

Phospholes. The Aromaticity Problem

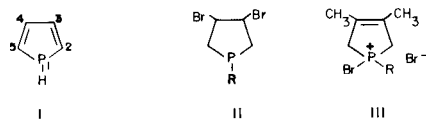
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Newer techniques of phosphole synthesis, particularly those which lead to simple phospholes substituted with active functional groups, are briefly surveyed. A detailed account of chemical, physico-chemical, spectroscopic and theoretical studies related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

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

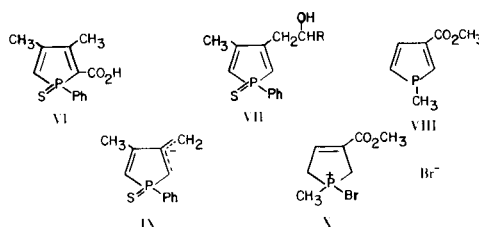


final stages, rely on dehydrobromination of species such as the dibromophospholane II and the *P*-bromo-3-phospholenium salt III obtained by a variety of reaction paths. Also, Mathey (6,7,8) has reported an elegant one-step synthesis of phospholes by addition of phenyldibromophosphine to conjugated dienes followed by treatment with DBU (2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]-azepine, Ring Index No. 10065). 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).

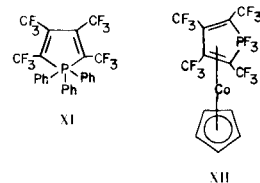


Of particular importance are the recent syntheses (4,5,10,11) of the first phosphole derivatives containing active functional groups on the ring. Examples of such phosphole derivatives are VI, VII, and VIII. These were prepared by treating anions such as IX with carbon dioxide, aldehydes or ketones (10,11)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

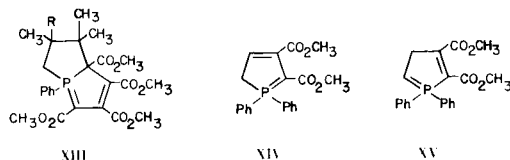
There have even been reports (12,13) of stable phospholes containing five-coordinate five-covalent phosphorus.



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 revised (14).



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



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. Therefore, we 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.

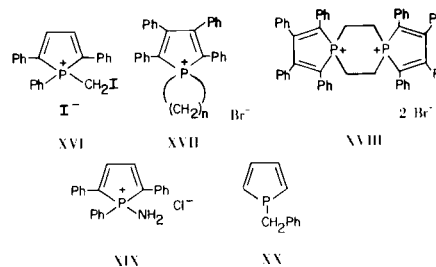
Chemical and Physico-Chemical Studies.

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 6π -electron 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, *et al.*, (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).

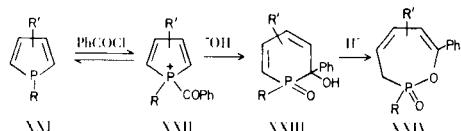


Again, these reactions would appear to indicate little or no lone pair - diene interaction in phospholes. On the other hand, Brown has pointed out (25) in an early theoretical study that comparisons in oxidation and quaternization reactions between phospholes and pyrroles (where these reactions do not 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.

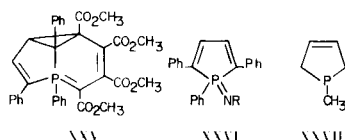
In this connection, it has been found (5) that rates of quaternization of various phospholes depend very much upon the substitution pattern. For example, 1-benzylphosphole (XX) quaternizes only very slowly (28% conversion after 11 days) with benzyl bromide and this implies much reduced tertiary phosphine 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 XXI \rightarrow 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 ylde.



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 ($EtO_2CNHOSO_2-p-C_6H_4NO_2$) 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.

