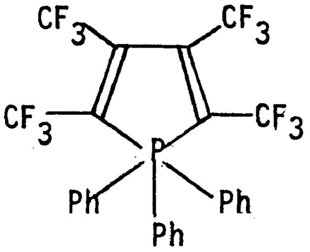




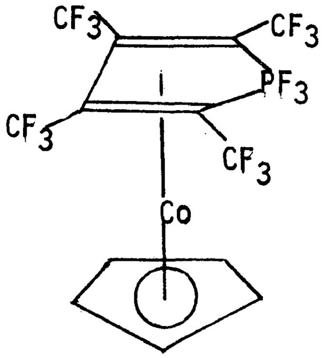
IX

X

There have even been reports (12, 13) of stable phospholes containing five-coordinate five-covalent phosphorus. Examples of these are XI and XII which were prepared by somewhat unusual methods involving metal-phosphine complexes. These phospholes are of particular interest since all such structures previously postulated have had to be revized (14).

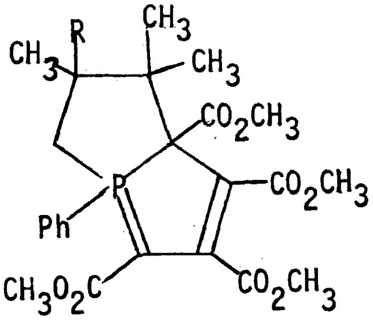


XI

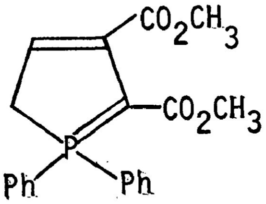


XII

Finally, in the area of phosphole synthesis, there have been further reports of the synthesis of 2H-phospholes of type XIII and XIV (15, 16) and also 3H-phospholes of type XV (16).



XIII



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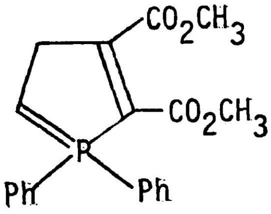


XV

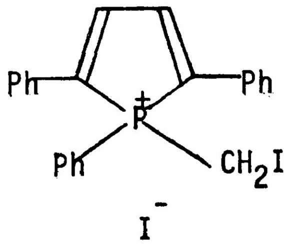
However, of the more than sixty papers on the chemistry of simple phosphole derivatives which have appeared during the past five years, more than half have been concerned directly or indirectly with the possibility of pyrrole-type aromatic character in the phosphole ring. These studies, many of which have been quite ingenious, have tackled the problem from a wide variety of viewpoints but some of the more important investigations have led to sharply conflicting conclusions. Indeed, much seems to hinge upon an adequate definition of aromaticity - particularly for heterocycles where pyramidal inversion may take place about the hetero atom. We therefore present in this article a review of the various studies of phosphole aromatic character which have appeared during recent years and, in order to give a full picture, some earlier work is also included. These investigations may be divided into the three broad classifications of chemical and physico-chemical studies, spectroscopic studies and theoretical treatments.

Chemical and Physico-Chemical Studies

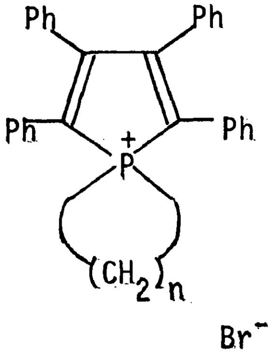
If the phosphole system possesses any significant degree of non-bonding pair delocalization, there are two possible arrangements. It could be a planar molecule with a fully delocalized Hückel 6 π-elecron system rather like pyrrole or thiophene (17) or it may have a rapidly inverting pyramidal arrangement about the phosphorus atom with appreciable lone pair - π system interactions in the pyramidal state and greater such interactions in the planar transition state. This latter view was advanced by Egan <u>et</u> <u>al</u>. (18) and it will receive considerable attention later in this article. A further factor to be considered is that the phosphorus atom possesses vacant 3d orbitals which may make some contribution to the π bonding. In any event, there should be two chemical consequences in that delocalization would lead to reduced reactivity of the conventional phosphine type at the phosphorus atom and would also suppress the dienoid character of the remainder of the ring. Indeed, the ring should behave at the carbon atoms to some extent as a π-electron rich heterocyclopentadiene.

Most studies of the reactivity of phospholes have been concerned with reactivity at the phosphorus atom. Thus, simple phospholes readily form oxides, sulfides or selenides (1) on treatment with hydrogen peroxide in ethanol or with elemental sulfur or selenium in suitable solvents under reflux. Oxide formation quite often occurs spontaneously (1, 3) in air if the phosphorus atom possesses an alkyl substituent. This is typical tertiary phosphine behaviour and might be taken to indicate little or no pyrrole-like aromatic character in the phosphole system. However, such a conclusion should be treated with caution for several reasons. For example, the P=O bond in phosphine oxides and related compounds containing the phosphoryl group is formed extremely readily and, indeed, the formation of such a bond provides much of the driving force for several well known and versatile organophosphorus reactions such as the Wittig and Michaelis-Arbuzov reactions. It is also an exceptionally strong bond (120-150 kcal/mole)(19). It would be more informative to compare rates of oxidation for phospholes and phosphines but this has not yet been done.

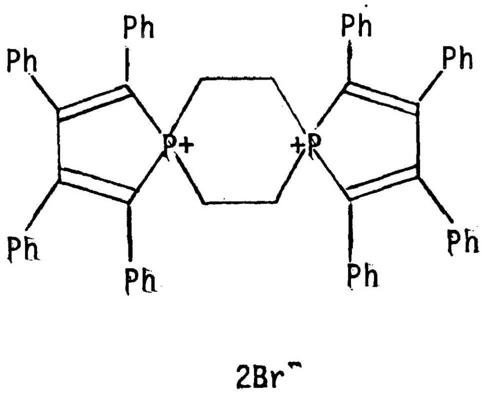
Another typical tertiary phosphine characteristic is the formation of quaternary phosphonium salts since phosphines are good nucleophiles. Both simple and more heavily substituted phospholes also form methiodides (3, 8, 20, 21, 22), P-haloalkylphospholium salts of type XVI (23) and types XVII and XVIII (22), P-dibromides (3, 20) and P-aminophospholium salts of type XIX (24).



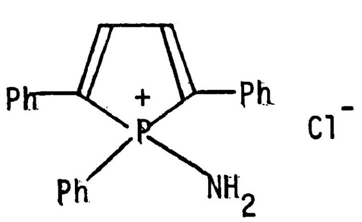
XVI



XVII



XVIII



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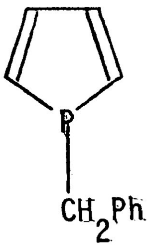
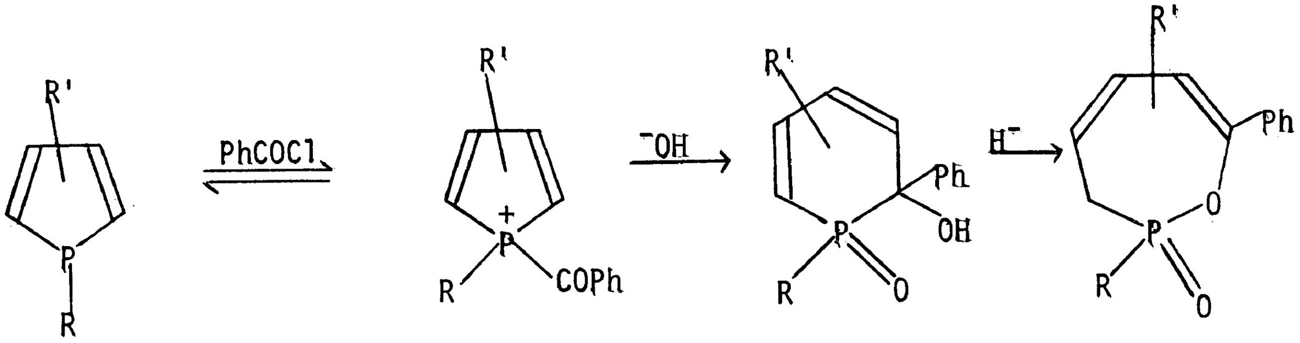


XX

Again, these reactions would appear to indicate little or no lone pair - diene interaction in phospholes. On the other hand, Brown has pointed out (25) in an early theoretical study that comparisons in oxidation and quaternization reactions between phospholes and pyrroles (where these reactions do not normally take place because of electron delocalization) could be misleading since the energy difference between the planar and tetrahedral states is less for phosphorus than for nitrogen. This theoretical study will receive further attention later in this article.

In this connection, it has been found (5) that rates of quaternization of various phospholes depend very much upon the substitution pattern. For example, 1-benzylphosphole (XX) quaternizes only very slowly (28% conversion after 11 days) with benzyl bromide and this implies much reduced tetiary phosphine character in XX. If, however, methyl groups are introduced into the 3- and the 3- and 4- positions of XX, the rate of quaternization progressively increases (5) implying increasing phosphine character and this has been attributed (5) to steric interactions and/or electronic effects involving the methyl groups. This tentative deduction has been supported (5) by studies of metal complex formation and by nmr studies and these will be discussed later in this review. It should also be noted that similar variations in phosphole substitution patterns result in differences in reactivity towards butyllithium (8) where the butyl anion may attack at the phosphorus atom (to give ligand exchange) or at the ring carbon atoms (to give phospholene anions). Again, this will be discussed more fully later.

It should be mentioned in passing, and in connection with phosphole quaternary salts, that Mathey et al. have developed (26, 27 28) an ingenious and very versatile double ring expansion of simple phospholes (though not 1,2,5-triphenylphosphole) based upon the equilibrium formation of a 1-benzoylphospholium salt in ether, hydrolysis of this salt under mildly basic conditions and treatment of the resulting 2-hydroxy-1,2-dihydrophosphorin with trace amounts of hydride ion to give a 1-oxa-2-phosphacyclohepta-4,6-diene derivative. The reactions are shown in the sequence XXl → XXIV.



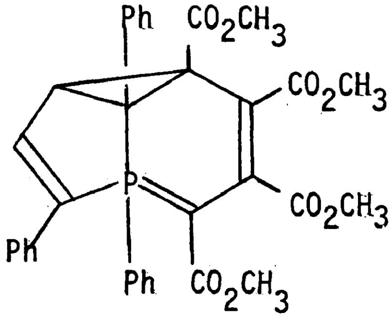
XXI

XXII

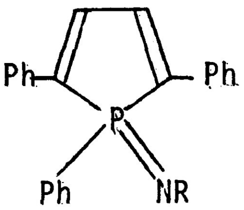
XXIII

XXIV

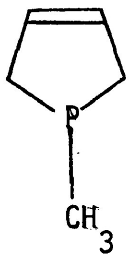
Several other reactions utilizing the lone-pair electrons are known to occur at the phosphorus atom of phospholes. For example, although 1,2,5-triphenylphosphole will not react (29) with dimethyl acetylenedicarboxylate under normal conditions (under reflux in benzene) to give either a Diels-Alder addition across the dienoid portion of the molecule or the expected very rapid (30) nucleophilic attack of the phosphorus atom upon the triple bond, a reaction of the phosphole with the acetylenic ester does slowly occur over a period of two days at room temperature when a very large excess of ester is used in the absence of diluting solvent. The main product has been assigned (14) the unusual tricyclic structure XXV and is clearly formed by very slow nucleophilic attack of the phosphorus upon the ester followed by rearrangement of an intermediate ylide.



XXV



XXVI



XXVII

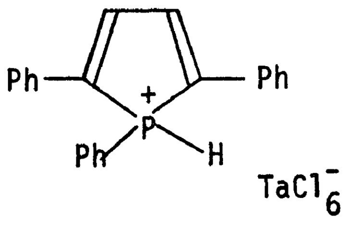
Also, Cadogan et al. (31) have found that 1,2,5-triphenylphosphole reacts with aryl-, methanesulfonyl-, arylsulfonyl-, ethoxycarbonyl-, phenoxycarbonyl- and diphenylphosphinyl azides by non-nitrene routes to give iminophospholes of type XXVI. On the other hand, benzoyl azide does not react directly with the weakly nucleophilic non-bonding electron pair of 1,2,5-triphenylphosphole although a reaction giving XXVI (R = Ph) does occur via decomposition of benzoyl azide followed by a Curtius rearrangement. Furthermore, 1,2,5-triphenylphosphole reacts with ethyl N-(p-nitrophenylsulfonyloxy)-carbamate ($EtO_2CNHOSO_2-p\text{-}C_6H_4NO_2$) only in the presence of triethylamine to give XXVI (R=$-CO_2Et$) by a nitrene mechanism whereas triphenylphosphine is known (31) to give an analogous product by direct lone-pair nucleophilic attack upon the nitrogen atom of the carbamate.

Finally, carbon bisulfide is known to form coloured complexes readily with tertiary phosphines except those with strongly electron withdrawing groups attached. However, 1-methylphosphole will not react (3) with carbon bisulfide although the acyclic analogue ethyldivinylphosphine reacts slowly to give the normal type of adduct.

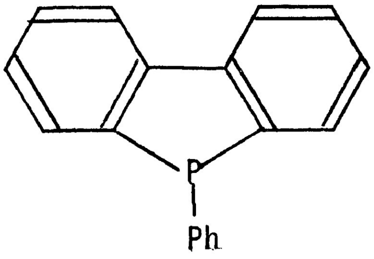
In summary then, the oxidation, quaternization and other studies outlined so far in this section indicate reduced lone-pair availability at the phosphorus atom of phospholes as compared with tertiary phosphines although little quantitative data for these reactions are available. A more quantitative idea of lone pair availability should, however, be provided by pK$_a$ and phosphole protonation studies as well as by investigations of metal complex formation by phospholes, and all three types of investigation have been carried out.

The first quantitative measurements on phosphole lone-pair availability were made by Quin *et al*. (3, 32) who observed (32) that, unlike the partially unsaturated analogue XXVII, 1-methylphosphole (XXI, R=Me, R^1=H) is not extracted from pentane solution by 2*N* hydrochloric acid and must therefore have a considerably lower basicity than would be expected for a normal tertiary phosphine. A direct measurement of the pK$_a$ value of 1-methylphosphole was therefore made (3) using ultraviolet absorption techniques and it was found that this phosphole has the unusually low pK$_a$ value of 0.5. This value is about 7 units less than is obtained for trialkylphosphines (pK$_a$ 7-8) and about 4.5 units less than that calculated (3) for similar divinylphosphines (pK$_a$ ~ 5.2). This evidence then strongly suggests considerable lone pair-diene interaction in the phosphole system although it should be noted that the undoubtedly aromatic pyrrole system has a somewhat lower pK$_a$ value of -3.8 (33).

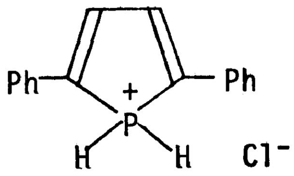
During this study, Quin stated (3) that it would be interesting to determine whether phospholes protonate at the phosphorus atom or at the ring carbon atoms as do pyrroles (33). In this connection, Chuchman *et al*. (34) found that exposure of the 1:1 σ complex of 1,2,5-triphenylphosphole (designated here as TPP) with tantalum(V) chloride, TPP(TaCl$_5$), in benzene solution to ethanol vapour causes precipitation of a very water sensitive orange solid unambiguously characterized as the P-protonated phospholium salt XXVIII. Similar behaviour was observed for the corresponding niobium(V) chloride complex but not, in general, with halides of other transition metals. The 1H-phospholium salt XXVIII is also formed quantitatively on passing dry hydrogen chloride into a dry benzene solution of (TPP)$\mathrm{TaC}\ell_5$. On the other hand, no phospholium salt of the type TPPH^+ $\mathrm{C}\ell^-$ could be formed when rigorously dried hydrogen chloride was passed into a dry benzene solution of TPP although both triphenylphosphine and 5-phenyl-5H-dibenzophosphole (XXIX) readily form P-protonated salts under these conditions. This again strongly indicates much reduced lone-pair availability in phospholes as compared with tertiary phosphines.



XXVIII



XXIX



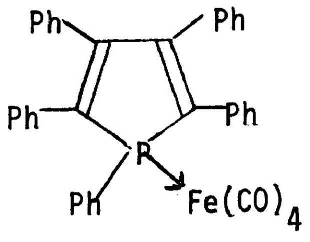
XXX

The stability of the salt XXVIII under anhydrous conditions was therefore attributed (34) to the exceptional stability of the $\mathrm{TaC}\ell_6^-$

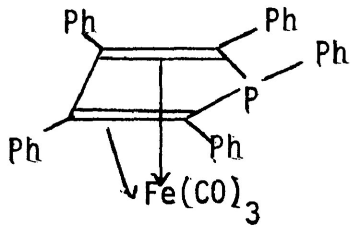
ion and a favourable lattice energy in the highly crystalline salt XXVIII. However, Braye *et al*. (22) at about the same time reported the formation of the 1*H*-phospholium salt XXX by treatment of the corresponding phosphole with hydrogen chloride under inert atmosphere conditions. No further comment was made.

It therefore seems that phospholes are much less readily protonated than tertiary or divinylphosphines, that protonation to give stable *P*-protonated salts can be made to occur under anhydrous conditions and that the ease of protonation as with quaternization discussed earlier depends upon the substitution pattern.

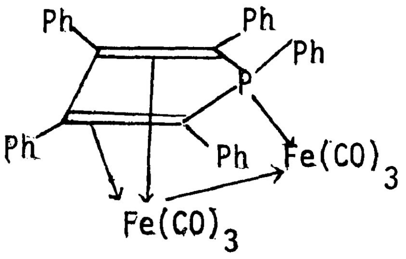
In related studies, there have been numerous investigations of the availability of the phosphorus lone-pair of electrons of phospholes in the formation of coordination compounds. These studies have been treated in considerable detail elsewhere (35) but a brief summary would be in order here. The first such studies of phosphole coordination chemistry were carried out with metal(0) carbonyls (36, 37, 38) and gave complexes such as XXXI, XXXII and XXXIII (36).



XXXI



XXXII



XXXIII

Cookson et al. (37) found that 1,2,5-triphenylphosphole (TPP) forms similar complexes to XXXI and XXXII in reactions with iron carbonyls and that reactions of this phosphole with $M(CO)_n$(M = Ni, Cr, Mo and W) give monosubstituted σ- bonded complexes of the type $(TPP)M(CO)_{n-1}$. More recently, Mathey (38) has reported the formation of a number of phosphole - Mn carbonyl complexes while a Shell patent records (39) the uses of certain phosphole-cobalt carbonyl complexes as catalyts in hydroformylation reactions. The implication there is that the non-bonding electrons are available for donation to transition metals which suggests that delocalization in phospholes may not be great. This conclusion was in fact drawn by one group (36) who noted that 1,2,3,4,-5-pentaphenylphosphole has both tertiary phosphine and conjugated diene characteristics in these reactions although it should be noted that the conditions required for the formation of several of the complexes (boiling isooctane for several hours) are quite drastic.

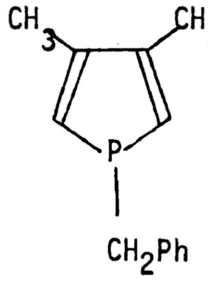
The studies described above, however, lack any kind of quantitative estimate of the lone pair availability in phospholes for metal complex formation and a much better idea of this availability is provided by similar studies of reactions between phospholes and transition metal halides - particularly the halides of metals which are good "class b" (40) acceptors.

An early study in this area (41) showed that 1,2,5-triphenylphosphole will form conventional σ complexes with Pd(II) and Pt(II) chlorides and bromides and with Hg(II) and Rh(III) chlorides under mild conditions. The only departure noted from conventional phosphine reactivity was that Rh(III) is not reduced to Rh(I). However, a series of detailed studies of phosphole coordination (42, 43, 44, 45, 46) has shown that although phospholes show some phosphine-like character in certain reactions leading to the formation of σ complexes with transition metals, there are also significant departures from normal phosphine behaviour in these and related reactions. For example, 1,2,5-triphenylphosphole (TPP) will not form (42) complexes with the chlorides of Ag(I), Mn(II), Fe(II), Co(II), Ni(II), Th(IV) and U(IV) even though conventional phosphine complexes of these metals are well known and are normally very easily formed. That this is not a steric effect in the bulky TPP molecule is shown (42) by the fact that TPP will readily reduce Cu(II) to form a Cu(I) complex $(TPP)CuC\ell$ and also by the fact that 1:1 σ complexes are formed between TPP and Nb(V) and Ta(V) chlorides and bromides although the phosphorus-metal bond in these complexes is extremely weak compared with those of normal phosphine complexes of these metals.

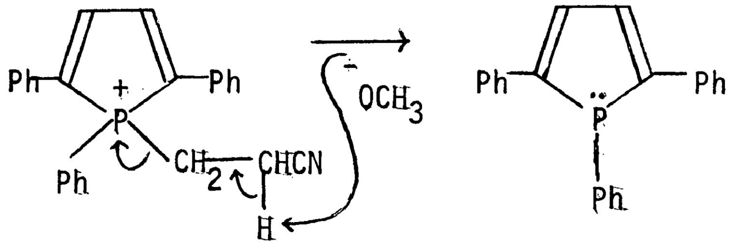
This reluctance of phospholes to form normal σ complexes with Ni(II) has also been observed by Quin _et al_. (3, 43) who showed that neither 1-methylphosphole (3) nor 1-benzylphosphole (XX) (43) - where steric factors would be relatively unimportant - will form conventional phosphine type σ complexes with Ni(II) chloride. Unexpectedly, however, 1-benzyl-3,4-dimethylphosphole (XXXIV) (43) readily forms a complex of the type $L_2NiC\ell_2$ (where L = phosphole ligand). It follows that inorganic donor character of the phosphole system depends greatly upon the substitution pattern in the phosphole ring. This dependence of lone-pair reactivity upon substitution pattern has also been observed with rates of phosphole quaternization (5) as has already been discussed. In this connection, it should again be stated that nmr studies of 3,4-dimethyl-1-benzylphosphole indicate an electronic structure somewhat different from that of other simple phospholes and this will be discussed more fully later.

Other complexes of 1,2,5-triphenylphosphole (TPP) and 1-phenylphosphole (PP) with Rh(III) chloride have been reported (44) and it is interesting to note that no reduction of Rh(III) to Rh(I) occurs in the formation of these complexes under relatively severe conditions even though triphenylphosphine reduces Rh(III) to Rh(I) extremely rapidly under mild conditions. Complexes of TPP with Rh(I) (44), Re(III) (45) and Ru(II) and (III) (46) have also been reported and, in each case, the phosphole system has been found to be a poor donor lacking in normal phosphine character although some of the Rh complexes have been found (44) to have homogeneous catalytic activity in hydrogenation reactions as do other Rh-phosphine complexes (47). This lack of normal phosphine donor character in phospholes has been discussed at length elsewhere (35, 46).

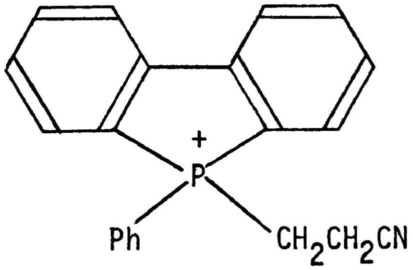
The problem of lone-pair availability has been tackled in a very ingenious manner by Farnham and Mislow(48) who theorized that if the non-bonding electron pair of phospholes is less readily available than that of ordinary tertiary phosphines because of lone-pair delocalization, then in certain reactions of quaternary phospholium compounds, cleavage of an exocyclic P-C bond to restore the lone-pair to the phosphorus atom should occur more readily with the phospholium system than with a phosphonium system. These workers therefore studied the kinetics of



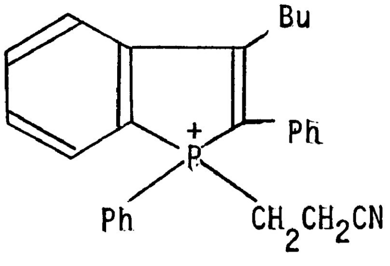
XXXIV



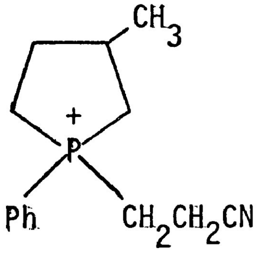
XXXV



XXXVI



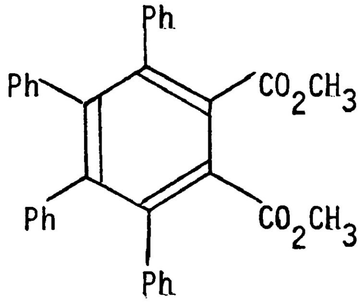
XXXVII



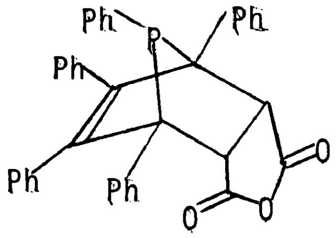
XXXVIII

the retrocyanoethylation of the cyanoethylphospholium grouping XXXV and compared the rate of the reaction with the rates of similar reactions with the related noncyclic (2-cyanoethyl)triphenylphosphonium ion and the systems XXXVI, XXXVII and XXXVIII. It was found that retrocyanoethylation of XXXV was considerably accelerated compared with the other systems studied and this was interpreted as being consistent with significant lone-pair delocalization in phospholes.

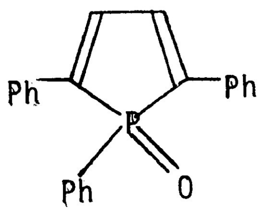
In contrast to the numerous studies of nucleophilic reactivity of the phosphorus atom of phospholes outlined in the preceding discussion, very few studies of the reactivity at the ring carbon atoms have been made. One obvious study would be an investigation of the dienoid character of phospholes in Diels-Alder reactions and there have been two such reports (36, 20). Thus, 1,2,3,4,5-pentaphenylphosphole reacts only under severe conditions (no solvent at > 150^0) with dimethyl acetylenedicarboxylate (36) and with maleic anhydride to give the adducts XXXIX and XL - i.e.



XXXIX



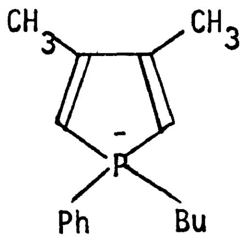
XL



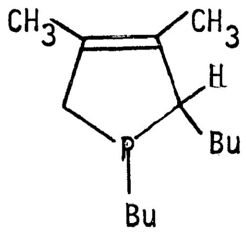
XLI

in the first case aromatization of the intermediate phosphorus bridged adduct occurs. Similar results have been observed (20) with 1,2,5-triphenylphosphole. Both the pentaphenylphosphole and the triphenylphosphole are, however, bulky systems and the reluctance of these systems to react as dienes in Diels-Alder reactions might be attributed to unfavourable steric interactions. That this is not the case is shown by the fact that the equally bulky 1,2,5-triphenylphosphole oxide (XLI) readily reacts (in benzene at 80°) with dimethyl acetylenedicarboxylate and maleic anhydride (20) and with acrylonitrile (37) to give the expected Diels-Alder adducts except that with the acetylenic ester, aromatization of the adduct again occurs to give XXXIX. This then suggests that the lack of Diels-Alder reactivity of phospholes is an electronic rather than a steric effect.

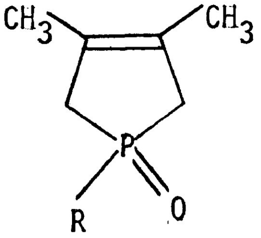
Three other reactions of phospholes at the ring carbon atoms have received brief attention (8, 26, 49). In the first of these, Mathey (8) found that 3,4-dimethyl-1-phenylphosphole reacts with butyllithium to give 1-butyl-3,4-dimethylphosphole *via* the adduct XLII - *i.e.* nucleophilic attack occurs upon the phosphorus rather than the usual electrophilic attack already discussed. This product reacts further with butyllithium at the 2- carbon atom to give the 3-phospholene XLIII. Both of these reactions are unusual for tertiary phosphines and vinylphosphines and Mathey (8) has suggested that these attacks on phosphorus and the 2-carbon atom in the phosphole system indicate both $p\pi$ and $d\pi$ interactions between the phosphorus and the diene system. This suggestion is supported by



XLII



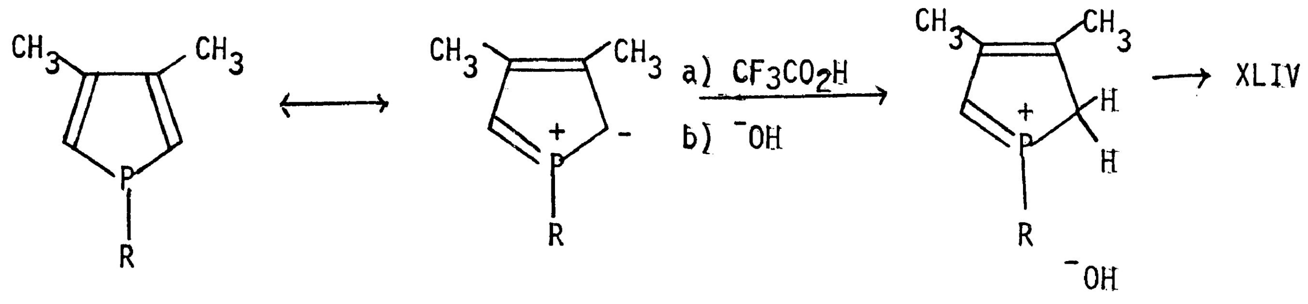
XLIII



XLIV

nmr data in the same paper and this will be discussed in the next section. It should however be noted that, in view of Quin's observations (43) regarding possible electronic peculiarities in 3,4-dimethylphospholes, the above systems chosen by Mathey (8) may not be representative of phosphole behaviour in general.

The second of these studies was also by Mathey (26), in a paper devoted to a variety of phosphole reactions, who showed that certain phospholes will react with trifluoroacetic acid to give an unisolated intermediate which, on neutralization of the acid solution, yields 3-phospholene oxides of the type XLIV. Mathey has suggested the mechanism XLV → XLVI → XLIV for this reaction - i.e. a mechanism involving π-delocalization of the non-bonding pair and in which protonation occurs on the 2-carbon atom of phospholes just as it does in the aromatic pyrroles (33). In this connection, however, it should be remembered that under



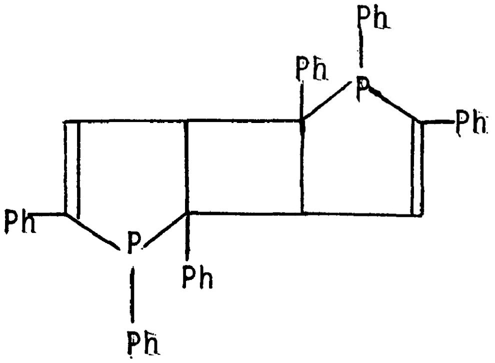
XLV

XLVI

different conditions, phospholes appear to protonate - at least in the solid state - at the phosphorus atom (22, 34) as already discussed and it may be again that the peculiarities of the 3,4-dimethylphosphole system (43) are responsible for the behaviour observed in trifluoroacetic acid.

The only other recorded study of the reactivity at the ring carbon atoms of phospholes was by Barton et al. (49) who found that 1,2,5-triphenylphosphole photodimerizes to give the adduct XLVII and the reaction was found to be general for a variety of 2,5-diphenylheterocyclopentadienes. This ease of dimerization for the phosphole system was taken to indicate little aromatic character in phospholes as compared with similar thiophenes which do not photodimerize under these conditions.

In concluding this section on chemical and physico-chemical studies, mention should be made of a thermochemical investigation. Bedford _et al_. found (50) that the $P{=}O$ bond dissociation energy in 1,2,3,4,5-pentaphenylphosphole 1-oxide is only about 100 kcal./mole which is exceptionally low compared with those of other phosphine oxides such as triphenylphosphine oxide (19a) (126 kcal./mole) and trimethylphosphine oxide (19b) (139 kcal./mole). It was therefore concluded that this low value is a measure of the phosphole conjugation energy relative to its oxide and this would indicate a resonance energy for phospholes of the same order of magnitude as for pyrroles.



XLVII

Spectroscopic and Related Studies

It can be seen from the discussion outlined in the preceding section that although relatively little quantitative data other than $\underline{p}K_a$ values, rates of quaternization and rates of retrocyanoethylation are available. the evidence is strongly indicative of a considerable degree of phosphorus lone-pair interaction with the diene system of phospholes. There is also some suggestion of d-orbital involvement. With the spectroscopic data of various types to be discussed in this section it will be seen that although much of the information is again suggestive of strong lone pair-diene interactions, certain pieces of evidence are mutually contradictory.

Considering nmr studies first, there have been several ^{1}H, ^{31}P and ^{13}C studies of phospholes and also estimates of the pyramidal inversion barrier in phospholes using nmr methods. In an early study, Märkl et al. (51) noted that in 2,5-dimethyl-1-phenyl-phosphole, both the ^{1}H chemical shifts of the ring protons and of the methyl groups are very like those in 2,5-dimethylthiophene and, since the latter is aromatic, it was suggested that these results are indicative of some aromatic character in the phosphole system. A little later both Märkl et al. (52) and Quin et al. (3, 32) reported on the ^{1}H nmr spectra of ring unsubstituted phospholes such as 1-phenylphosphole (52) and 1-methylphosphole (3, 32). In both instances it was noted that the ring protons resonate in the normal aromatic range and that the spectra were very similar to those of the corresponding pyrrole derivatives. In the case of 1-methylphosphole, a detailed analysis of the ^{1}H spectrum was made and it was found to show a typical AA'BB'X spectrum. No association was noted in neat samples of 1-methylphosphole. Values of $^{2}J_{P-H}$ for the phosphorus and α ring protons were found to have the extraordinarily high value of 38.5 Hz.

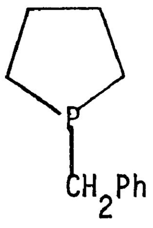
Further studies of the ^1H nmr spectra of phospholes were carried out by Mathey _et al_. (8) [following a preliminary report (7)] using a wide variety of substitution patterns and some tentative deductions regarding the dependence of the degree of aromatic character upon the substitution pattern were made. Thus, it was found that the ring protons of 1-butylphosphole, 1-butyl-3-methylphosphole and 1-butyl-3,4-dimethylphosphole are centred at $\tau = 3.20$, $\tau = 3.47$ and $\tau = 3.88$ respectively while the methyl groups resonate at $\tau = 7.90$ and $\tau = 8.19$ - _i.e_. as the substitution on the ring increases, the resonances shift to higher field. Similar effects were observed with 1-methylphosphole and 1,3,4-trimethylphosphole. This would suggest decreasing aromatic character along the series although inductive effects cannot be ignored. This observation agrees well with the studies of Quin _et al_. on the dependence of rates of quaternization (5) upon the substitution pattern of phospholes and also with the observation (43) that 3,4-dimethylphospholes will form Ni(II) complexes whereas other phospholes will not. The nature of the substituent upon the phosphorus atom seems also to have some effect upon the location of the ring proton resonances in the nmr spectrum (8). For example, 1-methylphosphole shows the ring protons centred on $\tau = 3.00$ while the 1-butylphosphole ring protons are centred on $\tau = 3.20$.

In a more recent paper, Quin _et al_. (5) have obtained similar results in a thorough study of a series of ten phospholes. For example, the ^1H - ^1H coupling constants for the ring protons of a variety of phospholes were found to be strikingly similar to those of structurally related thiophenes. Furthermore, the apparent "dearomatizing" effect (upfield shift of ring protons) of 3-methyl and 3,4-dimethyl substitution in the phosphole ring was also observed. However, Quin et al. (5) found that this effect appears also in similarly substituted pyrroles which would seem to refute the suggestion of Mathey et al. (8) that this type of substitution causes an increase in $(p\text{-}d)\pi$ conjugation in phospholes.

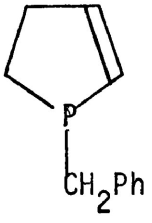
There have also been several ^{31}P nmr studies of phospholes. The first of these was by Quin et al. (3) who observed that in 1-methylphosphole, the ^{31}P chemical shift (neat liquid) is +8.7 ppm relative to external 85% phosphoric acid. In comparison with various phospholenes and vinylphosphines, this was found to be at unusually low field with the ^{31}P shift of 1-methyl-3-phospholene occurring at +41.8 ppm and those of ethyldivinylphosphine and trivinylphosphine at +20.8 and +20.7 ppm respectively. This deshielding of ^{31}P in phospholes was therefore tentatively attributed to lone-pair electron delocalization in the phosphole ring.

Mathey et al. have recorded (7, 8) the ^{31}P nmr spectra (using the external reference P_4O_6) of a number of phospholes and have discussed (8) these shifts in terms of the Letcher-Van Wazer treatment (53). On the basis of this treatment, it was concluded (8) that there is indeed some delocalization of the phosphorus lone-pair in phospholes and that the degree of delocalization decreases as methyl groups are introduced into the 3- and 3,4- positions of the phosphole ring. This is in agreement with the deductions made from ^{1}H spectra already discussed and also the chemical evidence provided by quaternization studies, pK_a measurements and metal complex formation.

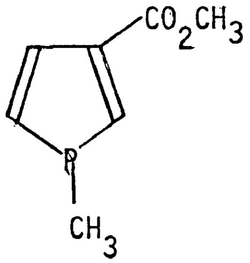
In a more recent paper Quin et al. (5) have presented the results of a detailed ^{31}P nmr study of phospholes. Again, the external standard was 85% phosphoric acid and it was found that phospholes possess a more deshielded ^{31}P atom than do 2-phospholenes or phospholanes. For example, the ^{31}P chemical shifts for 1-benzylphospholane (XLVIII), 1-benzyl-2-phospholene (XLIX) and 1-benzylphosphole (XX) are +14.4, 0.0 and -7.9 ppm



XLVIII



XLIX



L

respectively and this is suggestive of some delocalization of the lone-pair in phospholes. However, as the authors pointed out, caution must be exercised in making this prediction since conformational factors and the different bond angles about the phosphorus atom should be taken into consideration as mentioned by Mathey _et al_. (8). In general, ring unsubstituted phospholes show a ^{31}P chemical shift in the range -8.0 to -5.8 ppm while introduction of a ring methyl group causes, as might be expected on inductive grounds, some shielding of the phosphorus to give small positive chemical shifts. If, however, a methoxycarbonyl group is introduced into the 3- position of the ring as in L, strong deshielding of the phosphorus atom to -3 ppm again occurs and this indicates resonance interaction of the ester group with the ring and delocalization of the phosphorus lone pair. It was also noted that ring and substituent contributions to the ^{31}P chemical shift in phospholes are additive and allow calculation of ^{31}P chemical shifts for simple phosphole derivatives.

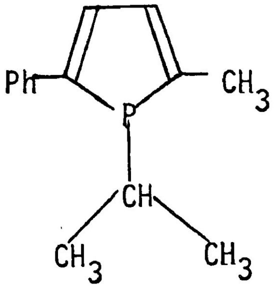
Finally, it was again observed (5) that although introduction of a methyl group into the 3- position of the phosphole ring results in a slight deshielding of the phosphorus atom, (taking into account the ring and substituent components of the shift) introduction of a second methyl group into the 4- position causes strong shielding. This has been attributed largely to steric interference rather than electronic effects and this effect is also observed in 4-methoxycarbonyl-1,3-dimethylphosphole where the ring methyl group inhibits conjugation of the methoxycarbonyl group with the phosphole system.

There have been three brief ^{13}C nmr studies on phospholes. The first of these (54) was devoted to a ^{13}C nmr study of 1-phenylphosphole - i.e. a phosphole without ring substituents. The $^{2}J_{C(3)-P}$ (C(3) = the ring carbon atom at position 3 in the phosphole nucleus) value in 1-phenylphosphole increases relative to that in the corresponding 1-phenyl-2-phospholene and this was taken to be indicative of a decrease in the average dihedral C-C-P-lone pair angle. This indicates a reduced pyramidal inversion barrier relative to that in the phospholene and hence some delocalization of the lone pair. This suggested delocalization was supported by the values of other ^{13}C—^{31}P coupling constants in the system and also the ^{13}C chemical shifts of both the phosphole ring carbon atoms and, in particular, the phenyl ring carbon atom attached to the phosphorus atom.

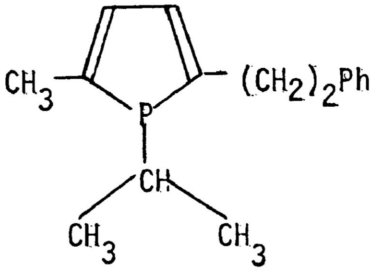
Quin et al. (5,55) studied ^{13}C—^{31}P coupling constants and ^{13}C chemical shifts in 1-methylphosphole, 1,2-dimethylphosphole, 1,3-dimethylphosphole and 1,3,4-trimethylphosphole and concluded that the almost identical shifts of all of the ring ^{13}C atoms in all of the phospholes studied are suggestive of some delocalization in the phosphole system even, presumably, in 1,3,4-trimethylphosphole where, on the basis of ^{1}H and ^{31}P nmr studies and chemical evidence, the usual 3,4- steric interaction of the methyl groups should occur. That this interaction does occur is also indicated (5, 55) by a 0.8 ppm difference in the chemical shifts of the 3- and 4- ring methyl groups in 1,3-dimethylphosphole and 1,3,4-trimethylphosphole - a difference very similar to that observed for the methyl groups of o-xylene and m-xylene.

Before leaving nmr studies of phospholes, the ingenious and apparently unambiguously definitive investigations of pyramidal inversion (and hence aromatic delocalization) in phosphole derivatives carried out by Egan *et al*. (18, 56) using ^1H nmr methods should be discussed. These workers observed (18) that the uniformly high pyramidal inversion barrier in acyclic phosphines (29 - 36 kcal./mole) is generally increased in cyclic phosphines because of angle strain. However, significant interaction of the phosphorus lone-pair in phospholes with the diene system should markedly reduce this inversion barrier relative to that of the corresponding saturated phospholane and partially unsaturated phospholene derivatives. Indeed, the aromatic stabilization could possibly be sufficient to offset the energy required to convert the normal pyramidal phosphorus arrangement to a planar ground state arrangement in phospholes as is observed in pyrroles. If this energy of aromatic stabilization is insufficient to produce a planar ground state, the potentially aromatic nature of the planar transition state should, as already stated, reduce the pyramidal inversion barrier at phosphorus in phospholes.

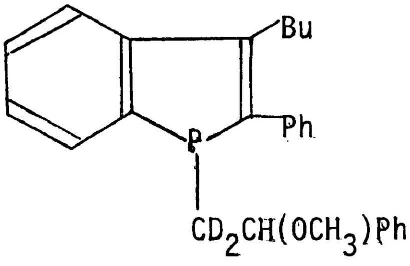
In order to study this inversion, Egan et al. (18, 56) prepared the dissymmetric phosphole LI and studied the ^1H nmr spectrum. At ca. 0°C, the isopropyl region of the spectrum showed the expected pattern for the diastereotopic isopropyl methyl groups - i.e. two doublets of doublets with each doublet of doublets arising from coupling of an isopropyl methyl group with the neighbouring isopropyl proton and the phosphorus atom. As the temperature is allowed to rise, the diastereotopic methyl groups tend to become equivalent through inversion of the phosphorus atom until at ca. 42° the two methyl signals have merged into a broad coalescence peak. Further heating leads to the appearance of one doublet of doublets. From these coalescence studies, the pyramidal inversion barrier ($\Delta G^{\ddagger}_{25}$) was estimated (18, 56) to be 16 kcal./mole in LI. Similar studies on other dissymmetric phospholes such as LII gave similar values for the pyramidal inversion barrier. These similar



LI



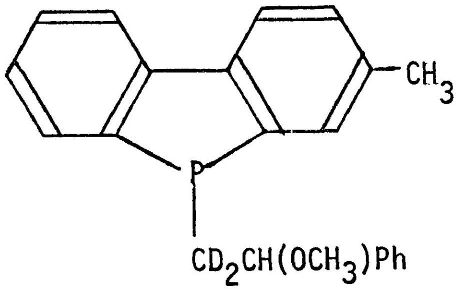
LII



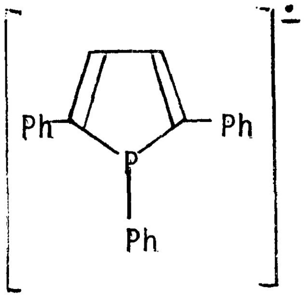
LIII

values were taken to indicate that the methyl groups of the isopropyl group are diastereotopic in all torsional arrangements and that pyramidal inversion is slow on the nmr time scale.

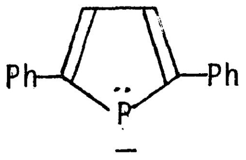
The studies were extended (56) to benzophospholes and dibenzophospholes such as LIII and LIV and it was found that the barrier to inversion is raised to ca. 24 kcal./mole and 26 kcal./mole respectively suggesting decreased lone-pair delocalization relative to simple phospholes. It was noted that these trends parallel those observed in the corresponding nitrogen and sulfur series.