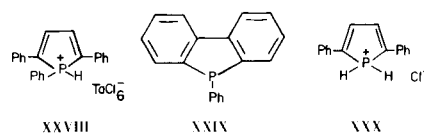
Finally, carbon bisulfide is known to form coloured complexes readily with tertiary phosphines except those

with strongly electron withdrawing groups attached. However, 1-methylphosphole will not react (3) with carbon bisulfide although the acyclic analogue ethyl-divinylphosphine 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

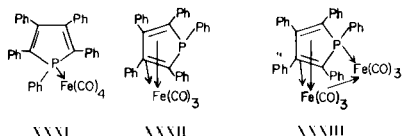


metals. The 1*H*-phospholium salt XXVIII is also formed quantitatively on passing dry hydrogen chloride into a dry benzene solution of (TPP)TaCl₅. On the other hand, no phospholium salt of the type TPPH⁺ Cl⁻ could be formed when rigorously dried hydrogen chloride was passed into a dry benzene solution of TPP although both triphenylphosphine and 5-phenyl-5*H*-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.

The stability of the salt XXVIII under anhydrous conditions was therefore attributed (34) to the exceptional stability of the TaCl₆⁻ 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(O) carbonyls (36,37,38) and gave complexes such as XXXI,



XXXII and XXXIII (36). 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-Mo carbonyl complexes while a Shell patent records (39) the uses of certain phosphole-cobalt carbonyl complexes as catalyts in hydroformylation reactions. The implication then 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 iso-octane 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.

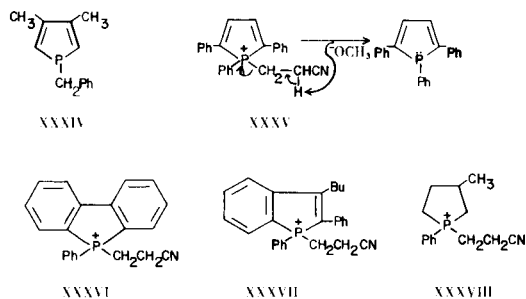
An early study in this area (41) showed that 1,2,5-triphenylphosphole will form conventional σ complexes with Pd(II) and Pt(II) chlorides and bromides and with Hg(II) and Rh(III) chlorides under mild conditions. The only departure noted from conventional phosphine reactivity was that Rh(III) is not reduced 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)CuCl 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 L₂NiCl₂ (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 indi-

cate 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).

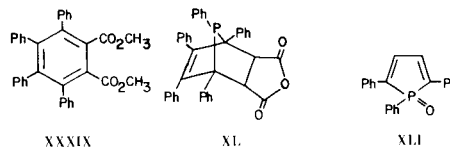
The problem of lone-pair availability has been tackled in a very ingenious manner by Farnham and Mislow (48) who theorized that if the non-bonding electron pair of phospholes is less readily available than that of ordinary tertiary phosphines because of lone-pair delocalization, then in certain reactions 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 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.

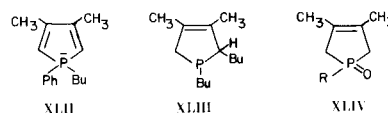
In contrast to the numerous studies of nucleophilic reactivity of the phosphorus atom of phospholes outlined in the preceding discussion, very few studies of the reactivity at the ring carbon atoms have been made. One obvious study would be an investigation of the dienoid

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 $>150^\circ$) with dimethyl acetylenedicarboxylate (36) and with maleic anhydride to give the adducts XXXIX and XL - *i.e.*, 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.

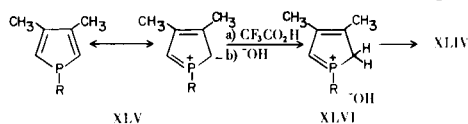
Three other reactions of phospholes at the ring carbon atoms have received brief attention (8,26,49). In the first of these, Mathey (8) found that 3,4-dimethyl-1-phenylphosphole reacts with butyllithium to give 1-butyl-3,4-dimethylphosphole *via* the adduct XLII - *i.e.*, nucleophilic attack occurs upon 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 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,