LIV



LV

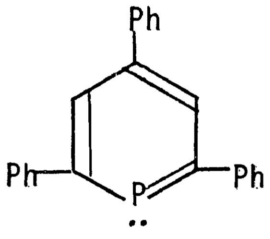


LVI

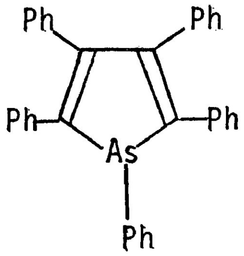
Turning now to electron spin resonance studies of phosphole systems, Kilcast and Thomson have carried out three such investigations

(57, 58, 59) involving the reactions of phospholes with alkali metals. In the first of these, it was found that 1,2,5-triphenylphosphole and 1,2,3,4,5-pentaphenylphosphole both react with potassium in dimethoxyethane and tetrahydrofuran to give solutions which show three strong and interconvertible esr signals. These were shown to be associated with the cleaved P-phenyl group (probably polymerized) rather than phosphole anion radicals of type LV which might be expected from the reactions. It should be mentioned that Braye _et_ _al_. have carried out similar chemical studies and have shown (22) that at room temperature or under reflux, complete cleavage of the phenyl group occurs to give phosphole anions of type LVI.

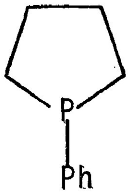
In their second (58) and third (59) reports, Kilcast and Thomson showed that at -60^{o} to -80^{o}, 1-methyl-2,5-diphenylphosphole, 1,2,5-triphenylphosphole and 1,2,3,4,5-pentaphenylphosphole all react with sodium and potassium in ethereal solvents to give anion radicals - probably of type LV - which decompose rapidly above -30^{o}. These radicals all showed a well separated (~30G) doublet in the esr spectrum, each component of which showed considerable fine structure. The large couplings were assigned to the phosphorus atom and were found to be significantly larger than for other phosphines. Indeed, the couplings were found to be similar those in related λ^{3}-phosphorin (_e.g._ LVII) radical ions. Since the λ^{3}-phosphorins appear to be true aromatic species (though with some electronic peculiarities (35)),



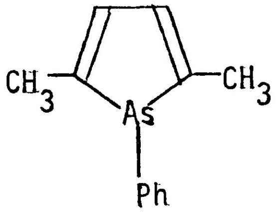
LVII



LVIII



LIX



LX

this suggests that phosphole radical anions also have some aromatic character. This is supported by the esr spectrum of the radical anion derived from 1-methyl-2,5-diphenylphosphole where the methyl group splitting is strongly suggestive of a methyl group attached to an aromatic ring.

With regard to ultraviolet spectroscopic studies of simple phospholes, only very brief investigations have been reported and the results of these are somewhat contradictory. In the first of these studies it was only noted (32) that 1-methylphosphole shows an ultraviolet spectrum which in some ways is similar to that of N-methylpyrrole. In a later publication by the same group (3) this statement was amplified somewhat with the observations that the spectrum of 1-methylphosphole is unlike that of a tertiary phosphine and shows no resemblance to that of a divinylphosphine. The observed transition at 286 nm in the spectrum of 1-methylphosphole was therefore taken to be unique to the phosphole system and was regarded as indicative of lone-pair delocalization.

In a still later publication, Quin et al. (5) showed that this transition is present in the ultraviolet spectra of all phospholes so far studied and that a methoxycarbonyl group on the phosphole ring causes a shift of 22 nm to longer wavelength indicating that the transition is due to the π-system of the phosphole. Introduction of methyl groups into the 3- and 4- positions of the phosphole ring cause small blue shifts and this was taken to indicate steric inhibition of conjugation as suggested by the chemical and nmr evidence already discussed.

With rather more complex molecules, Raciszewski et al. (60) observed that the ultraviolet spectra of 1,2,3,4,5-pentaphenylphosphole, 1,2,5-triphenylphosphole and 1,2,3,4,5-pentaphenylarsole (LVIII) are very similar to one another but are totally different from that of the partially aromatic 1,2,3,4,5-pentaphenylpyrrole suggesting at least reduced aromatic character in the phospholes. Ultraviolet fluorescence data for these molecules were also recorded (60).

In a much more recent study devoted mainly to a Faraday Effect investigation, Bruniquel *et al*. (61) noted that progressive *C*-methylation of 1-butylphosphole at the 3- and 4- positions leads to small blue shifts of the first ultraviolet transition. This behaviour was thought to be more consistent with a butadiene type of system rather than an aromatic system although, as noted above, Quin *et al*. attributed the effect to progressively increasing steric inhibition of conjugation. In the Faraday Effect study of phospholes discussed in the same paper (61), it was found that the observed magnetic molecular rotations are smaller than those calculated on the basis that phospholes are localized diene-lone pair arrangements. If, however, the phosphole system showed significant lone-pair interaction with the dienoid portion of the molecule, larger rotations than those calculated would be expected and this result again suggests a localized structure for simple phospholes.

In an entirely different approach, Schäfer *et al*. (62) have carried out a photoelectron spectroscopic study of 1-phenylphosphole, 2,5-dimethyl-1-phenylphosphole, the phospholanes (*e.g.* LIX) corresponding to these phospholes and 2,5-dimethyl-1-phenylarsole (LX). In the case of 1-phenylphosphole, the n and π levels of the phosphole ring were found to be nearly degenerate with an ionization potential (IP) of 8.45 eV while in 2,5-dimethyl-1-phenylphosphole the π-level drops to an IP of 8.0 eV while the n-level remains at 8.5 eV - i.e. in this second phosphole, the HOMO (highest occupied molecular orbital) is a π orbital and not the n orbital. Similar results were found for LX. Furthermore, the ionization potentials for the lone pairs of the corresponding phospholanes were found to be virtually identical with those of the phosphole lone pairs. This would appear to be conclusive proof of the localized nature of phospholes although the extrordinarily low pyramidal inversion barrier noted by Egan et al. (18, 56) still requires explanation. This last point will be discussed further later. In a later study on the photoelectron spectra of phosphines in general, Schmidt et al. (63) produced results which fully support the above conclusions. It is also worth noting that the orbital sequence deduced for phospholes from these photoelectron spectroscopic studies would account for the low basicity of phospholes and the reluctance of the lone-pair to react towards a variety of organic and inorganic reagents.

Finally, in this account of spectroscopic and related investigations of delocalization in phospholes, there have been two reported X-ray crystal and molecular structure determinations of simple phosphole derivatives. In the first of these (64, 65), it was found that in 1-benzylphosphole, the phosphorus atom is pyramidal and slightly out of the plane of the five-membered ring but that the ring

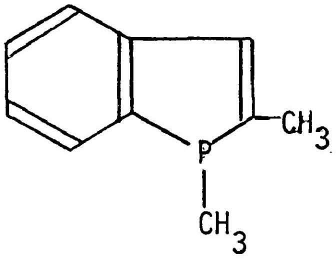
P-C bonds are shorter than the sum of the normal single bond covalent radii. This was taken to indicate perhaps some non-bonding electron interaction with the π-system. The C-C bond lengths in the phosphole were, however, found (65) to be similar to those in cyclopentadiene and, using these bond lengths as a measure of aromaticity, the tentative order of aromaticity was suggested to be be pyrrole > thiophene > furan > phosphole. On the other hand, it was noted that much depends upon the criteria used to measure aromaticity.

In the second molecular and crystal structure determination of a phosphole, it was found (66) that in 1,2,5-triphenylphosphole there is no significant shortening of the ring P-C bonds as compared with normal tertiary phosphines. Furthermore, as with 1-benzylphosphole, the ring is nonplanar and the arrangement about the phosphorus atom is pyramidal. The ring carbon atoms also have typical butadienoid distances. As has been observed elsewhere (65), clearly much depends upon the substitution pattern of the phosphole ring and, indeed, the dependence of behaviour upon the substitution pattern has been observed with most of the studies outlined earlier in this review.

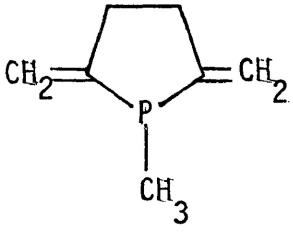
Theoretical Studies

There have been six theoretical studies which have a bearing upon the problem of the electronic structure of phospholes and again, sharply conflicting conclusions have been put forward. The first of these investigations was by Brown (25) who estimated by HMO calculations that the phosphole system (a planar model) should have a conjugation energy of about 25 kcal./mole which is about the same as that of the pyrrole system.

In a more recent study, Rauk *et al*. (67) carried out semi-empirical calculations of pyramidal inversion barriers of first and second row elements using the Pople CNDO/2 approach. In this very thorough treatment, inversion barriers for about 100 structures were calculated and good agreement between calculated and experimental values was observed. The agreement extended to inverting atoms adjacent to (p-p)π unsaturation and, in the case of phospholes such as 1,2,5-trimethylphosphole and benzophospholes such as LXI, the results were in excellent agreement with inversion barriers measured by the nmr coalescence technique reported by the same group (18, 56). This again was taken to support the earlier suggestion (18, 56) that in the pyramidal ground state of phospholes there



LXI



LXII

is significant interaction of the lone-pair orbital with the diene system and that this interaction increases markedly in the planar transition state.

As a check on the accuracy of this deduction, further calculations on the degree to which cyclic conjugation specifically lowers the inversion barrier in phospholes were carried out using models (such as 1-methyl-2,5-dimethylenephospholane (LXII)) which are unconjugated cyclically and tautomeric with the phospholes studied. The lowering of the barrier was found again to agree well with that observed. The effects of $(2p\text{-}3d)\pi$ conjugation were judged to be unimportant in determining inversion barrier heights.

Shortly after the above results were published, Hase et al. (68) reported the results of a detailed study of the electronic structure of phospholes and arsoles using the extended CNDO/2 method. Considerable information regarding conformational effects, orbital energies, orbital sequences and orbital density plots was recorded. According to this study, the difference in the pyramidal inversion barriers of phosphole and arsole is only 3.4 kcal./mole although actual values for the barriers were not given and, as will be seen shortly, this value has been challenged by other workers. Furthermore, the orbital sequences in phosphole and arsole were calculated, the effects of substituents were noted and the implication was that phospholes and arsoles are pyramidal molecules in the ground state with little $n\text{-}\pi$ interaction.

In reply to this work and also to the earlier work by the same group (62) regarding photoelectron spectroscopic studies of phospholes, Andose et al. (69) have stated that on various grounds (e.g. possible incorrect assumptions regarding phosphine inversion barriers and possible incorrect values chosen for the equilibrium out of plane angle in phospholes) they consider the calculations of Hase et al. (68) to be questionable and in a detailed argument concerning measured and calculated pyramidal inversion barriers, they reiterate that there is excellent evidence for (3p-2p)π delocalization in phospholes and arsoles. It was, however, conceded that only energy differences between pyramidal and planar states are available by the method of calculation used and that in view of the photoelectron spectroscopic data reported by Schäfer et al.(62) there may well be little n-π interaction in the pyramidal ground state of phospholes and that aromaticity may be confined largely to the planar transition state. It was further stated (69) that the criterion of a lowering of the inversion barrier because of planar state delocalization "differs crucially" from measurements and calculations which are concerned only with a pyramidal arrangement about the phosphorus atom. Andose et al.(69), however, found it "inconceivable" that delocalization is restricted entirely to the planar transition state and claimed that the pyramidal inversion barrier work unambiguously demonstrates n-π interactions in both the pyramidal and planar states of phospholes. On the other hand, it was stated that much depends upon an adequate and generally accepted definition of aromaticity which is not at present available.

To add to the already confused picture obtained from theoretical studies, in a still more recent paper Kaufmann and Mathey (70) have used the LCAO-MO-CNDO/2 method to calculate the effect of conformational changes upon delocalization (if any) in phospholes. It was concluded that inversion barriers are indeed lowered by delocalization in the planar transition state, that this delocalization is of the (3p-2p)π type, that (2p-3d)π conjugation plays a key role even in the pyramidal state and that substituents on the phosphorus atom have some effect. Thus, it was calculated that lone-pair interaction with the diene system is greater in 1-methylphosphole than in 1-t-butylphosphole. In short, aromaticity in phospholes is strongly angularly dependent. There is, therefore, considerable agreement between Andose et al. (67, 69) and Kaufmann et al. (70).

Finally, a very thorough and extremely detailed treatment of phospholes by the LCGO procedure has appeared very recently. On the basis of this study (71), it was concluded that phosphole is non-planar as a consequence of increased $3s_p$ contributions to the pyramidal arrangement. Furthermore, it was stated that phosphole has no resonance energy and the previously published ^{1}H nmr information (already discussed) was interpreted as being more consistent with a butadienoid system. Also, the ionization potential (IP) data calculated were found to be in good agreement with those experimentally determined by Schäfer et al. (62). The authors conceded (71) that if these deductions are correct, the observed low pyramidal inversion barrier in phospholes still requires explanation and proposed that it is a valence force field effect which does not require delocalization in the planar transition state. It was, however, stated that these calculations do not rule out aromatic character in phosphole radical anions of the type reported by Kilcast and Thomson (59).

In summary, early studies (mainly chemical) of aromaticity in phospholes suggested that there is little delocalization of the phosphorus lone-pair. Later, more detailed, chemical, physico-chemical and spectroscopic investigations indicated very much reduced lone-pair availability for chemical reactions and provided considerable evidence that this is due to lone-pair interaction with the diene system. However, the deductions from very recent photoelectron spectroscopic and theoretical results are in considerable disagreement. Clearly, further studies are desirable and, as has been remarked elsewhere (71), some reliable thermochemical data would be very helpful.

Addendum

Two further points remain to be noted. The first is that the foregoing survey has now been published virtually in its entirety (72).

The second point is that as the remainder of this thesis was written on a part time basis over a period of more than a year, further publications in the area of phosphole chemistry have appeared. Two of these (refs 75 and 87) are of importance to the theme of this thesis but, rather than risk the introduction of errors and ambiguities by minor revision of this introductory chapter, mention of these papers has been made at appropriate places in the next chapter.

RESULTS AND DISCUSSION

Introduction

The first chapter of this thesis discussed recent developments in phosphole chemistry with particular reference to the aromaticity problem and several interesting points arose during this discussion. One such point is the question of how reactive is the phosphorus non-bonding electron pair in simple phosphole derivatives. Thus, although phospholes with very simple substitution patterns are unusually weak bases (3,32) and normally very poor donors towards transition metal ions (3,42-46), the phosphorus non-bonding electron pair of such phospholes is sufficiently reactive towards benzoyl chloride in the presence of water for the phospholes to undergo ring expansion reactions (26-28) in good yield.

A second interesting point is that although the phosphole pyramidal inversion studies carried out by Mislow's group (18,56,67,69) provide strong evidence for at least an aromatic planar transition state, several (though not all) photoelectron spectroscopic (62) and theoretical studies (68,71) suggest that phospholes are non-aromatic systems. Furthermore, in order to reconcile an apparently very low pyramidal inversion barrier with an apparently non-aromatic phosphole planar transition state, the suggestion has been made (71) that the low barrier is a result of a vaguely defined valence force field effect.

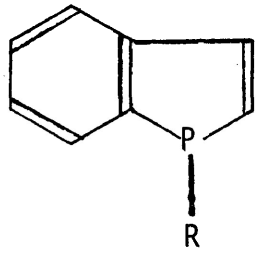
The author of this thesis therefore attempted (with some success) to clarify further these two points. Thus, a preliminary study was carried out regarding the nucleophilic character of the phosphorus atom of simple phospholes, with different substitution patterns, towards the well known electrophile dimethyl acetylenedicarboxylate (DMADC). The objectives here were threefold. First, in view of Mathey's observations (26-28) regarding simple phosphole nucleophilic character, it was felt advisable to check whether the earlier observation (29) that the phosphorus atom of 1,2,5-triphenylphosphole is not reactive, under normal conditions, towards DMADC is general for simple phospholes.

Second, in view of earlier observations regarding phosphole reactivity towards quaternization (5), the influence of substitution--particularly in the 3- and 3,4-positions of the phosphole nucleus--upon reactivity at the phosphorus atom should receive further attention.

Third, since tertiary phosphines in general give such a wide variety of structural types (normally ylides) in reactions with the acetylenic ester (for a discussion of these, see refs. 30 and 73), it would be interesting to see what new heterocyclic systems could be made from these reactions.

Regarding the second point arising from the introductory chapter, it was felt desirable to check that the activation energies measured by Egan _et al_. (18,56) are, in fact, due to pyramidal inversion at the phosphorus atom of the phosphole system and not to some other process. This check, of course, should be carried out using a method entirely different from that used by Egan _et al_.

While carrying out the phosphole reactivity studies mentioned above, it also occurred to the author that the simple phospholes used in the study could possibly be used in a general two-step synthesis of the, at present, relatively inaccessible (73) phosphindole (benzo[b]phosphole) system LXIII. A brief account of a preliminary study in this area is therefore also given in this chapter of the thesis.



LXIII

Although the pyramidal inversion study mentioned above was carried out after the phosphole reactivity studies were started, it follows on so naturally from the end of the introductory chapter that it will be discussed here first.

Pyramidal Inversion Studies

In the introductory chapter of this thesis, it was pointed out that there is considerable disagreement as to the possibility of lone pair delocalization in phospholes, and that further studies would be desirable. Of the six theoretical studies mentioned, four (25,67,69,70) point to at least some degree of aromaticity. The remaining two theoretical studies (68,71) imply that phospholes are pyramidal molecules in the ground state with little n-π interaction, but only one (71) of these two has attempted to explain the observed low pyramidal inversion barrier in phospholes. This tentative explanation involves a valence force field effect which does not require delocalization in the planar transition state. This explanation is rather vague and the fact remains that it is not a proven fact but rather a theory devised to explain experimental results which conflict to some extent with theoretical calculations.

It therefore seems that few conclusions can be drawn from such conflicting results. To add to the confusion, Burdon, et al. (74) have recently warned against "uncritical acceptance" of CNDO/2 calculations as improper choice of geometries or improper convergence of density matrices may cause errors in the calculations of molecular charge and/or spin distributions.

In a very recent development carried out since the introductory portion of this thesis was written, a group of authors, who in previous papers (61,62,63,68) had produced allegedly strong evidence against aromaticity in phospholes, have reversed their stand and stated (75) that phospholes are indeed "aromatic" systems despite their pyramidal ground state. In this twofold study, photoelectron spectroscopic data and theoretical results obtained by the extended CNDO/S and the MINDO/2 procedures were analysed. Therefore, before this author's own results are reported, a discussion of this latest highly significant paper will be presented.

The theoretical calculations consider conjugation between cis-butadiene and PR subunits within the phosphole molecule. The CNDO/S calculations have shown that the hyperconjugative interaction between the $\pi(b_1)$ orbital of the butadiene unit and P-C orbital of the PR unit is the predominant interaction between occupied orbitals, that the vacant $\pi^*(b_1)$ orbital contains nearly equal contributions from the n and P-C orbitals of the PR unit, and that for the pyramidal model the d_{xz} orbital may accept electrons reducing π charge transfer from the PR unit to the butadiene part of the phosphole molecule.

Calculations on planar and pyramidal models of the phosphole molecule showed that the conjugation energy is only 30-40% less in the pyramidal molecule. Since the parameterization of the CNDO/S method is chosen with the aim of reproducing electronic spectra, these authors decided to check the stabilization (conjugation) energies produced by the CNDO/S method using the MINDO/2 method, the parameters of which are chosen to describe correctly the enthalpies of formation. Although the conjugation energies obtained by the MINDO/2 method were about 70% of the CNDO/S values, it was felt that the agreement is quite reasonable. Because of combined $n\pi^*$ and $n\pi$ interactions it was felt that the n orbital energy was not a good indicator of phosphole aromaticity and photoelectron spectra of some simple phospholes and phospholanes were re-examined. The experimentally derived orbital interaction diagram for the interaction of the cis-butadiene and PR units confirms the theoretical findings of strong $P\text{-}C/\pi(b_1)$ hyperconjugative and weak $n/\pi(b_1)$ conjugative interactions, with negligible π charge transfer from the PR unit to the neighbouring π system.

Because of the conflicting opinions on the matter of phosphole aromaticity and the general agreement that further studies were required, it was decided, as mentioned in the introduction to this chapter, to conduct a preliminary investigation of some simple phosphole systems in an attempt to help clarify the confused situation.

In particular, because the nmr studies carried out by Egan et al. (56) on pyramidal inversion barriers in phospholes provided the most conclusive physical evidence for the aromaticity of phospholes, it was decided to attempt to check these results by an independent method. Dielectric relaxation measurements provide a technique which, like the nmr technique (56) is able to provide thermodynamic parameters for a dipole or molecular relaxation. Various accounts of this technique occur in the literature (e.g. ref. 76a and 76b) but essentially the Eyring equation is used to analyse the variation of dielectric loss maximum with temperature and an enthalpy of activation (which can be associated with an energy barrier) for the dipole orientation process can be obtained. The Eyring rate equation below gives the rate constant for reorientation:

$$\kappa = \frac{kT}{h} \exp\left(\frac{\Delta S^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H^{\ddagger}}{RT}\right)$$

where k is Boltzmann's constant, h is Planck's constant, R is the ideal gas constant, $\Delta S^{\ddagger}$ is the entropy of activation and $\Delta H^{\ddagger}$ is the enthalpy of activation. The quantity κ is related to the frequency of maximum dielectric loss as follows:

$$\kappa = \tau^{-1} = 2\pi f_{max}$$

where τ is the relaxation time of the reorientation process.

This method has the potential advantage of applicability to non-dissymmetric phospholes unlike the nmr method used by Egan et al. (18,56) where dissymmetric phospholes must be used. This allowed measurements to be made on simple, relatively readily available phospholes. The only apparent restriction (other unexpected restrictions will appear later in this discussion) on the compounds to be used is that they should have a permanent dipole moment. The reason for this is that the dielectric relaxation method is based upon the reorientation of a dipole in an alternating applied electric field.

The dielectric constant of a dipolar compound will decrease as the frequency of the applied electric field increases until eventually the molecular dipole orientation cannot keep pace with the changes in direction of the applied field. Thus, the permittivity (ε_0) (dielectric constant) of a polar compound at static or low frequency will be greater than the permittivity (ε_∞) at very high frequencies. The decrease in permittivity is due to a time lag between the response of the dipoles to the voltage oscillations. This time lag is a relaxation, and the frequency range between which the permittivity decreases from ε_0 to ε_∞ is termed a region of anomalous dispersion or, simply, the relaxation region. In the relaxation region, the permittivity ε^* is a mathematically complex quantity. $\varepsilon^* = \varepsilon' - i\varepsilon''$ where ε' is the real permittivity and ε''

is the imaginary part or loss factor. In dielectric relaxation studies ε'' is referred to as the dielectric loss or dielectric absorption, and is a measure of the conductance of the medium. The dielectric loss reaches a maximum in the relaxation region and the frequency of the maximum loss (f_{max}) gives the relaxation time (τ) of the dipole orientation process in seconds.

$$\tau = \frac{1}{2\pi f_{max}}$$

The quantities ε' and ε'' can be derived experimentally and, in their simplest form, are derived from the equations:

$$\varepsilon' = \frac{C}{C_0} \qquad \varepsilon'' = \frac{1}{\omega R C_0}$$

where C_0 is the capacitance of an empty condensor and C and R are respectively the capacitance and resistance of the condensor filled with the polar sample under investigation. The quantity $\omega = 2\pi f_{max}$.

Thus, by experimentally determining ε' and ε'' at a number of frequencies a plot can be made of tan δ vs. log f where tan δ is the ratio $\varepsilon''/\varepsilon'$. The maximum of this plot gives f_{max} and hence the relaxation time. The particular relaxation time measured may represent any one of a number of processes such as group rotation, pyramidal inversion or molecular relaxation involving the whole molecule. These, of course, would normally be of different activation energies and measurement of the activation energy should define the process. This is done by plotting tan δ vs. log f from measurements made over a range of temperatures.

Assuming the relaxation can be represented by the Eyring rate expression rewritten as

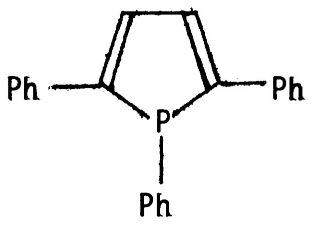
$$\tau = \frac{h}{kT} \exp\left(\frac{\Delta H_E^{\ddagger}}{RT}\right) \exp\left(- \frac{\Delta S_E^{\ddagger}}{R}\right)$$

a plot of log τT vs. T^{-1} may be used to evaluate $\Delta H_E^{\ddagger}$ and $\Delta S_E^{\ddagger}$ the Eyring enthalpy and entropy of activation respectively. If the only mode of dipole relaxation is pyramidal inversion, $\Delta H_E^{\ddagger}$ is the enthalpy of activation (energy barrier) which must be overcome for the phosphole molecule to flip from one pyramidal arrangement to the other. The free energy of activation $\Delta G_E^{\ddagger}$ is then given by $\Delta G_E^{\ddagger} = \Delta H_E^{\ddagger} - T\Delta S_E^{\ddagger}$.

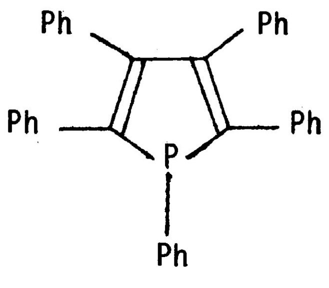
For the phosphole pyramidal inversion studies undertaken by this author, the sample phospholes to be investigated were incorporated into a polystyrene matrix by dissolving the sample and the polystyrene in a suitable solvent, evaporating the solvent, then pressing the polystyrene matrix into a flat disc. The dielectric measurements were then made by placing the disc between the electrodes of a capacitance bridge.

This particular method was chosen because only a small amount of sample is needed, the measurements can be made over a wide frequency range, and it was felt that if the phosphole were incorporated into a polymer matrix it would be more feasible to observe an intramolecular relaxation such as pyramidal inversion rather than rotation of the entire phosphole molecule (molecular relaxation). Also, the polymer environment has the effect of slowing such processes down to the extent that they can be observed at relatively low frequencies.

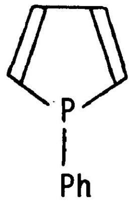
Since apparently no restrictions limited the phospholes to be investigated, simple, readily available phospholes and phosphole derivatives were chosen. Those investigated were 1,2,5-triphenylphosphole(LXIV), 1,2,3,4,5-pentaphenylphosphole(LXV), 1-phenylphosphole (LXVI), 3-methyl-1-phenylphosphole(LXVII), 3,4-dimethyl-1-phenylphosphole(LXVIII), 3,4-dimethyl-1-phenylphosphole sulfide(LXIX), and 1-n-butyl-3,4-dimethylphosphole(LXX).



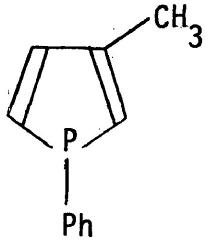
LXIV



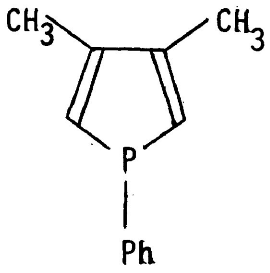
LXV



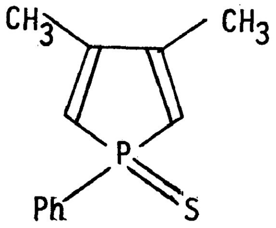
LXVI



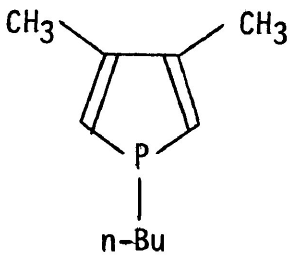
LXVII



LXVIII



LXIX



LXX

The energy barriers mentioned in the following discussion are expressed in terms of the enthalpy of activation $\Delta H_E^{\ddagger}$ since it is felt that for phospholes with a particularly large R group on the phosphorus atom, the polymer chain may have to move to allow the pyramidal inversion of the phosphole. Probably, this would increase the entropy term greatly giving an abnormally low value for $\Delta G_E^{\ddagger}$, and this could lead to misleading deductions regarding pyramidal inversion. Since the entropy terms were small or negligible in the nmr study (18,56) on pyramidal inversion barriers (indeed, Egan <u>et al</u>. (56) give their results almost entirely in terms of $\Delta G_E^{\ddagger}$ since, by their method, $\Delta H_E^{\ddagger}$ is less easy to obtain) it is felt by this author that the $\Delta H_E^{\ddagger}$ values obtained here would be more significant for the purpose of comparison of these results with those obtained by the nmr coalescence method. It is also felt that because of the possible interference of the polymer chain in the pyramidal inversion, the $\Delta H_E^{\ddagger}$ values obtained in this study would if anything be slightly high, and would give an upper limit for the pyramidal inversion barrier.

Only two of the phospholes mentioned above (LXVIII and LXX) showed a maximum in the dielectric loss curve which may (see later discussion) be attributable to a pyramidal inversion. The other phospholes unexpectedly exhibited a conduction band in the plot of tan δ vs. log frequency which obscured any peak attributable to a pyramidal inversion, thus constituting an unforseen restriction in the use of this method for phospholes. A typical such plot of tan δ vs. log frequency for 3-methyl-1-phenylphosphole is shown in Figure 1. The loss curve in Figure 1 is typical (77a) of a molecule in which D.C. conductivity is involved. Thus, the total dielectric dispersion is that due to dipole reorientation plus a loss associated with D.C. conductivity. It can be seen that such losses for the above phosphole are very high at low frequencies. This is in line with theory, which relates the total loss ε_T'' to D.C. conductivities by the equation $\varepsilon_T'' = \varepsilon'' + \frac{K\sigma}{f}$ where σ is the conductivity, K is a constant, and f is the frequency. The conductivity, σ, depends on mobility of charge carriers and the temperature.

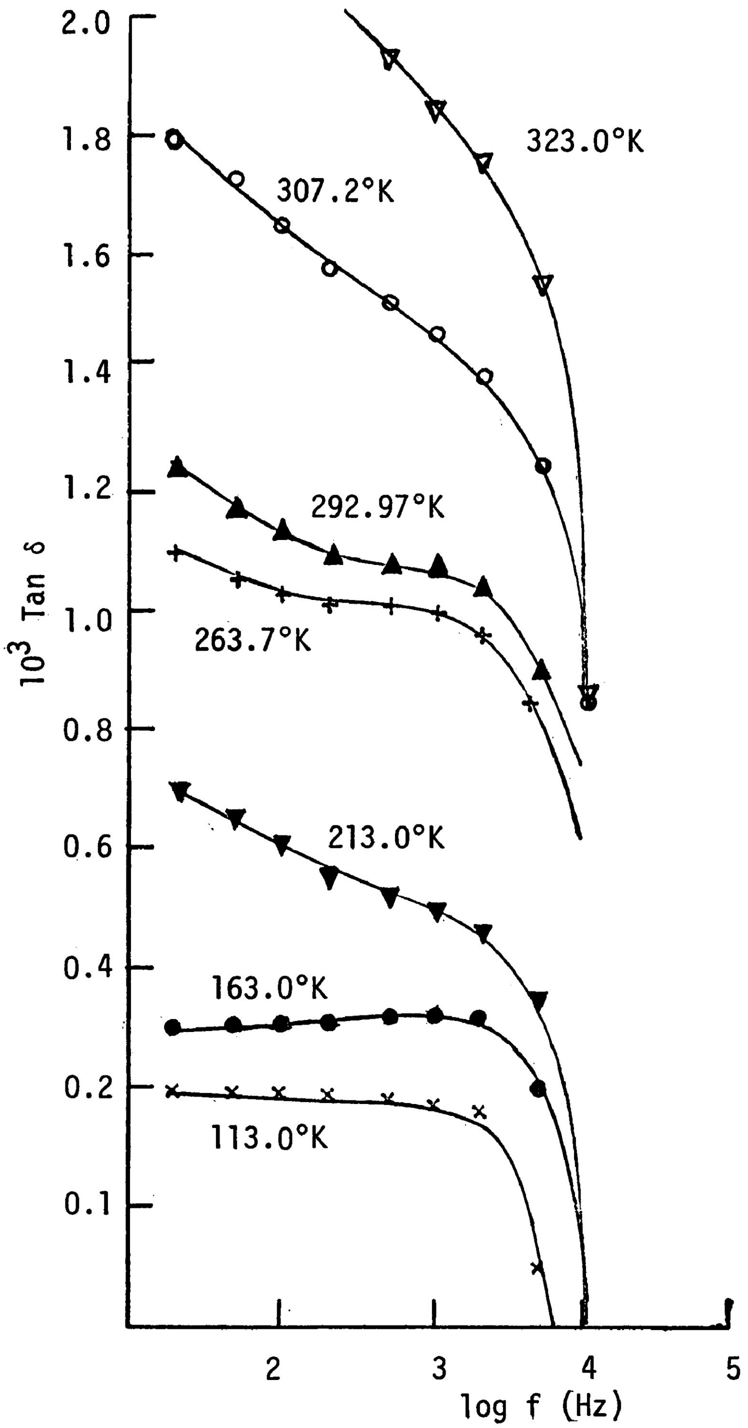


Figure 1 - Plot of Tan δ vs. log frequency for 3-Methyl-1-phenylphosphole.

Note the change in scale on the Tan δ axis.

In this connection, there is a possible correlation between the population patterns of molecular orbitals and D.C. conductivity. In the case of 1-phenylphosphole (LXVI), for which the n and π levels of the phosphole ring were found (62) to be nearly degenerate, with ionization potentials of 8.45 eV and 8.5 eV respectively, a conduction band is observed and it is possible that the conduction effects observed are at least in part due to this degeneracy. This will be discussed more fully a little later.

Depending on the substitution pattern of the phosphole ring, the ionization potentials may vary. For example, for 2,5-dimethyl-1-phenylphosphole the n and π levels were found (62) to be well separated by 0.5 eV. Dielectric studies of this compound, not available to this author, would therefore be desirable since conduction effects may be much less.

That methyl groups on the phosphole ring cause significant changes in the electronic structure of phospholes has been noted by other authors (5,8,43) in both chemical and spectroscopic investigations. This point has been discussed in the introduction to this thesis.

Thus, in summary, it was only the two phospholes with methyl substituents in both the 3- and 4- positions which showed maxima in the dielectric absorption curves. The plot of tan δ

vs. log frequency for 1-n-butyl-3,4-dimethylphosphole is shown in Figure 2. By calculating the relaxation time, τ, at a number of temperatures it is possible to obtain $\Delta H_E^{\neq}$ for whatever relaxation process is being observed from a plot of log τ vs. T^{-1}. The plot for 1-n-butyl-3,4-dimethylphosphole is shown in Figure 3. The value obtained, $\Delta H^{\neq} = 30.5 \pm 2.6$ kcal./mole, is rather high for a pyramidal inversion barrier in an aromatic phosphole where values of $\Delta H_E^{\neq}$ of around 15-20 kcal./mole would be expected as measured by Egan <u>et al</u>. (18,56). However, it is rather low for inversion about a phosphorus atom constrained by a five-membered ring where values around 40 kcal./mole would be expected (56). This point will be discussed further shortly. In passing, it should be noted that although the various graphical plots are hand drawn for convenience, actual $\Delta H_E^{\neq}$ values were obtained by a computer refinement of the data.

A much lower value of $\Delta H_E^{\neq} = 19.5 \pm 5$ kcal./mole was obtained for 3,4-dimethyl-1-phenylphosphole for which the appropriate graphical plots are shown in Figures 4 and 5. This is in excellent agreement with the inversion barriers of simple phospholes (<u>ca</u>. $\Delta H_E^{\neq} = 17$ kcal./mole found by Egan <u>et al</u>.(56) using the nmr coalescence technique and also for such barriers calculated (67,69) by theoretical methods. However, it is also well within the range of experimental $\Delta H_E^{\neq}$ values for <u>molecular</u> relaxations of molecules of similar size. For example, by this same method $\Delta H_E^{\neq}$ for the energy barrier tentatively assigned to the molecular

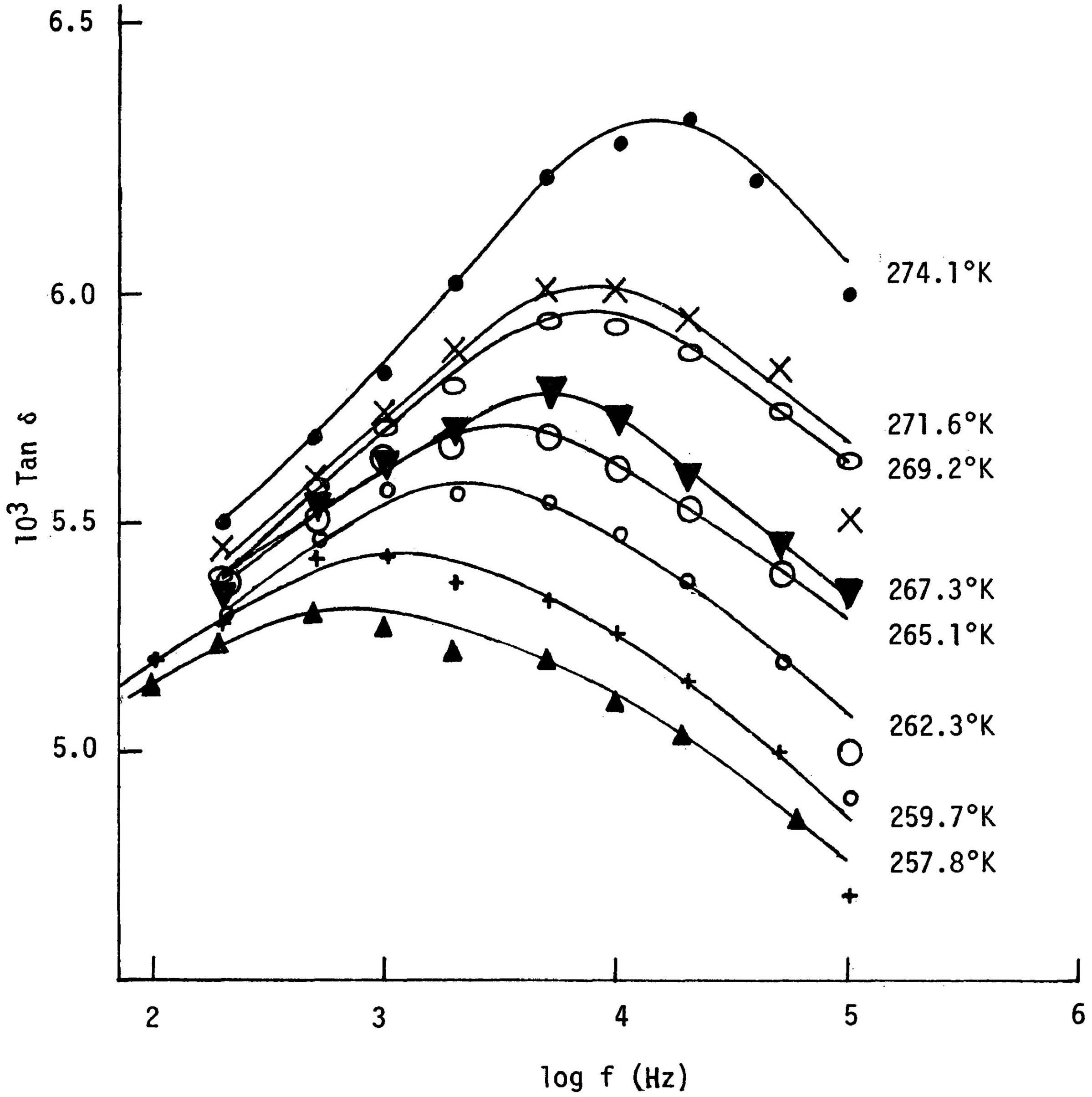


Figure 2 - Plot of Tan δ vs. log frequency for 1-Butyl-3,4-dimethylphosphole.

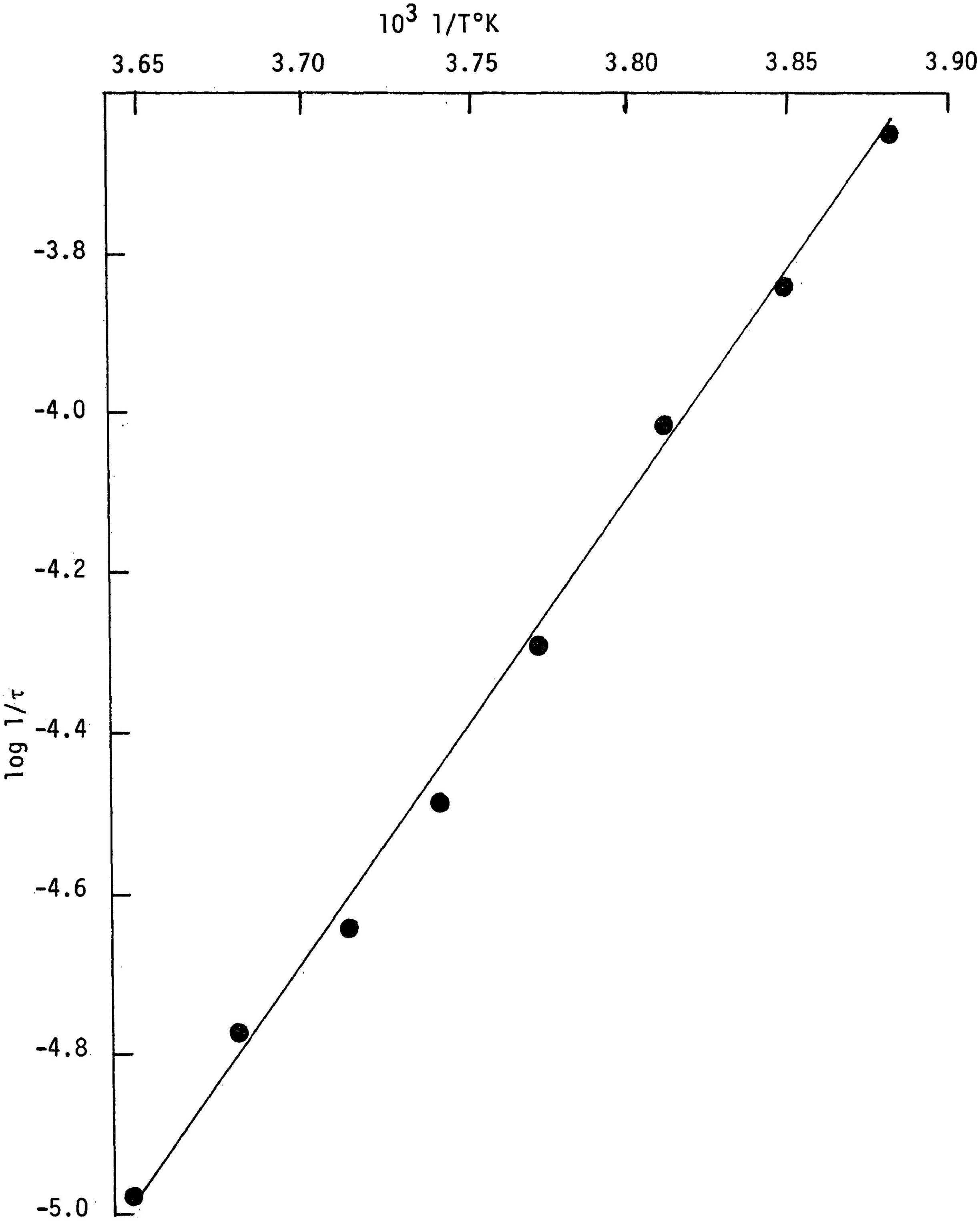


Figure 3 - Plot of log 1/τ vs. 1/T°K for 1-Butyl-3,4-dimethylphosphole.