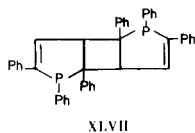
who showed that certain phospholes will react with trifluoroacetic acid to give an unisolated intermediate which, on neutralization of the acid solution, yields 3-phospholene oxides of the type XLIV. Mathey has suggested the mechanism XLV \rightarrow XLVI \rightarrow XLIV for this reaction - *i.e.*, 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 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-penta-phenylphosphole 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). Therefore, it was 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 pK_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 ^1H , ^{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-phenylphosphole, both the ^1H 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 ^1H 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 ^1H 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 $^2J_{\text{P-H}}$ 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 centered 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,

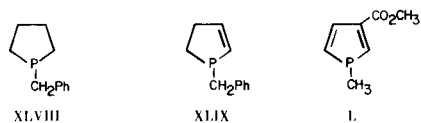
1-methylphosphole shows the ring protons centered on $\tau = 3.00$ while the 1-butylphosphole ring protons are centered on $\tau = 3.20$.

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 $^1\text{H} - ^1\text{H}$ 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-d) π 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 ethyl-divinylphosphine and trivinylphosphine at +20.8 and +20.7 ppm, respectively. Therefore, this deshielding of ^{31}P in phospholes was 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 ^1H spectra already discussed and also the chemical evidence provided by quaternization studies, $\text{p}K_a$ 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, respectively.



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 I, 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.

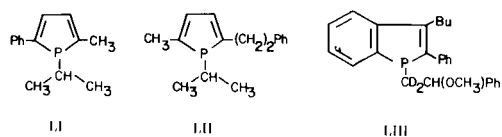
There have been three brief ^{13}C nmr studies on phospholes. The first of these (54) was devoted to a ^{13}C nmr study of 1-phenylphosphole - *i.e.*, a phosphole without ring substituents. The $^2J_{\text{C}(3),\text{P}}$ (C(3) = the ring carbon atom at position 3 in the phosphole nucleus) value in 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 $^{13}\text{C} - ^{31}\text{P}$ 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 $^{13}\text{C} - ^{31}\text{P}$ 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-trimethyl-

phosphole where, on the basis of ^1H 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 phospholes 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.

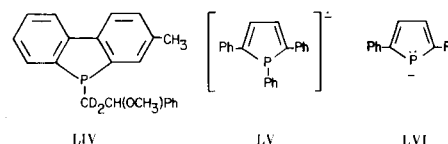
In order to study this inversion, Egan, *et al.*, (18,56) prepared the dissymmetric phosphole LI and studied the ^1H nmr spectrum. At *ca.* 0° , the isopropyl region of the spectrum showed the expected pattern for the diastereotopic isopropyl methyl groups - *i.e.*, two doublets of doublets with each 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 (ΔG_{25}^\ddagger) 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 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.

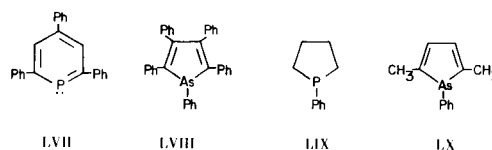
The studies were extended (56) to benzophospholes and dibenzophospholes such as LIV and LIV and it was found that the barrier to inversion is raised to *ca.*, 24



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.

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° to -80° , 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° . 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 to 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)), 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 extraordinarily 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 pyrrole > thiophene > furan > phosphole. On the other hand, it was noted that much depends upon the criteria used to measure aromaticity.

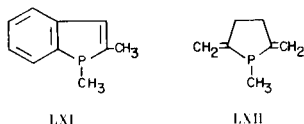
In the second molecular and crystal structure determination of a phosphole, it was found (66) that in 1,2,5-triphenylphosphole there is no significant shortening of the ring P-C bonds as compared with normal tertiary phosphines. Furthermore, as with 1-benzylphosphole, the ring is nonplanar and the arrangement 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 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-3d) π 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- π 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 ^1H 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 studies are in considerable disagreement although the LCGO studies by Palmer and Findlay (71) provide a powerful argument for a non-aromatic phosphole system in either the pyramidal or planar states. Clearly further studies are desirable and, as has been remarked elsewhere (71), some reliable thermochemical data would be very helpful.

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