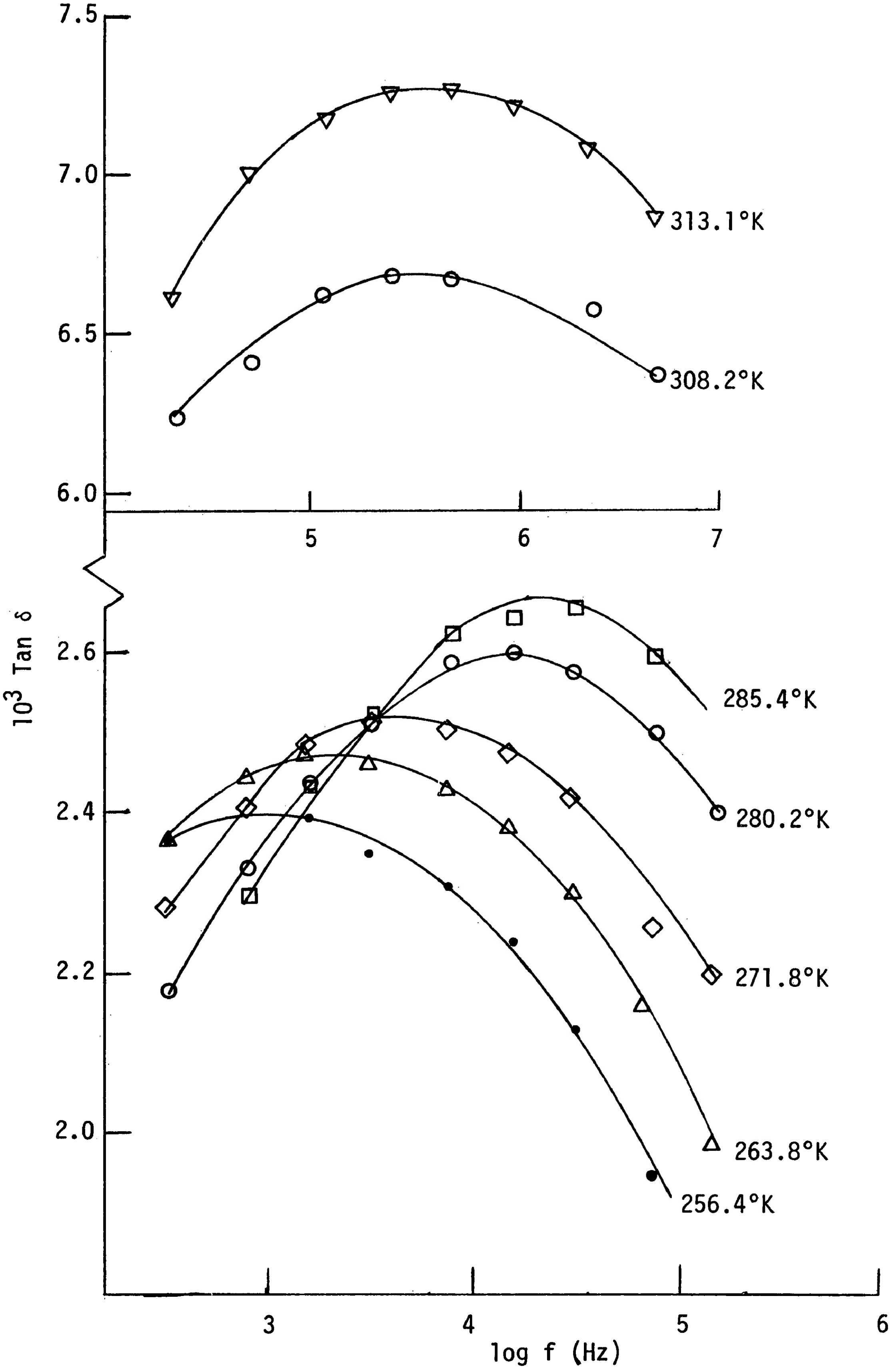


Figure 4 - Plot of Tan δ vs. log frequency for 3,4-Dimethyl-1-phenylphosphole

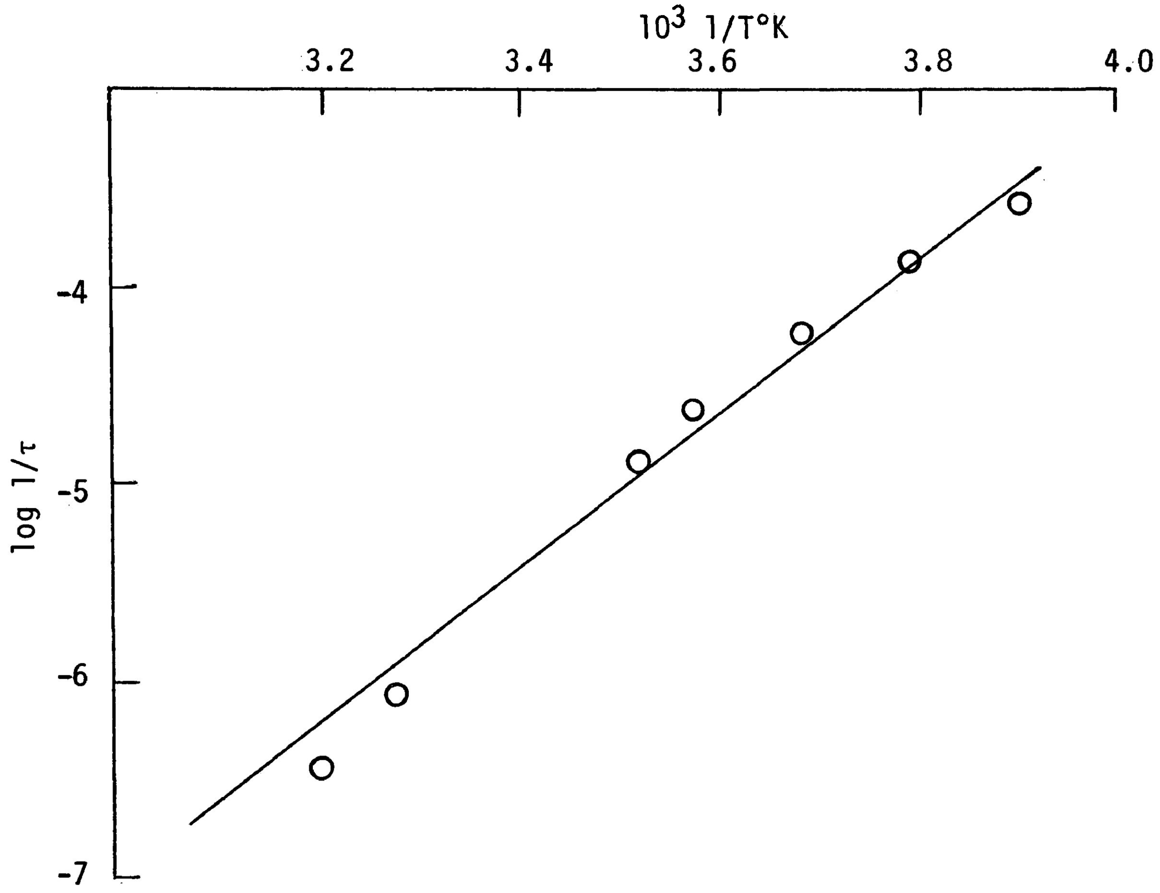


Figure 5 - Plot of log 1/τ vs. 1/T°K for 3,4-Dimethyl-1-phenyl phosphole.

relaxation of benzophenone was found to be about 17 kcal./mole (77b). It should, however, also be noted that the energy of such a molecular relaxation is very sensitive (76b) to the rotational volume and values as high as $\Delta H^{\neq} = 130$ kcal./mole for molecules such as tetracyclone have been obtained.

As a check on this point, it was then decided to investigate possible relaxation in the sulfide of 3,4-dimethyl-1-phenylphosphole because this molecule, being rigid, would exhibit only a molecular relaxation and group rotation of much lower energy. The value of the activation energy for the molecular relaxation of the phosphole sulfide was found to be 17.3 kcal./mole. Since the margin of error for 3,4-dimethyl-1-phenylphosphole puts the $\Delta H_E^{\neq}$ value for this compound well within comparable range of the value found for the sulfide, no firm conclusion can be drawn as to whether this activation enthalpy is for a molecular or intramolecular process. Indeed, the two processes may well be of almost identical energy. It may be noted, however, that Egan et al. (56) quoted an activation enthalpy of 17.1 ± 0.4 kcal./mole for 1-isopropyl-2-methyl-5-phenylphosphole in what was almost certainly a pyramidal inversion as measured by the nmr coalescence technique.

As mentioned earlier, $\Delta H_E^{\neq}$ for 1-butyl-3,4-dimethylphosphole was found to be 30.5 ± 2.6 kcal./mole, which is almost certainly too high for a molecular relaxation, since the measured value reported above for 3,4-dimethyl-1-phenylphosphole sulfide is considerably lower and yet this latter molecule is of similar if not larger size than 1-n-butyl-3,4-dimethylphosphole. For molecules of a given shape, $\Delta H_E^\ddagger$ of molecular relaxation should increase, as noted by Davies and Edwards (79), with the size of the molecule. It is true that the value of $\Delta H_E^\ddagger$ obtained for the 1-butyl compound, if, as is probable, this is due to a pyramidal inversion, is somewhat higher than the $\Delta H^\ddagger$ values obtained by Egan <u>et al</u>. (56) from the nmr coalescence studies. However, it is still significantly lower than those estimated (56) for non-aromatic phosphole systems where the phosphorus inversion, constrained by a five-membered ring, may have a $\Delta H_E^\ddagger$ value as high as 40 kcal./mole (ref. 56 gives 34 kcal./mole for $\Delta G^\ddagger$) as outlined earlier.

Also, two other factors must be considered. The first is that, as already mentioned, the value of $\Delta H_E^\ddagger$ of 30.5 kcal./mole represents an upper limit for whatever process is occurring because inversion or other major rearrangement of a large molecule like 1-butyl-3,4-dimethylphosphole may also involve some rearrangement of the polymer matrix. The true energy barrier may well be somewhat lower. The second is that in chemical and ^{31}P nmr studies (7,8) discussed in the first chapter of this thesis, 3,4-disubstituted phospholes showed significantly different character from simple phospholes. This may be a steric effect involving the 3- and 4- substituents which reduces the aromatic character and therefore, perhaps, increases the pyramidal inversion barrier. This may also explain in part why D.C. conduction is less important for the two 3,4-disubstituted phospholes, which showed normal loss curves. It is clear, however, that considering all of the available evidence, the D.C. conduction does not appear to be a direct consequence of the presence of benzene rings attached to the phosphole ring since 3,4-dimethyl-1-phenylphosphole does not show this conduction. Neither is it a property specifically associated with n,π degeneracy in the orbital sequence (a possibility briefly mentioned earlier) since both 1-phenylphosphole (which shows a conduction band) and 1-n-butyl-3,4-dimethylphosphole (which does not) apparently have (75) the same type of degeneracy.

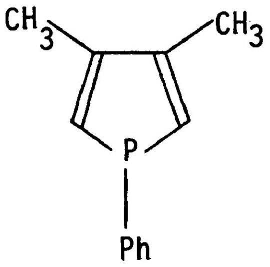
Probably the best molecule to study by the dielectric absorption method would be 1-methylphosphole which contains no phenyl groups and where no 3,4- steric interaction is possible although the orbital sequence is not yet known. Unfortunately, this compound is not easily prepared and handled and a study of this system must await a more detailed investigation.

In summary, the results obtained for 1-n-butyl-3,4-dimethylphosphole (LXX) and 3,4-dimethyl-1-phenylphosphole (LXVIII) are consistent with a pyramidal inversion process although, in view of the results obtained with the sulfide of LXVIII, the value of $\Delta H_E^{\ddagger}$ obtained for LXVIII itself could possibly be attributed to a molecular relaxation. If these results are indeed due to pyramidal inversion, then considerable support is given to the results obtained by nmr coalescence techniques (18,56).

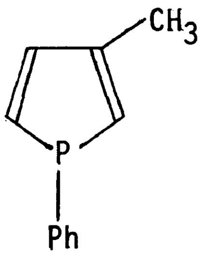
Phosphole Reactivity Studies

Introduction

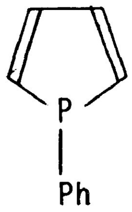
It was mentioned in the introduction to this chapter, that in view of the conflict between Mathey's results (26-28) with ring expansions *via* reactions at the P atom and earlier studies (29,31) regarding phosphole reactivity using more heavily substituted phospholes, a preliminary investigation would be undertaken of reactivity of simple phospholes at the P atom. The phospholes chosen were 3,4-dimethyl-1-phenylphosphole (LXVIII), 3-methyl-1-phenylphosphole (LXVII) and 1-phenylphosphole (LXVI) and these are shown below. The investigation, as explained in the introduction, involved reaction of the phospholes with dimethyl acetylenedicarboxylate (DMADC) and the phospholes used were chosen with a view to determining the effect of the substitution pattern upon reactivity.



LXVIII



LXVII



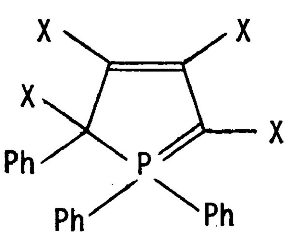
LXVI

3,4-Dimethyl-1-phenylphosphole (LXVIII)

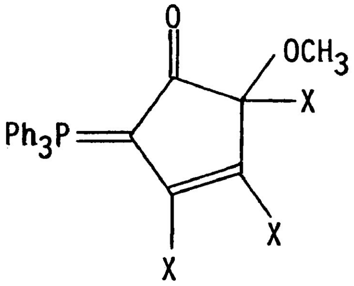
Investigation was begun with this phosphole because previous studies (5,43,55) have indicated that it could be expected to be more reactive than other phospholes. For instance, Quin et al. (43) showed that 3,4-disubstitution (as in 1-benzyl-3,4-dimethylphosphole) causes greater reactivity at the P atom in phosphole-metal complex formation. This apparent change in reactivity is also reflected in an increased rate of quaternary salt formation (5). Furthermore, nmr studies (5,55), discussed in the first chapter, have also indicated that the electronic structure of the 3,4-disubstituted phospholes is somewhat different from that of other simple phospholes.

It was found that this phosphole reacts smoothly and rapidly with DMADC at room temperature in benzene to give mainly one product as orange crystals in 39.2% yield. This is in contrast to 1,2,5-triphenylphosphole (29) which will not react with DMADC in benzene, even under reflux, but will react with a very large excess of the undiluted ester at room temperature over two days to give XXV. Elemental analyses in excellent agreement with a 1:2 adduct of the phosphole with DMADC were obtained. The molecular formula and molecular weight were confirmed by mass spectrometric analysis, which showed the molecular ion peak at m/e 472.

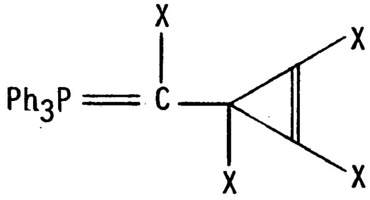
The infrared spectrum showed clearly that the adduct obtained is probably an α-carbonyl stabilized ylide since it showed C=O stretching vibrations at 1750, 1737, 1703, 1670 and 1525 cm^{-1}. This type of pattern is typical (14) of such systems. For example, the tricycloallylidenephosphorane XXV showed strong absorption bands at 1740, 1710, 1660, 1650,and 1520 cm^{-1}. Phosphines and phospholes are known to form a variety of α-carbonyl stabilized ylidic 1:2 adducts with DMADC and the range of known (78,79,80,14,15) structural types is shown below. Early studies of reactions of phosphines with acetylenes have been reviewed elsewhere (30).



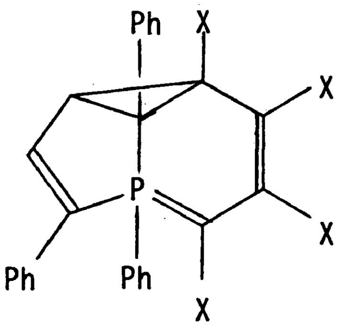
LXXI



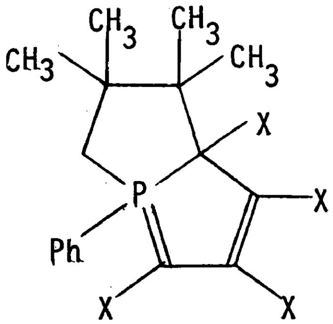
LXXII



LXXIII



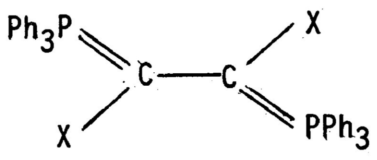
XXV



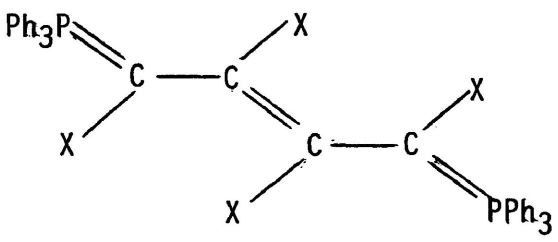
LXXIV

X=CO_2CH_3

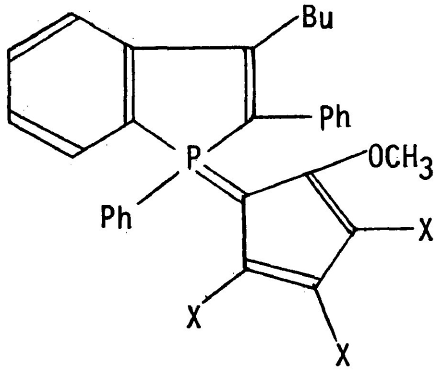
Other ylidic structures derived from this type of reaction are known, but are either not α-carbonyl stabilized, or are not 1:2 adducts. Thus, 2:1 adducts *e.g.* LXXV (81), 1:1 adducts *e.g.* LXXVI (81), or 1:2 adducts less one O atom *e.g.* LXXVII (82) have been obtained. Furthermore it is difficult to visualize other structural types which are both α-carbonyl stabilized ylides and 1:2 adducts. By analogy with the above structures, and, for the moment ignoring reaction pathways, the adduct of 3,4-dimethyl-1-phenylphosphole and two molecules of DMADC should



LXXV



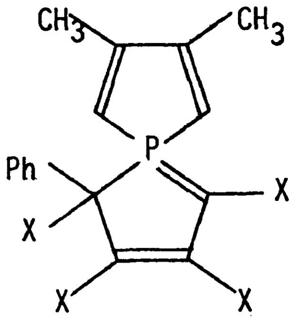
LXXVI



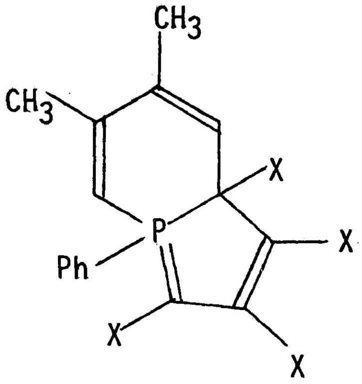
LXXVII

$X = CO_2CH_3$

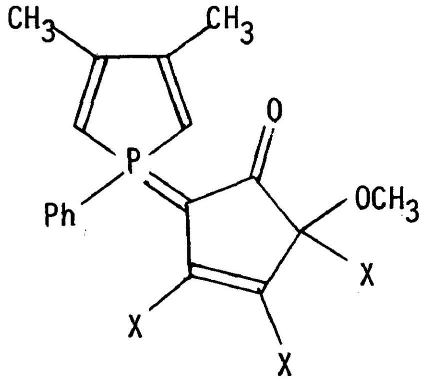
be one of the following:



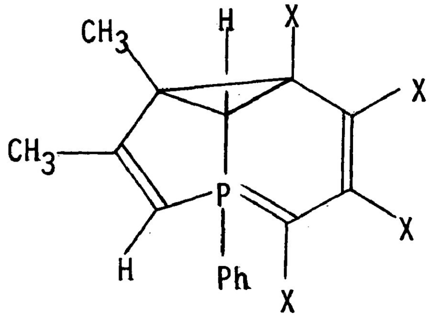
LXXVIII



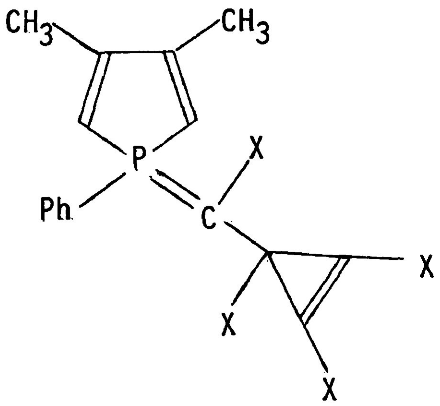
LXXIX



LXXX



LXXXI

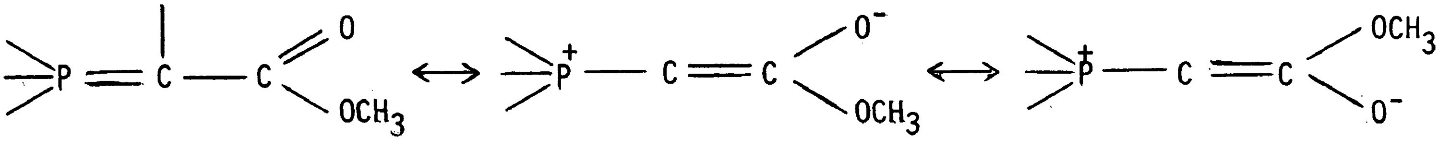


LXXXII

X=CO_2CH_3

Examination of the nmr spectrum in $CDCl_3$ allows us to narrow this choice still further. The spectrum at 32° shows five aromatic protons as a complex multiplet at τ 2.00 - 2.55; two olefinic protons as apparently two overlapping doublets (appearing as a triplet with a broadened central peak) at τ 3.50 - 4.40, with J ~ 20-22 Hz for each doublet (the resolution is such that one doublet of J = 45 Hz could straddle another doublet with J = ca. 4 Hz, but this is much less likely); four ester methoxy signals at τ 6.01, 6.38, 6.45 and 7.01, with the peak at τ 6.45 much shorter and much broader than the other peaks; and two allylic methyl signals as broadened singlets at τ 7.78 and 7.97.

This immediately eliminates structure LXXXI which contains only one olefinic proton. The nmr spectrum also eliminates LXXX since on warming the $CDCl_3$ solution to +50°C, the ester methyl peak at τ 6.45 becomes much sharper and taller while at +10°C it becomes much shorter and broader. The only other change is that at +50°C, the olefinic signals become slightly better resolved to give two doublets centred on τ 3.70 and τ 4.12 with J = 24 Hz (or, less likely, J = 45 Hz straddling J = 4 Hz) in each case. The behavior of the ester methyl peak is typical (14) of α-ester carbonyl stabilized ylides where restricted rotation about the ylidic carbon-carbonyl bond occurs as shown in LXXXIIIa and LXXXIIIb giving two preferred conformers. This results in a broadened methoxy signal (often two signals at low temperatures) which sharpens at higher temperatures when rotation about the C—C bond is rapid.



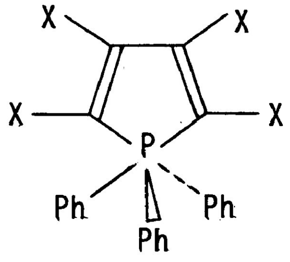
LXXXIIIa

LXXXIIIb

Further confirmation of this comes from the nmr spectrum of the adduct in DMSO-d_6. At room temperature the spectrum shows much the same pattern as in $CDCl_3$ except that the two olefinic protons appear as a doublet of two broadened peaks with J = 21 Hz. This eliminates the less likely alternative couplings mentioned above. As the temperature is raised to 150°C, the four ester methoxy peaks all become very sharp and of equal height, while the olefinic signal becomes two doublets with all peaks of equal area, the lower field pair having J = 21 Hz and the higher field pair having J = 20 Hz. This behavior could not be shown by LXXX where stabilization would be through a ketonic carbonyl group which would not show these conformational effects.

The nmr spectrum in CF_3CO_2H also confirms the ylidic nature of the system since extra indistinct peaks appear in the range τ 4.0 - 5.3 (somewhat less than 1 proton) and major modifications occur in the ester methoxy region. This is typical (14) of α-carbonyl stabilized ylidic systems in acid solution where protonation may occur at the α-carbon atom or the γ-carbon atom in systems such as LXXI (78).

This narrows the choice of structures to one of LXXVIII, LXXIX and LXXXII. Structure LXXXII can almost certainly be eliminated because stable structures of this type are unknown. In the reaction of Ph_3P with DMADC (1:2) in ether at -50°C, the analogous structure LXXIII has been postulated (80) as a transient intermediate which rearranges first to LXXXIV and then to LXXI. Structure LXXIII is not otherwise characterizable. Since there is no obvious extra stabilizing factor in LXXXII, it therefore seems unlikely that LXXXII would be stable as a solid to well above 100°C and stable indefinitely in solution if LXXIII rearranges almost instantaneously at -50°C. Furthermore, the mass spectrum of the adduct shows no fragment peak corresponding to the parent phosphole, 3,4-dimethyl-1-phenylphosphole,

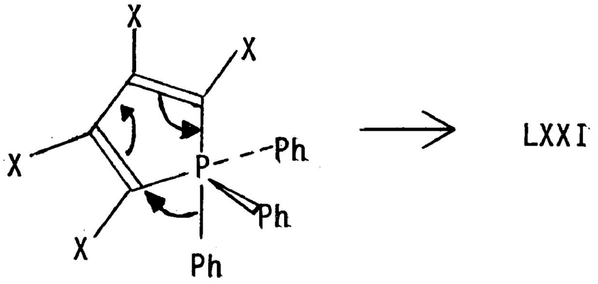


LXXXIV

$X=CO_2CH_3$

as would be expected by simple fission of the ylidic link in LXXXII as had been observed (79,83) for similar triphenylphosphonium ylides.

The structure therefore appears to be LXXVIII or LXXIX which are analogues of the well known (78,15) LXXI and LXXIV respectively. The formation of such structures is thought to go via structures of type LXXIII and then type LXXXIV with rearrangement of a good leaving group from an apical position to the carbon atom adjacent to the P atom thus:



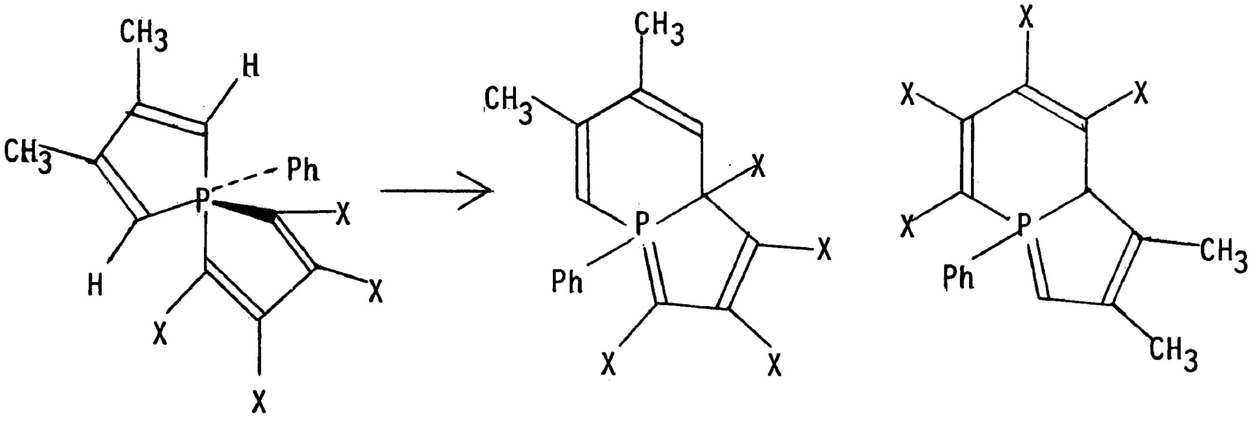
LXXXIV

$X=CO_2CH_3$

It should be noted that the five-membered ring takes up an apical-equatorial arrangement since this gives lower angle strain than a di-equatorial position (15).

If, as seems likely, the adduct under discussion is formed by a similar mechanism the intermediate would be LXXXV in which, for angle strain reasons, both five-membered rings would occupy apical-equatorial arrangements with the phenyl group in an equatorial position.

Migration from an apical position would therefore give LXXIX as shown or, as an alternative, a phosphonium ylide LXXXVI which is not α-carbonyl stabilized and which is not compatible with most of the spectroscopic evidence.



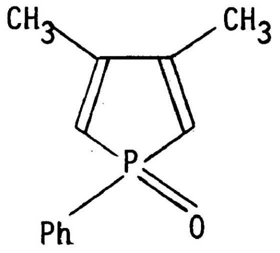
LXXXV LXXIX LXXXVI

$X=CO_2CH_3$

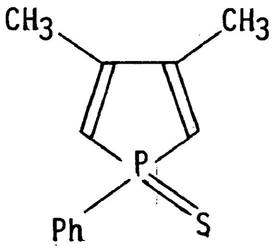
Conversely, formation of LXXVIII would require either migration of the equatorial phenyl group or some pseudorotational process in LXXXV which temporarily places the phenyl group in an energetically unfavourable apical position. Alternatively, the rearrangement may not involve an intermediate such as LXXXV although this seems unlikely in view of other related reactions leading to LXXI, LXXIV and several related structures (78,15).

On mechanistic grounds then, LXXIX is the favoured structure of the adduct, but this is by no means proved. The ultraviolet spectrum is consistent with either LXXVIII or LXXIX since both contain the same chromophoric unit as LXXI. Thus, the uv spectrum in 95% ethanol shows three main regions of absorption with λ_{max} (ϵ) at 223 (19320), 269 (8900) (inflection), 277 and 289 (10,000) (inflections), and 331 (12780)nm. This is very similar to that of LXXI (78) which shows λ_{max} (ϵ) at 228 (28000), 268 (8200) (inflection), 275 (6800) (inflection) and 344 (19000) nm. Furthermore, protonation of LXXI in concentrated HCl causes the long wavelength band at 331 due to the ylidic carbonyl system virtually to disappear. This happens also with the adduct LXXVIII or LXXIX.

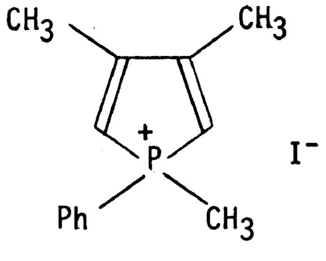
Re-examination of the nmr spectral evidence shows conclusively that the structure is LXXIX as expected. The peak pattern in the methoxy region is very similar to that shown (78) by LXXI and virtually identical to that shown by LXXIV (15) which contains the basic structural unit of the five-membered ylidic ring. The two low field doublets at τ = 3.70 and τ = 4.12 (J = 20 - 24 Hz depending on solvent) suggest that the two olefinic protons are not coupled to one another and are close to, if not adjacent to, the P atom in view of the large coupling constant. This would appear to favour LXXVIII except for two things. First, the olefinic protons in LXXVIII are very similar to those in phosphole oxides, phosphole sulfides and phospholium salts, e.g. LXXXVII, LXIX and LXXXVIII, where the chemical shift of these protons is in the range τ 2.9 - 4.0 (as observed here) but where the coupling constant between the P atom and the ring protons is in the range $^{2}J_{P-H}$ = 31 - 33 Hz. It therefore seems that J_{P-H} in the adduct under discussion is probably too low for the structure LXXVIII. However, at first sight, the fact that the J_{P-H} coupling constants are equal for the two protons would seem to rule out LXXIX, but this is not the case. For example, in the structure LXXXIX which contains a six-membered ring analogous to that in LXXIX, the values of J_{P-H} for the two ring protons are virtually equal (28) at 14 and 15.5 Hz although the value is somewhat lower than that observed for the adduct under discussion (J = 20 - 24 Hz depending on solvent and temperature). Structures similar to LXXXIX show (28) J_{P-H} values as high as 17 Hz.



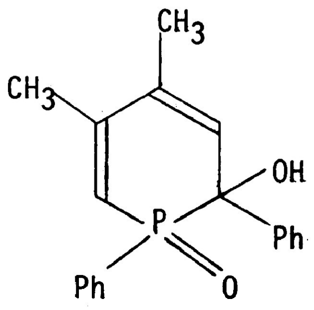
LXXXVII



LXIX



LXXXVIII



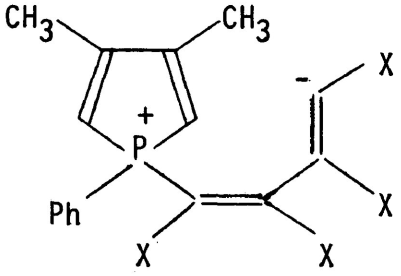
LXXXIX

The proton signals are, however, in almost the same locations, τ 3.76 and 3.87 for LXXXIX as compared to τ 3.74 and 4.12 for the adduct tentatively assigned structure LXXIX. Also, the methyl proton signals of LXXXIX at τ 7.83 and 7.98 coincide almost exactly with those of the adduct (τ 7.78 and 7.97).

The major difference between LXXVIII and LXXIX is that in LXXIX the P-Ph group is intact whereas in LXXVIII this group has been cleaved by migration. Compounds containing the P-Ph group usually reflect this in the mass spectrum with a peak at m/e 108. In the spectrum of the adduct tentatively assigned structure LXXIX, there is a weak peak at m/e 108 (ca. 3% of base peak at m/e 472) and the meaning of this is doubtful. However, there is a much stronger peak at m/e 109 (27% of base peak and much stronger than most peaks in the spectrum which is relatively featureless below m/e 400). This could conceivably be due to the fragment Ph-P-H formed by some rearrangement type of fragmentation. A routine spectrum, of course, cannot decide this issue but a precise mass determination can. Such a precise mass determination shows that this peak is indeed due to an ion of formula C_6H_6P since the calculated mass is 109.0207 and that found is 109.0198. There can therefore be little doubt that the adduct contains the P-Ph unit and that it has structure LXXIX.

3,4-Dimethyl-1-phenylphosphole therefore reacts with DMADC .

much more readily than does 1,2,5-triphenylphosphole (TPP) to give a product of an entirely different structural type. (TPP gives XXV by 1,3-cyclization as discussed in the introduction to this thesis). The reaction is also much faster than with TPP. This difference in behavior may be due to the fact that in the dimethylphosphole, the 3- and 4- positions of the phosphole ring are substituted and are sterically more resistant to attack by the negative centre in the intermediate zwitterion XC.



XC

$X=CO_2CH_3$

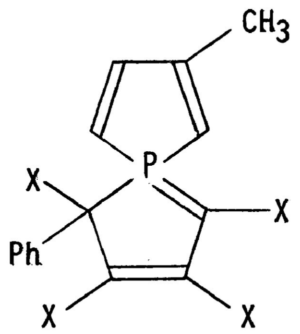
Alternatively, the difference may be due to the differences in the relative energies of the various orbitals in the phosphole system. These energies are very sensitive to the substitution pattern (62,68). Further discussion of this point has been made in the previous section.

One further point regarding the nmr spectrum is that in the spectrum of LXXXIX, the lower field methyl signal (at τ 7.83) had been assigned to the methyl group <u>para</u> to the phosphorus atom and it is possible that a similar assignment can be made for LXXIX.

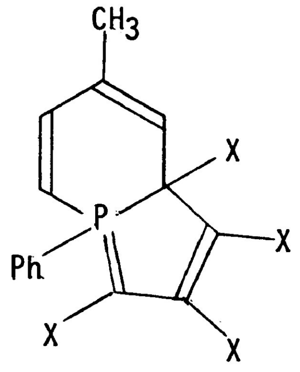
3-Methyl-1-phenylphosphole (LXVII)

Like the 3,4-dimethyl analogue, 3-methyl-1-phenylphosphole reacts readily with DMADC in benzene at room temperature to give a yellow product (in 21.0% yield) which analysed very well for a 1:2 adduct of the phosphole with the ester. As with the dimethyl phosphole, the ir spectrum shows the adduct to be an α-carbonyl stabilized ylide since it shows carbonyl stretching frequencies typical of such systems at 1747, 1704, 1665 and 1530 cm^{-1} as already discussed for the 3,4-dimethyl system. The molecular weight of a 1:2 adduct was confirmed by the mass spectrum which showed the molecular ion peak at m/e 458.

Again, for the reasons outlined earlier, there are several possible structures (XCI - XCVII) for the adduct and, once again, most of these may be eliminated on spectroscopic evidence.

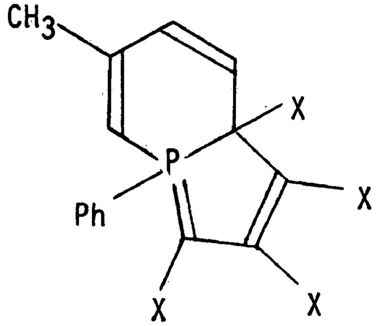


XCI

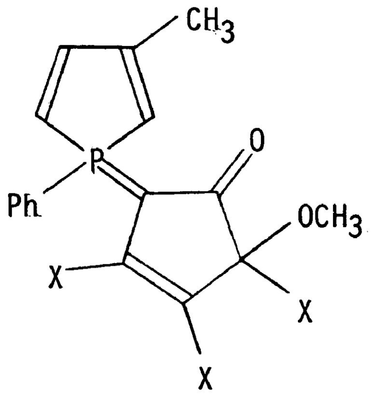


XCII

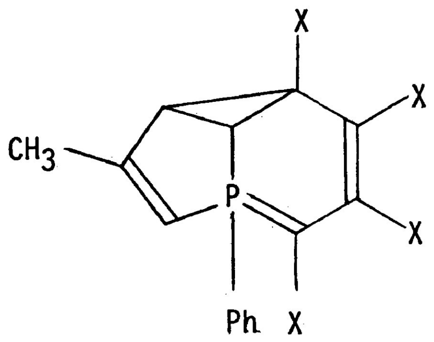
$X=CO_2CH_3$



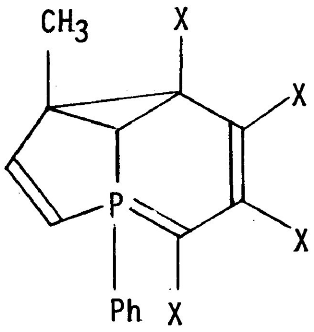
XCIII



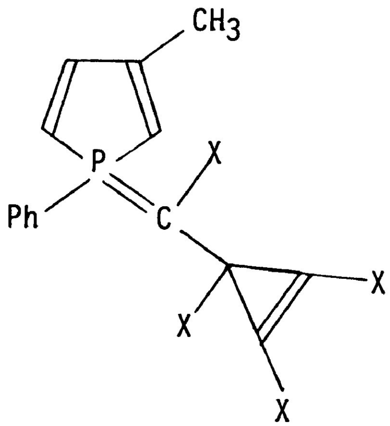
XCIV



XCV



XCVI



XCVII

$X=CO_2CH_3$

The nmr spectrum in $CDCl_3$ at room temperature shows five aromatic protons as a broad based peak at τ 2.43, three olefinic protons as a complex multiplet at τ 3.18 - 4.50, four ester methoxy groups as four singlets at τ 6.08, 6.41, 6.51 and 7.07 and three methyl protons as a singlet at τ 7.87. It should also be noted that the methoxy signal at τ 6.51 is broader and shorter than the others. In several samples, a small amount of some aliphatic impurity appeared in the nmr spectrum as a very complex multiplet of very weak peaks (total integration 1-2 protons) in the range τ 8.10 - 9.50. In general, the spectrum is very similar in appearance to that of LXXIX.

This spectrum immediately eliminates XCV and XCVI since neither contains three olefinic protons. This, at first sight, is a little surprising since the 4- position in the phosphole is not blocked (as is the case with the 3,4-dimethyl analogue) and one might expect the phosphole to react in the same manner as does 1,2,5-triphenylphosphole (which gives XXV, as mentioned earlier) to give XCV.

As before, variable temperature nmr studies eliminate structure XCIV since they clearly show that the adduct is an ester carbonyl stabilized ylide. Thus, cooling the $CDCl_3$ solution causes all of the ester methoxy peaks to broaden with the greatest effect being on the peak at τ 6.51 as with LXXIX. This eliminates structure XCIV since it is not an ester stabilized ylide.

Treatment of the $CDCl_3$ solution with trifluoroacetic acid gives little information except that the ester methoxy group signals are shifted to much lower field (τ 5.98, 6.18, 6.21, 6.66) and these peaks are more nearly of equal area. This again suggests an ylidic structure. The nmr spectrum in pure trifluoroacetic acid is too poorly resolved to give any positive information.

Structure XCVII may also be dismissed. Again, as with the analogous structure LXXXII which was postulated earlier as a possible product from the reaction of 3,4-dimethyl-1-phenylphosphole with the acetylenic ester, there are no special stabilizing factors in structure XCVII which would make it a stable compound and the mass spectrum shows no peak corresponding to the parent phosphole as would be expected by simple fission of the ylidic link in XCVII.

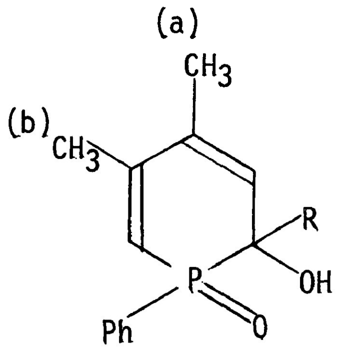
As before, then, we are left, at this stage, with the three possible structures XCI, XCII and XCIII. For the same reason as advanced earlier (probable nature of intermediate and general mechanism for rearrangement of five co-ordinate phosphorus species] the adducts XCII and XCIII would seem more likely structures but XCI certainly cannot be dismissed at this stage.

The uv spectrum in 95% ethanol is consistent with any of the three possible structures showing again three main regions of absorption at λ_{max} (ϵ) 223 (20,150), 262 (9100) (inflection), 269 and 275 (10,000) (inflections) and 332 (12,750) nm. This spectrum is virtually identical to that of LXXIX and strongly suggests that the structure of the adduct under consideration is XCII or XCIII. As before, the spectrum of the adduct in concentrated HCl shows that the band at 331 nm due to the ylidic carbonyl system has disappeared as expected.

Thus, while the evidence favours XCII or XCIII, it is as yet not conclusive. Further evidence comes from the mass spectrum which shows relatively few strong peaks except the molecular ion peak and nearby peaks caused by fragmentation of the ester groups. Again, although there is no strong peak at m/e 108 (there is a weak one which is ca. 7% of the molecular ion peak) corresponding to the Ph-P group, there is as before a strong peak (28% of molecular ion peak) which is probably due to the Ph-P-H group. No precise mass determination was made in this instance but the general similarity of this peak and the whole spectrum to those of LXXIX is striking. If, as it seems highly likely, the Ph-P grouping is intact in the adduct, then structure XCI is eliminated..

It is highly probable then that the adduct formed from 3-methyl-1-phenylphosphole and two molecules of DMADC is one of the ring expanded structures XCII and XCIII. The reaction is therefore virtually identical to that of 3,4-dimethyl-1-phenylphosphole discussed earlier, and completly different from that of 1,2,5-triphenylphosphole which gives structure XXV as the major product. That is to say, neither of the two phospholes under discussion here acts as a vinylphosphonium salt in the later stages of the reaction as does the 1,2,5-triphenylphosphole system. This suggests that 1,2,5-triphenylphosphole is a non-typical phosphole in its reactions as has been shown by Mathey in his ring expansion studies (26,27,28), by Hughes and Srivanavit in their studies of iodomethylphospholium salt hydrolyses (23) and by Tse in his studies of phosphole co-ordination chemistry (84). Since many early studies on phosphole chemistry were with the readily accessible 1,2,5-triphenylphosphole system, the deductions from these studies should be treated with caution.

Having narrowed the structure of the yellow adduct down to a choice between the two closely related systems XCII and XCIII, it might be possible to distinguish between the two isomers from the available data. The nmr spectral data may allow us to do this. Examination of the nmr (28) spectra of ten compounds of type XCVIII which are structurally



XCVIII

very closely related to XCII and XCIII shows that the signal of the methyl group (a) always falls in the range τ 7.90 - 7.83 (with the majority at τ 7.90 - 7.86) while the signal of the methyl group (b) falls in the range τ 8.03 - 7.96 even though the nature of the R group varies widely. The methyl group of the yellow adduct appears at τ 7.87 which puts it in the range of the methyl group (a) and well outside that of (b). A tentative assignment is therefore made that the yellow adduct has the structure XCII with XCIII as a somewhat less likely alternative. Perhaps it should also be noted again that the adduct of 3,4-dimethyl-1-phenylphosphole discussed earlier and assigned structure LXXIX shows the methyl signals in the nmr spectrum (in $CDCl_3$) at τ 7.78 and 7.97 with the lower field signal presumably again due to the methyl group <u>para</u> to the phosphorus atom.

<u>1-Phenylphosphole (LXVI)</u>

As with the other two phospholes described, 1-phenylphosphole reacts readily with DMADC but this time gives three products. Unfortunately, yields were relatively low and purification was extremely difficult and it has proved impossible to establish the structures of these compounds beyond all reasonable doubt. Two of the products were obtained every time the reaction was carried out and they proved to be a yellow 1:2 adduct of the phosphole with the ester and what appears to be a colourless hydrolysis product of this or an isomeric adduct. It should be mentioned here also that hydrolysis products of 1:2 adducts were sometines isolated in small quantities from the phosphole-acetylenic ester reactions described earlier but determination of the structures of these hydrolysis products was not attempted because they were usually obtained in only very small yield and because the hydrolysis of bicyclic and tricyclic ylides in general and of XXV in particular is the subject of a separate investigation (85). The third adduct (colourless) was obtained only once and was again found to be a 1:2 adduct of the phosphole with the ester.

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

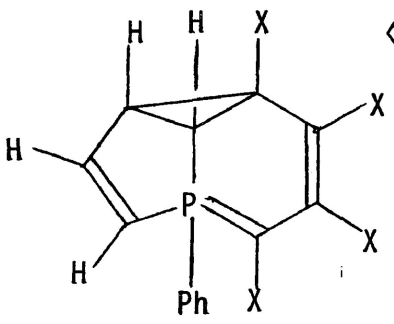
The uv spectrum would appear to rule out structures of type LXXIX and XCII obtained from the other two phospholes discussed here since, although the spectrum is broadly speaking what we would expect from a carbonyl stabilized ylide, it is completely different in general appearance from the spectra of LXXIX and XCII which are virtually identical in appearance, locations of maxima and extinction coefficients. The spectrum of the yellow adduct under discussion shows λ_{max} (ε) at 225 (18,130), 248 (13,630) and 332 (9820) nm. Furthermore, the peak at 248 nm is very broad and has a very long tail off to the long wavelength side. Since the spectra of LXXIX and XCII are so similar, it is difficult to see how the removal of one more methyl group could cause such large changes. It therefore appears that 1- phenylphosphole reacts by a different route than do the 3-methyl and 3,4-dimethyl substituted systems.

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

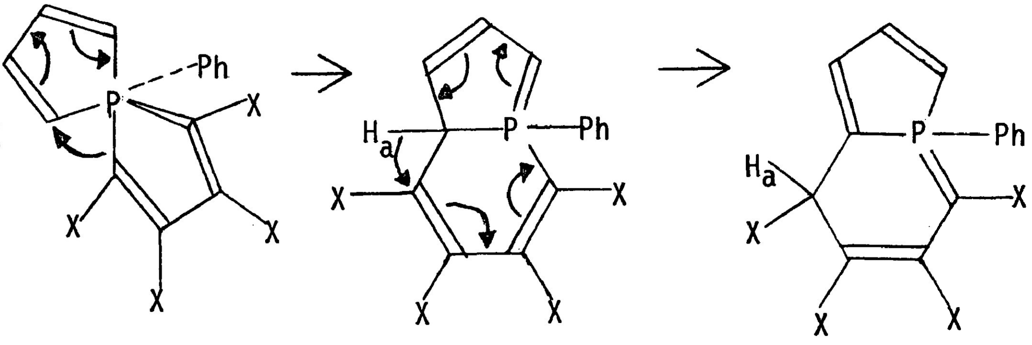
The problem comes with the integration of the signals since slightly different results are obtained with different samples and with slightly different conditions. If one considers the individual signals, the ratios of the areas aromatic:olefinic:ester methyl region: other high field protons is 5:a little over 2:12:a little less than 1. This is one too few protons for a 1:2 adduct. If one takes into consideration the fact that the olefinic and aromatic proton signals overlap, and are difficult to integrate separately, the integrations become aromatic + olefinic:ester methyl region:other high field protons = 8:13: a little less than 1. This is one too many protons for a 1:2 adduct. What _is_ clear is that there are no longer four olefinic protons as would be expected if the four protons on the five-membered ring of the phosphole remained on double bonds- _i.e._ at least one of the ring carbon atoms of the phosphole has been attacked in some way. This would appear to rule out structures related to LXXXII and XCVII.

The only remaining structural type is that of LXXXI and XCV and one might be tempted to assign this type of structure (in this case C) to the yellow ylidic adduct of 1-phenylphosphole with DMADC. However, this structure also does not fit the admittedly poor spectrum very well. If we consider the first of the integrations listed above, there are two problems. First, although there would be two olefinic protons as required, there would be a maximum of one cyclopropyl proton at high field and structure C requires two. Furthermore, this particular proton

$X=CO_2CH_3$



C



CI CII CIII

signal occurs at much too high a field in the spectrum for cyclopropyl protons of this type. Thus, in the spectrum of XXV, the similar cyclopropyl proton occurs in the ester methyl region at τ 6.43. If one assumes that the other cyclopropyl proton signal is hidden under the ester methyl signals, the remaining integrations become very poor and too high. In the opinion of this author, the high field peaks are due to traces of the solvents used in the chromatographic separation (diethyl ether and petroleum ether) and some evidence for this is given by the fact that different samples show different integrations in this range although the signal intensities could never be reduced to zero even by prolonged pumping.

Considering the second set of integrations mentioned above, eight aromatic and olefinic protons are clearly incompatible with structure C as well as all the other structures considered so far. The question therefore arises as to whether there is another possible reaction pathway not yet considered for these reactions. In fact there is one other pathway considered and rejected by Tebby et al. (14) in the determination of the structure of the tricyclic ylide XXV. In this reaction, an intermediate 1:2 adduct of type CI would be formed similar to the structure LXXXV proposed as an intermediate in the formation of LXXIX (a similar intermediate is presumably formed in the reaction leading to XCII). This would rearrange by apical migration of a suitable leaving group as does LXXV but, this time, the migrating group would be a carbon atom bearing an ester group as shown in the sequence CI → CII. However, CII is not a carbonyl stabilized ylide and rearrangement to the lower energy system CIII might occur as shown and as suggested by Tebby in related systems. Tautomeric rearrangements of this type in cyclic ylides are known (16).

The structure CIII would be a carbonyl stabilized ylide and therefore compatible with the ir evidence and the temperature dependence of the nmr spectrum. Furthermore, the uv spectrum would probably differ somewhat in general appearance from those of LXXIX, XCII and also of XXV (14) as is observed. Finally, the nmr spectrum would show eight aromatic and olefinic protons as is apparently observed. Of course, the proton H_a in structure CIII still has to be assigned in the nmr spectrum of the adduct. This proton would be both allylic and adjacent to an electron withdrawing ester group. Protons of this type occur (16) generally in the ester group region of the spectrum and we would expect the signal to be masked by the methoxy signals in the spectrum. This would give 13 protons in this region as is observed if the second set of integrations mentioned earlier is correct and it should be noted again that the signals in this region of the spectrum are more complex than in the spectra of LXXIX and XCII.

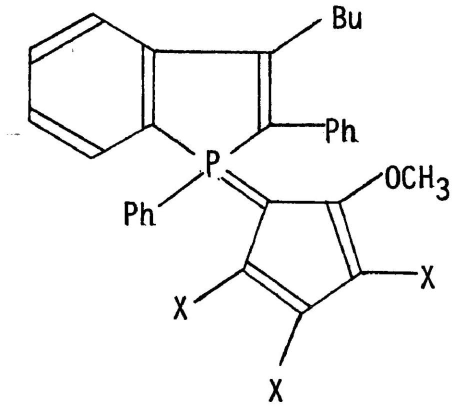
The weight of the evidence therefore favours CIII as the structure of the yellow 1:2 adduct from 1-phenylphosphole and DMADC although the less than satisfactory nmr integrations make this assignment only tentative at this stage. Numerous attempts were make to obtain better nmr stectra but the difficulties in obtaining really pure samples in reasonable quantity rendered these attempts unsuccessful. Clearly this pathway is not followed by the other two phospholes in reactions with the ester since the nmr spectra show no ring-carbon attack has occurred.

Considering finally the colourless 1:2 adduct of the phosphole with the ester obtained on only one occasion, a more definite, though not conclusive, structural assignment may be made. Only 90 mg. of the compound was obtained and the structure assignment therefore rests mainly on a very detailed spectroscopic analysis together with an excellent C,H analysis. No phosphorus analysis could be obtained since all of the sample was used up in spectroscopic studies. However, the mass spectrum did confirm the molecular weight as 444.

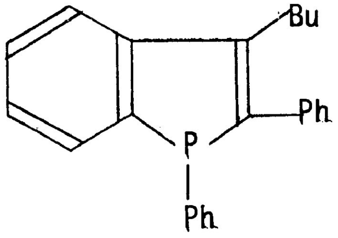
The ir spectrum shows quite clearly that unlike the yellow 1:2 adduct, the colourless 1:2 adduct is not a carbonyl stabilized ylide since no carbonyl peak occurs in the 1530 cm^{-1} region and all carbonyl absorption occurs as a broad band centred on 1740 cm^{-1} with maxima at 1760, 1736 and 1725 cm^{-1}.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

The most information is given by nmr spectra of the adduct under various conditions. The room temperature nmr spectrum is very well defined and shows 5 aromatic protons as a complex multiplet between τ 2.20 and 2.76, 3 olefinic protons as a series of at least 12 sharp peaks of various areas in the range τ 2.84 - 4.00, 1 tertiary or olefinic proton as a doublet of doublets between τ 5.35 and 5.60 with the two coupling constants having values of J = 8Hz and J = 2Hz respectively, and three very sharp methoxy signals at τ 6.17 (3 protons), 6.24 (6 protons) and 7.06 (3 protons). There is no significant change in the methoxy region over the temperature range -40°C to +32°C and this confirms that the compound is not an ester carbonyl stabilized ylide.

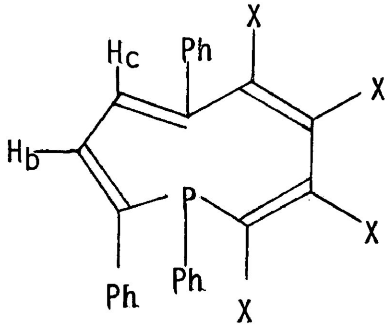
This information so far suggests that the product is either an ylide which is not α-carbonyl stabilized or is not an ylide at all. Products of either type from reactions of tertiary phosphines with DMADC are rare and in fact, only one stable product of each type is known. Thus, the ylide LXXVII is formed from 3-butyl-1,2-diphenylphosphindole(CIV) and two molecules of DMADC (82) while the nine-membered ring CV is formed by thermal rearrangement (boiling chloroform) of the tricyclic ylide XXV (14,29). Clearly the adduct under consideration cannot be an adduct of type LXXVII which is a 1:2 adduct less one oxygen atom. Furthermore, the mass spectrum doesn't show a peak corresponding to the phosphole as occurs with LXXVII which shows a phosphindole peak. The ylide LXXVII is stabilized by the cyclopentadienyl



LXXVII



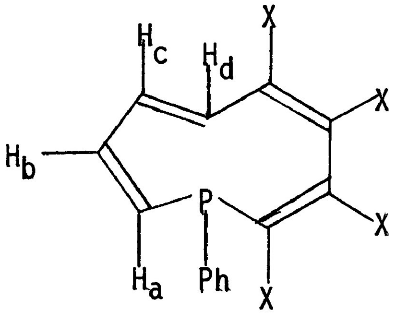
CIV



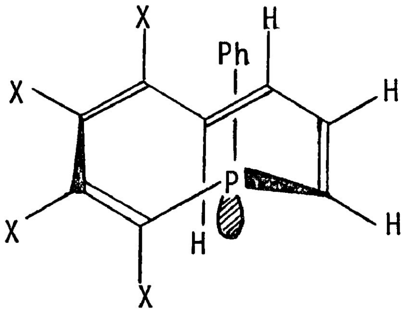
CV

grouping. Also, an ylide not stabilized by an electron withdrawing group is out of the question since such systems are well known to be extremely air and water sensitive.

The possibility therefore remains that the structure of the adduct is CVI which would be analogous to CV and would presumably be formed in a similar manner. Analysis of the nmr spectrum shows that this is almost certainly the case.



CVI



CVII

$X=CO_2CH_3$

Ideally, one could determine whether the phosphorus atom of the adduct is a tertiary phosphine type by ^{31}P nmr spectrometry but such facilities were not available to us. However, the main aromatic proton ^{1}H resonance occurs at τ 2.62 which is at markedly higher field than is observed in the cyclic ylidic adducts LXXIX (τ 2.41) and XCII (τ 2.36) already discussed. This indicates that the P atom is less positively charged and this would be consistent with a tertiary phosphine structure rather than an ylide. The limited quantities available did not allow chemical conversion to the phosphine oxide as can be done with CV (14,29). The P-phenyl grouping is clearly intact since the mass spectrum shows a strong peak at m/e 109 as do the other systems discussed in this chapter. There is also a reasonably strong peak at m/e 108.

Comparison of the nmr spectra of the adduct under discussion here and the adduct CV show marked similarities between the two spectra. Thus, the four OMe proton signals in the spectrum of CV occur at τ 6.16, 6.23, 6.30 and 7.09 (29) while those in the colourless 1:2 adduct occur at τ 6.17, 6.24 (two OMe groups) and τ 7.06 - i.e. the OMe signals in the two spectra are in virtually identical locations. Next, the proton marked as H_c in structure CV occurs (because of shielding due to conformational effects in the nine-membered ring discussed extensively elsewhere (14)) as a doublet at τ 5.12. This proton is therefore coupled with H_b, which occurs as a triplet with $J_{H-H} = J_{P-H} = 9Hz$ at τ 3.62, but not with the phosphorus. If the 1:2 adduct has structure CVI, conformational and shielding effects should be much the same as in CV and the protons H_c and H_b should appear in much the same locations although the signals would be more complex because of the additional protons present.

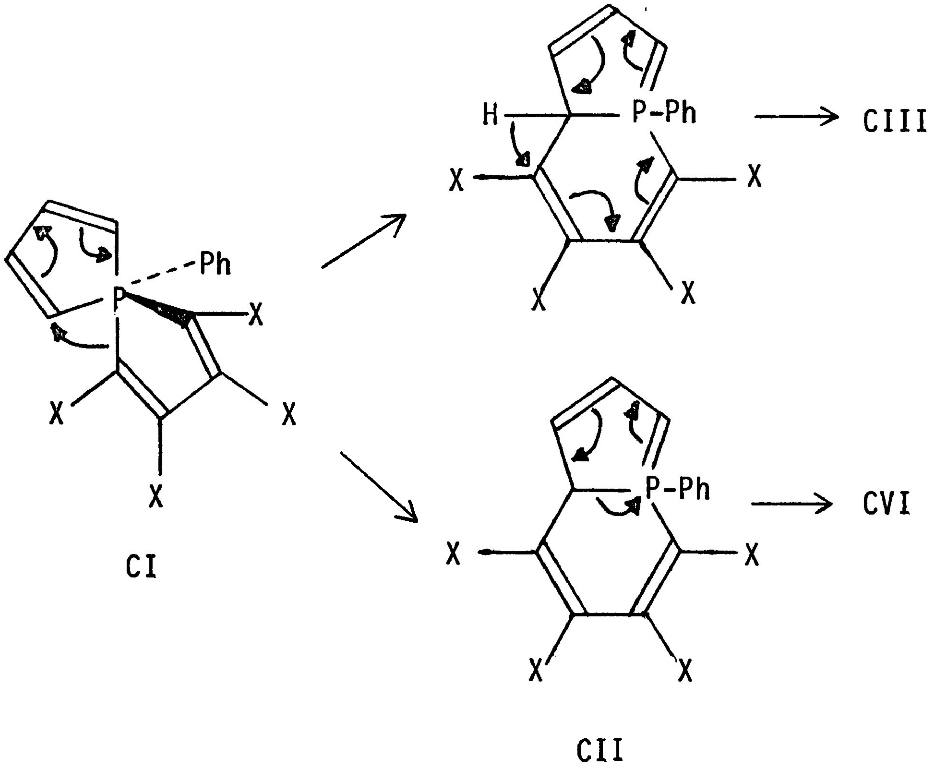
Examination of the olefinic region of the spectrum of the 1:2 adduct shows the presence of a high field, probably olefinic proton as a doublet of doublets centred on τ 5.48 with the coupling constants of value 8 Hz and 2 Hz respectively. This proton therefore agrees well in both location and one coupling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

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

The evidence is therefore strong that the colourless 1:2 adduct has structure CVI and that the structure probably has the same conformational arrangement (as discussed in ref. 14) as the analogous structure CV - i.e. probably as shown in CVII. Another point which suggests that the structures of CV and the adduct are related is the presence in the ir spectra of a weak conjugated C=C bond absorption at 1642 cm^{-1} in the spectrum of CV and at 1625 cm^{-1} in the spectrum of the colourless adduct.

As mentioned earlier, it proved impossible to prepare this compound again for final and conclusive determination of the structure but there is one further observation of possible significance. Structure CV is derived from the tricyclic ylide structure XXV by thermal rearrangement (14,29). Not surprisingly, both CV and XXV have identical mass spectra (14). However, the mass spectra of the yellow ylidic 1:2 adduct tentatively assigned structure CIII and the colourless 1:2 non-ylidic adduct of probable structure CVI are considerably different and this would be a further argument against the alternative structure C for the yellow adduct though not necessarily an argument in favour of CIII.

On a concluding note, one might think that the phosphacyclononatetraene (phosphonin) CVI would be formed from C (just as CV is derived from XXV) even though C could not be isolated. While it is probable that this is the case, it is also possible that both CIII and CVI are derived from CI and the hypothetical non-stabilized ylide CII as follows:



X = CO_2CH_3

Further work on this problem would be worthwhile.

Conclusions

While not all structures discussed in this subsection of the thesis concerning phosphole - acetylenic ester reactions have been determined beyond all possible doubt, certain general observations may be made.

First, it is clear that simple phospholes are reasonably good nucleophiles in reactions with DMADC and, in the main, the products are ester carbonyl stabilized bicyclic ylides. This is relatively unexpected behavior in view of the extremely low basicity determined (3) for 1-methylphosphole, the poor donor (35) and nucleophilic (29) character of 1,2,5-triphenylphosphole and the negligible donor character (3,43) of 1-benzylphosphole discussed in Chapter I. It would appear that simple 1-alkylphospholes (*e.g.* 1-methylphosphole) and very heavily substituted phospholes (*e.g.* 1,2,5-triphenylphosphole) are atypical of phospholes in general as was suggested by Mathey's hydrolytic ring expansions of simple phospholes with benzoyl chloride (26-28) mentioned earlier. This probable atypicality of heavily substituted phospholes has been noted by others in terms of metal complex formation (38).

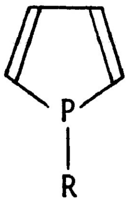
Second, the results obtained here are in agreement with those of similar very recent studies regarding inorganic donor character of simple phospholes towards nickel(II) chloride and other transition metal halides (86) which again show the phospholes to be quite good donors behaving broadly like tertiary phosphines - i.e. although simple phospholes might well be aromatic species in the pyramidal ground state, the degree of aromaticity would appear to be relatively low if phospholes behave like tertiary phosphines. In this connection, it is interesting that although a very recent paper by Epiotis and Cherry (87), published since Chapter I was prepared, shows fairly conclusively that phospholes are aromatic (in the sense of a low ground state enthalpy arising from a Hückel type lone-pair delocalization), the degree of aromatic character was not estimated. These results, like those of Holah *et al*. (86) with Ni(II) chloride - simple phosphole systems mentioned above, indicate only a small degree of lone-pair delocalization in the pyramidal ground state.

Next, although the phospholes 3,4-dimethyl-1-phenylphosphole, 3-methyl-1-phenylphosphole and 1-phenylphosphole react like 1,2,5-triphenylphosphole to give cyclic ylides, the type of ylide obtained is entirely different. Thus, whereas with 1,2,5-triphenylphosphole dimethyl acetylenedicarboxylate cyclized onto the phosphorus atom and the β ring carbon atom to give XXV, this does not occur with the simple phospholes which ring expand *via* a 1,2-shift in a trigonal bipyramidal intermediate such as LXXXV to give structures like LXXIX, XCII and possibly CIII. Only 1-phenylphosphole shows any evidence of cyclization in the manner of 1,2,5-triphenylphosphole (to give CVI) and this is clearly a relatively minor pathway. Again, heavily substituted phospholes appear to show atypical behaviour.

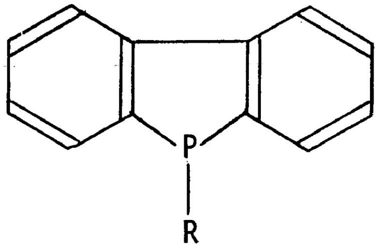
Finally, some of these reactions may be synthetically useful since bicyclic systems of phosphorus and carbon are rare, particularly those with phosphorus at a ring junction. Another synthetic application of simple phospholes is described in the next section.

The Synthesis of Phosphindoles from Phosphole Derivatives

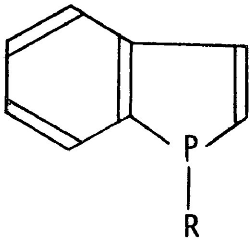
As mentioned briefly in the introduction to this chapter, the simple phospholes under study were considered also as possible starting materials in a synthetic approach to phosphindoles. The reason for this is that although phospholes (CVIII) and dibenzophospholes (CIX) have been studied extensively over the past 15 years (1,2,35,72), the related phosphindole (benzo[b] phosphole) system (LXIII) has received very little attention. This does not reflect a lack of interest in this system but, rather, it is a consequence of the fact that simple derivatives of phosphindole are very difficult to synthesize. Thus, there are only six reports in the literature regarding the chemistry of phosphindoles.



CVIII

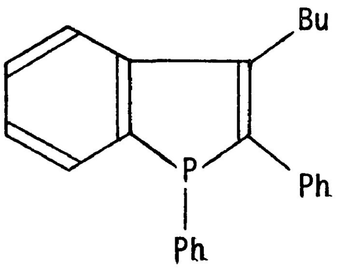


CIX

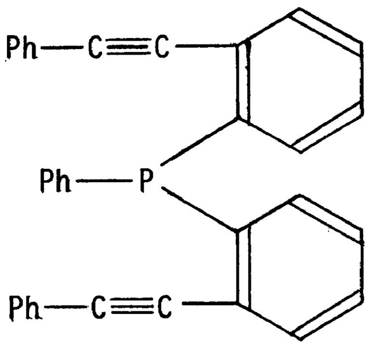


LXIII

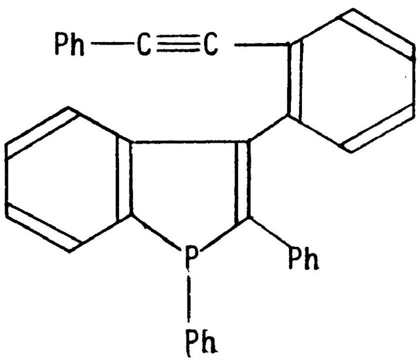
The first of these (88) concerned the synthesis of the heavily substituted (and therefore non-typical) phosphindole CX by a route which, unfortunately, is not general for the phosphindole system. A route to the much simpler phosphindole LXIII (R=Ph) and the corresponding oxide was later developed by Chan and Wong (89) but the method, though inge-



CX

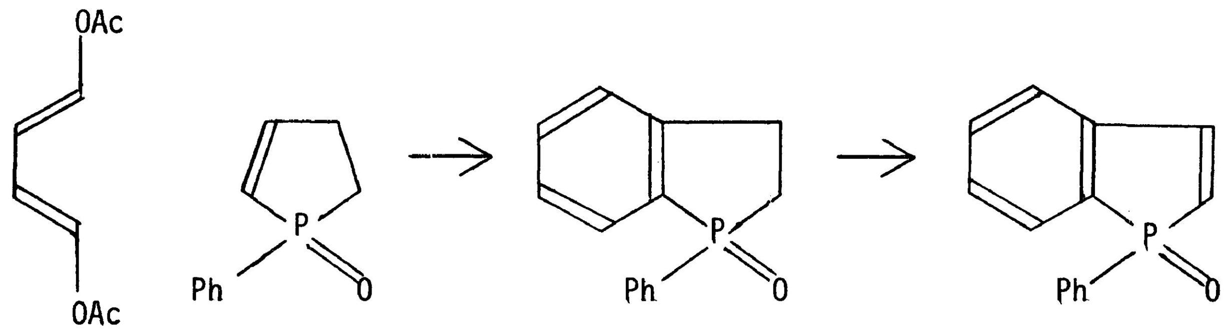


CXI



CXII

nious, has several steps. In this synthesis, 1-phenyl-2-phospholene 1-oxide (CXIV) is treated with *trans*-*trans*-1,4-diacetoxybutadiene (CXIII) to give the dihydrophosphindole (dihydrobenzo[*b*]phosphole) oxide CXV, which must then be brominated and dehydrobrominated to yield 1-phenylphosphindole 1-oxide (1-phenylbenzo[*b*]phosphole 1-oxide) CXVI which may be reduced with trichlorosilane to give the phosphindole. This synthesis, although potentially general to some extent, involves expensive and not easily accessible reagents and apparently yields only relatively small quantities of end product. The only other reported synthesis (90) of the phosphindole system is the rather unusual photocyclization of CXI to give the heavily substituted system CXII.

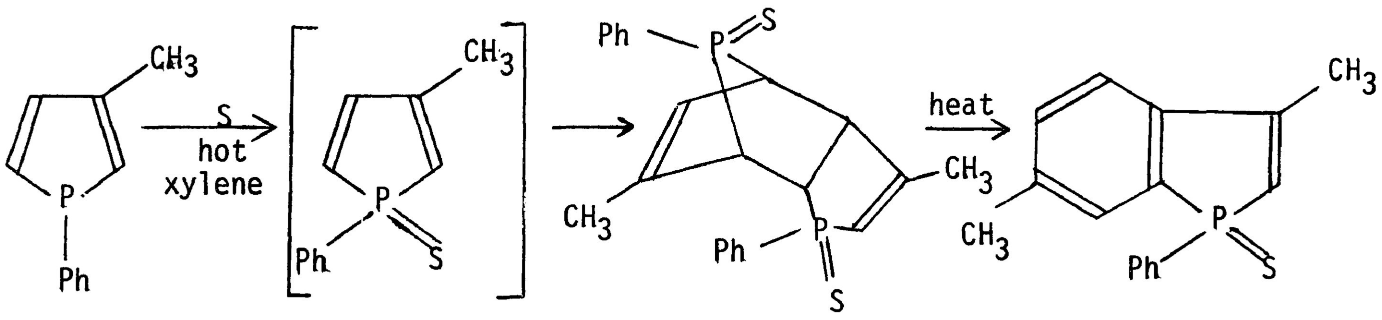


CXIII CXIV CXV CXVI

The remaining three published reports concern the chemistry of the phosphindole CX. Thus, the first of these (56), concerned primarily with pyramidal inversion studies in compounds of types CVIII, CIX and LXIII, briefly reported ligand exchange at the phosphorus atom of CX using lithium cleavage of the P-Ph group. The other two reports (82,91) discussed reactions at the phosphorus atom of CX with particular reference to reactions with dimethyl acetylenedicarboxylate (82) and ring expansion reactions (91). Crystallographic studies of CXII and certain of its quaternary salts have also been made (92).

Since it is desirable to extend studies of the inorganic donor character (35) and organic nucleophilic character (1,72 and this thesis) of phospholes CVIII and dibenzophospholes CIX to phosphindoles LXIII, the development of a more convenient, general and higher yield route to simple phosphindole derivatives has become necessary. With regard to this problem, synthesis of the dimethylphosphindole sulfide CXIX has now been attempted and achieved.

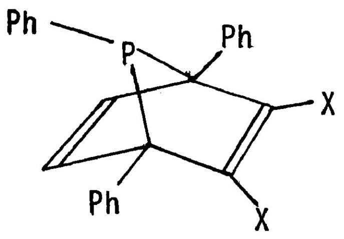
The synthetic route, outlined in the sequence LXVII→CXVII→CXVIII→CXIX, was chosen for several reasons, First, simple phospholes



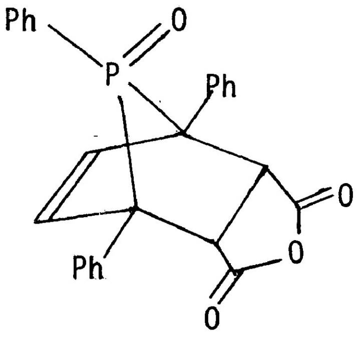
LXVII CXVII CXVIII CXIX

are now readily accessible (5,6,7,8) and would be satisfactory starting materials for such a synthesis. Second, it is well known (6,7,8,52,93,94) that simple phosphole oxides and sulfides of type CXVII spontaneously dimerize to give structures of type CXVIII in high yield. In this connection, it should be noted that an X-ray crystal structure determination of the dimer of 1-ethoxyphosphole oxide has confirmed (95) the structural type. Third, it is well known (20,36, 37,96) that Diels-Alder adducts (such as CXX and CXXI) of both phospholes (where drastic conditions are required for the Diels-Alder reaction) and phosphole oxides with dienophiles such as dimethyl acetylenedicarboxylate (20,36), maleic anhydride (20,36), acrylonitrile (20,37) and benzyne (96) readily and sometimes spontaneously lose the bridging phosphorus-containing group on heating. The product is a six-membered carbocyclic, usually aromatic, system such as CXXII.

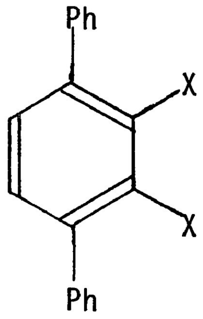
It therefore seemed likely that reduced-pressure pyrolysis of phosphole oxide or sulfide dimers of type CXVIII should yield dihydrophosphindole derivatives of type CXXIII or, more likely in view of the severity of the conditions required for pyrolysis, phosphindole sulfides such as CXIX. It should, however, be noted in passing that in earlier photochemical studies (97) of the similar dimer of 1-phenylphosphole oxide undertaken as an extension of studies of phopholene oxide pericyclic reactions, although the phosphorus containing bridge was eliminated and could be trapped as a methanol adduct, no trace



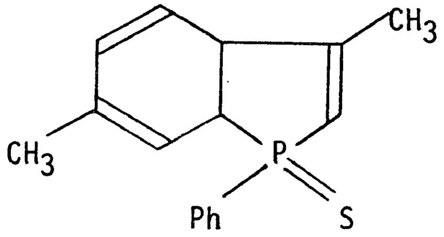
CXX



CXXI



CXXII



CXXIII

X=CO_2CH_3

of the expected dihydrophosphindole was found. Sensitized irradiation led (97) to the formation of a complex cage structure. No such problems were encountered during the pyrolysis study and reduced pressure (1-2 Torr) distillation of the known phosphole sulfide dimer CXVIII (prepared by the method of Mathey (7) and chosen because, for trial experiments, this compound seemed the most convenient to prepare) gave the crude phosphindole sulfide CXIX. Purification was effected by chromatography on neutral aluminum using carbon tetrachloride as eluent to give the phosphindole CXIX as a colourless glass in 65% yield. Microanalytical data were in good agreement with the proposed structure and confirmation of the proposed structure was provided by spectroscopic data.

Thus, the mass spectrum showed the molecular weight to be 270 as expected and showed at $(M+2)^+$ the isotopic peak characteristic (98) of compounds containing one sulfur atom. The molecular formula was confirmed by a precise mass determination for the molecular ion peak which showed a mass of m/e 270.0629 ($C_{16}H_{15}PS$ requires 270.0632). At very high gain, the mass spectrum showed what appeared to be small traces of an impurity of molecular weight 284. The fragmentation pattern is consistent with a phosphindole type system. A small peak occurs at m/e 255 (M-15) corresponding to the loss of one methyl group. The characteristic isotopic peak of sulfur containing compounds is also present at m/e 257. The next significant peak, occurring at m/e 238, may be attributed to loss of sulfur from the molecular ion. This is confirmed by the lack of the sulfur isotope peak which would appear at m/e 240. Peaks corresponding to the loss of sulfur and one methyl group and sulfur and both methyl groups are present at m/e 223 and m/e 208. The latter peak is of very high intensity. A significant peak at m/e 193 is most likely due to loss from the molecular ion of the phenyl group and sulfur atom from the phosphorus atom. Fragmentation of the five-membered ring by further loss of the methyl group and the carbon atom to which it is attached would then give an ion of mass 133. A fairly strong peak is indeed observed at this mass. A slightly stronger peak also occurs at m/e 140. This may be due to a different fragmentation pattern in which the phenyl-phosphorus-sulfur fragment is extruded. Such an ion would have a mass of 140. The remaining fragment of mass 130 would not be expected to show a strong peak since the Ph-P=S fragment would be expected to be the charge carrying fragment and, in fact, only a small peak is observed at m/e 130. A stronger peak at m/e 115 may be attributed to loss of a methyl group from the mass 130 fragment. The last fragment of significant size, at m/e 91, is most likely due to a radical of the six-membered aromatic ring which bears the methyl group.

The ultraviolet spectrum of CXIX in ethanol shows λ_{max} (ε) 231 (24615), 300 (1480) and 310 (1330) nm, a pattern similar to that of 1-phenylphosphindole (89)[233 (24600), 260 (11300), 300 (1480) and

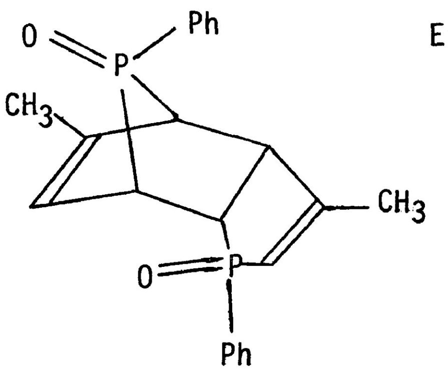
315 (3670) nm]. Any peak in the 250 - 260 nm region was obscured by the sharp increase in absorption due to the strong peak at 231 nm.

The infrared spectrum (Nujol) of the phosphindole CXIX is consistent with that expected of a benzo-heteroaromatic, the only peaks in the observable region being due to C-H stretching and bending vibrations of the methyl group and aromatic C-C and C-H groups. The P=S absorption would be expected to absorb below the measureable range of the infrared spectrum using NaCl plates.

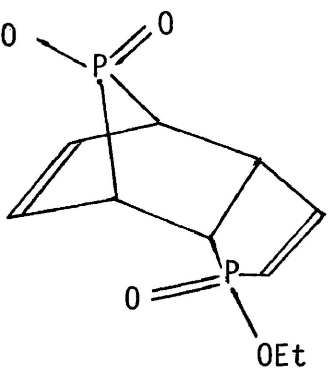
The nmr spectrum in deuteriochloroform also supports the structure assigned since it shows eight aromatic protons as a broad, complex multiplet at τ 1.90 - 3.10, one olefinic proton as a doublet (J = 29 Hz) centred on τ 3.86 and with each peak of the doublet broadened and apparently slightly split (*ca*. 1 Hz), three allylic or benzylic methyl protons as a sharp singlet at τ 7.57 and three allylic or benzylic methyl protons as a very closely spaced and slightly distorted triplet (J = 1.5 Hz) centred on τ 7.67. Spectra of different samples also showed traces of impurity peaks as a very complex multiplet in the range τ 7.6 - 9.0 with total integrations varying between one and two protons depending upon the sample. Repeated chromatographic treatments failed to remove this material completely but a substantial reduction in the already small amount of this impurity could be achieved.

The nmr spectrum is, therefore, in excellent agreement with the expected structure. For example, $^{2}J_{P-H}$ for the phosphorus-olefinic coupling in the five-membered ring measured as 29 Hz agrees very well with similar couplings obtained (7) in 3,4-disubstituted phosphole sulfides and phospholium salts where values of 30 - 32 Hz have been obtained. Also, the location of the olefinic proton signal of CXIX in the nmr spectrum at τ 3.86 is almost identical with the locations (τ 3.90 - 4.00) of the signals of similar protons in the spectra of 3,4-disubstituted phosphole sulfides (7). Furthermore, the fact that one of the methyl group signals appears as a distorted triplet (J = 1.5 Hz) suggests that the signal is due to the methyl group on the five-membered ring of CXIX and that $^{4}J_{P-CH_3}$ and $^{4}J_{HC=C-CH_3}$ are approximately equal in magnitude. These couplings are entirely consistent with the proposed structure CXIX since such couplings of very similar magnitude (1 - 2 Hz) have been observed for the structurally similar 3,4-dimethylphosphole sulfides (7). It should again be noted that the two principal peaks of the olefinic proton signal in the nmr spectrum of the compound assigned structure CXIX are, as expected from the above argument, broadened and slightly split by about 1 Hz.

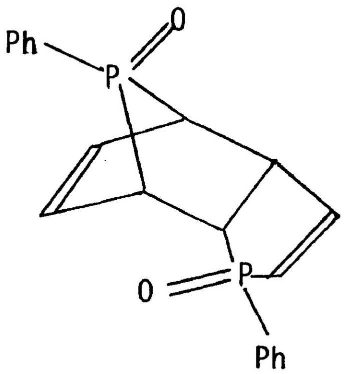
There can, therefore, be little doubt that the product obtained by the pyrolysis of the phosphole sulfide dimer CXVIII is the phosphindole sulfide CXIX. Clearly, this method is potentially general for the synthesis of a variety of phosphindole derivatives since other such systems related to CXVIII (*e.g.* CXXIV, CXXV and CXXVI) are readily prepared (8,52,94) and should undergo thermal fragmentation similar to that undergone by CXVIII. Furthermore, dimeric phospholium salts are also known (99) and these might also react similarly.



CXXIV

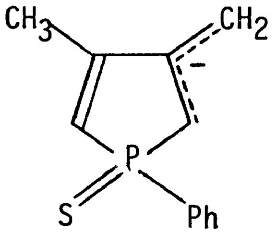


CXXV



CXXVI

Since ligand exchange at the phosphorus atom of the phosphindole CX has already been performed (56), it seems likely that, after reductions of the phosphindole sulfide CXIX to the corresponding phosphindole, (not yet attempted by this author but currently under study by others in the same research group) other ligands may be placed on the phosphorus atom by this method. In addition, it may be possible to introduce other functional groups to the 2- and 3- positions of the phosphindole system. Such reactions have been performed (10,11) on 3,4-dimethyl-1-phenylphosphole sulfide, from which the anion IX can be generated. Should this type of reaction prove possible with 3,6-dimethyl-1-phenylphosphindole it would allow changes in substitution pattern and provide an opportunity to study a variety of substituted phosphindoles. Together with ligand exchange at the phosphorus atom, this would provide a route to a wide variety of phosphindoles providing an opportunity for more extensive investigation of the chemical properties of this system.



IX

Conclusions and Suggestions for Further Work

At this point in a thesis of this type it is usually customary to make conclusions and suggestions for further work. However, since this thesis followed three parallel lines of study, these points have been discussed at the end of each subsection in the results and discussion section.

EXPERIMENTAL

Introduction

The experimental work described in this thesis was carried out by the author during the period September 1974 - September 1976. The results and discussion and much of the interpretation were completed on a part time basis during the period October 1976 - September 1977.

General Procedures

The ir spectra were recorded on a Beckman IR 12 spectrophotometer for samples mulled in Nujol using sodium chloride demountable cells.

The uv spectra were obtained using a Unicam SP 800A recording spectrophotometer, using 1 cm. fused silica cells. Ethanol (95%) or concentrated hydrochloric acid was used as solvent. The calibration of the spectrophotometer was checked against a holmium filter.

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

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

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

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

Column chromatography was carried out using neutral alumina as the adsorbent.

Benzene for reactions was dried by distillation from calcium hydride.

Nitrogen (certified pure) was dried by passage through concentrated sulfuric acid followed by passage through sodium hydroxide pellets.

Dielectric Studies

The dielectric measurements were carried out on a General Radio capacitance bridge, type 1615-A. The useful frequency range of this instrument is from 10^2 to 10^5 Hz. The three terminal cell consists of a guarded electrode 1.45 inches in diameter, a lower electrode, and a guard ring 2 inches in diameter. The electrodes are mounted on two square blocks of 5 inch thick boron nitride. Four brass rods 0.5 inches in diameter pass through the four corners of the blocks, holding them together. Springs on each of the four rods press the electrodes against the 0.07 inch thick sample disc. The entire cell is mounted in an air-tight aluminum container with walls 0.5 inches thick. The walls of the aluminum container are surrounded by a heating coil. The top of the container is flat and another aluminum container may be filled with liquid nitrogen and placed on top for cooling purposes. Varying thicknesses of paper could be placed between the two containers to control the rate of cooling.

By connecting the heater to the output of an RIIC temperature controller, the temperature could be controlled to within 0.1° K. The cell is flushed with dry nitrogen passed through the cell through very thin antenna tubing to avoid undue thermal conduction. The electrical connections were made in a similar manner. The entire cell assembly was enclosed within a styrofoam container with a wall 1.5 inches thick.

The sample placed within the cell is contained in a polystyrene matrix and is in the shape of a thin disc. The sample disc for these experiments was prepared by dissolving about 4 grams of polystyrene pellets, average molecular weight 230,000, in about 15 ml. of <u>trans</u>-1,2-dichloroethylene (b.p. 320.7° K). Solute (polar compound) equivalent to about five per cent of the weight of polystyrene was added. The mixture was thoroughly stirred and then evaporated in a vacuum oven at 358° K, until a constant weight was achieved. A polystyrene matrix prepared in this way usually contains less than one per cent solvent. The polystyrene matrix was pressed at 388° K between 2 inch diameter tungsten carbide blocks in a die to give a perfectly flat matrix of about 0.07 inch thickness. The disc was then stored for one day in a dessicator to reduce mechanical strain. The polar solute concentration in a polystyrene disc may be calculated in moles per litre (C) as follows:

$$C = \frac{\text{wt. of solute used}}{\text{mol. wt. of solute}} \times \frac{\text{wt. of disc}}{\text{wt. of polystyrene + solute used}} \times \frac{1}{\text{vol. of disc}}$$

The cell assemblies were calibrated by using a standard quartz specimen made by Rutherford Research Products Co., N.J. Polystyrene discs prepared as described previously were measured to determine the correction factors to be applied to the dielectric losses of polar solutes. These dielectric loss values for polystyrene are considerably smaller than those due to the polar solute(100).

Syntheses

Starting Materials

Simple phospholes were prepared by the method described by Mathey (6,7,8). Briefly, equimolar amounts of phenyldibromophosphine and the appropriate butadiene derivative were mixed together and stored in the body of a refrigerator for several days, the length of time depending upon the diene used. When reaction was complete, heating the adduct under reflux with two moles of DBU in a benzene-methylene chloride mixture effected dehydrobromination giving the crude phosphole in solution. This solution was hydrolysed with water, taken down to low bulk and the phosphole extracted with n-hexane. The solvent was distilled off at atmospheric pressure and the pure phosphole distilled under reduced pressure. Further experiments were carried out as soon as possible after the distillation to avoid deterioration of the phosphole. The phospholes LXIV and LXV were also made by literature (20) methods.

Reaction of 3,4-Dimethyl-1-phenylphosphole (LXVIII) with Dimethyl Acetylenedicarboxylate

With ice-bath cooling and vigorous stirring under nitrogen, a solution of dimethyl acetylenedicarboxylate (3.28 g., 0.0321 moles) in dry benzene (75 ml.) was treated dropwise with a solution of 3,4-dimethyl-

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

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

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

With ice-bath cooling and vigorous stirring under nitrogen, a solution of dimethyl acetylenedicarboxylate (2.90 g., 0.0205 moles) in dry benzene (50 ml.) was treated dropwise with a solution of 3-methyl-1-phenylphosphole (1.73 g., 0.010 moles) in dry benzene (50 ml.). Reaction was immediate and the resulting dark brown mixture was heated under reflux for 30 minutes under a slow stream of nitrogen. The concentrated mixture was chromatographed on neutral alumina using benzene as eluent. Further elution with benzene/diethyl ether mixtures of steadily increasing diethyl ether content resulted in a yellow band moving slowly down the column. The yellow band was finally eluted with diethyl ether. Concentration of the ether fractions and addition of low-boiling petroleum ether resulted in the precipitation of a yellow powder (0.964 g., 21.0% yield) identified as the ylide XCII, m.p. 157-159°C; ir (Nujol) ν_{max}: ν_{CO} 1747, 1704, 1665 and 1530 cm^{-1}; uv λ_{max}: 223 nm (ε, 20150), inflection 262 nm (ε, 9100), inflection 269 nm (ε, 10000), inflection 275 nm (ε, 10000), 332 nm (ε, 12750); nmr (deuteriochloroform): τ 2.43 (m, 5H, aromatic), 3.18 - 4.50 (m, 3H, olefinic), 6.08 (s, 3H, OMe), 6.41 (s, 3H, OMe), 6.51 (s, 3H, OMe), 7.07 (s, 3H, OMe), 7.87 (s, 3H, Me); ms: m/e 458 (M^+).

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

Reaction of 1-Phenylphosphole (LXVI) with Dimethyl Acetylenedicarboxylate

With ice-bath cooling and vigorous stirring under nitrogen, a solution of dimethyl acetylenedicarboxylate (2.32 g., 0.0163 moles) in dry benzene (50 ml.) was treated dropwise with a solution of 1-phenylphosphole (1.42 g., 0.008 moles) in dry benzene (50 ml.). Reaction was immediate as with the other phospholes and the resulting dark brown mixture was chromatographed on neutral alumina using benzene as eluent. Further elution with benzene/diethyl ether mixtures as described earlier resulted in a pale yellow band moving down the column. The pale yellow band was finally eluted with diethyl ether. Concentration of the ether fractions resulted in slow crystallization (overnight) of colourless needles(0.098 g., 2.70% yield) of what is almost certainly the nine-membered ring compound CVI, m.p. 140-143°C; ir (Nujol) ν_{max}: ν_{CO} 1760, 1736, 1725 cm^{-1} (also 1625 cm^{-1} - presumably C=C); nmr (deuteriochloroform), τ 2.20 - 2.76 (m, 5H, aromatic), 3.00 - 4.00 (m, 3H, olefinic), 5.35 - 3.60 (m, 1H, olefinic), 6.17 (s, 3H, OMe), 6.24 (s, 6H, OMe), 7.06 (s, 3H, OMe); ms: m/e 444 (M^+).

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

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

Analysis calculated for $C_{22}H_{21}O_8P$: C, 59.46; H, 4.73; P, 6.98. Found C, 60.40; H, 4.91; P, 4.98% (P in a later impure sample).

Synthesis of 3,6-Dimethyl-1-phenylphosphindole Sulfide (CXIX)

The phosphole sulfide dimer CXVIII of 3-methyl-1-phenylphosphole (LXVII) was prepared by the method of Mathey (7) and pumped on a high vacuum pump to remove traces of solvent. At reduced pressure (ca. 1 - 2 Torr), the phosphole sulfide dimer CXVIII (0.865 g.) was heated with an open flame. At 200 - 210°C a pale green liquid was distilled from the melt. This liquid quickly became viscous and solidified to a glass. The solidified distillate was dissolved in carbon tetrachloride and chromatographed on neutral alumina using carbon tetrachloride as eluent. A colourless band followed the solvent front. Fractions containing this band were pumped on an oil pump to remove solvent and these gave a colourless glass (0.37 g., 65% yield) identified as the phosphindole sulfide CXIX, ir (Nujol) ν_{max}: 1605, 1590, 1565, 1320, 1160, 1105, 1030, 890,825, 780, 745, 725, 715 (shoulder), 695, 670 cm^{-1}; uv λ_{max}: 209 nm (ε, 22180), 231,nm (ε, 24615), 300 nm (ε, 1480), 310 nm (ε, 1330); nmr (deuteriochloroform): τ 1.90 - 3.10 (m, 8H, aromatic), 3.86 (d, 1H, olefinic), 7.57 (s, 3H, Me), 7.67 (t, 3H, Me); ms: m/e 270 (M$^+$).

Analysis calculated for $C_{16}H_{15}PS$: C, 71.11; H, 5.56; P, 11.48; S,11.85. Found: C, 70.12; H, 6.07: P, 11.39; S, 11.96%.

Note: Each of the foregoing reactions was, in fact, carried out many times in order to establish optimum conditions as far as possible. It should also be remarked that in the reactions of 1-phenylphosphole with dimethyl acetylenedicarboxylate, further elution of the chromatography column with diethyl ether gave, in most cases, a 1:2:1 adduct of the phosphole, the ester and water as indicated by the mass spectrum. For the reasons outlined in the Results and Discussion section, this compound was not further investigated.

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CORRIGENDA

The structure number XCIX was not assigned to any structure in this thesis. The structure numbers proceed from XCVIII to C.

The compound assigned the structure number CX is identical to the compound previously assigned structure number CIV.