

## The Chemistry of Phosphole Derivatives

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Synthetic approaches to, and the chemistry of, phospholes, benzophospholes and dibenzophospholes are reviewed and particular attention is paid to the possible aromatic character of the phosphole ring. Systems containing the 2*H*- and 3*H*-phosph(V)ole nucleus are surveyed as are phosphole derivatives containing pentavalent and six-coordinate phosphorus. Stereochemical considerations in the more complex phosphole derivatives are discussed.

Furan, thiophenes and pyrroles have been known for many decades and have been extensively investigated and reviewed. However, the related phosphole (I) system has been comparatively little explored until recently and the first phosphole derivative was not isolated until 1953 (1) when Wittig and Geissler prepared the dibenzophosphole derivative, 9-phenyl-9-phosphafluorene (II), from pentaphenylphosphorane ( $\text{Ph}_5\text{P}$ ) and by other methods.

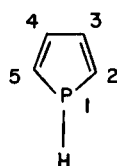
The main interest of the phosphole system lies in its potentially aromatic character as compared with the common heterocyclopentadienes, the behaviour of phospholes as secondary or tertiary phosphines, and in the chemical behaviour and stereochemistry of phosphole derivatives containing pentavalent phosphorus.

Early developments in the field of phosphole chemistry have been briefly surveyed by Märkl (2) and Hudson (3) but no recent systematic review of the topic has appeared.

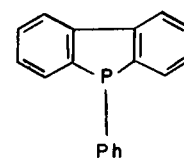
### Simple Phospholes: Synthesis.

There has been no report of the synthesis of phosphole (I) itself and all phospholes so far reported bear at least one substituent.

The first reports of simple phosphole derivatives (*i.e.* phospholes without fused rings) came in 1959 independently from three groups of workers (4,5,6) and during the last few years, several routes to various phosphole derivatives have been developed. However, few of these syntheses can be regarded as general.



I



II

The synthetic approaches to simple phosphole derivatives can be divided into four main methods and the first of these involves dehydrohalogenation of a phospholane (III), a 2-phospholene (IV) or a 3-phospholene (V) type of intermediate. Thus, the approach of Donadio and Howard (4,7) was the addition of bromine to the 2-phospholene (VI) followed by dehydrobromination of the intermediate dibromophospholane to give the corresponding phosphole oxide (VII).

Westheimer (8) employed a similar procedure in the synthesis of 1-ethoxyphosphole oxide (VIII) by the dehydrobromination of the 2-phospholene derivative (IX) by treatment of IX with base or by conversion of IX into the corresponding quaternary ammonium iodide by treatment with dimethylamine and methyl iodide followed by Hofmann degradation.

These phosphole oxides are highly reactive and, like cyclopentadiene, dimerise readily at room temperature.

Märkl (9) and Quin (10) used similar approaches to the synthesis of 1-phenylphosphole and 1-methylphosphole, respectively. In each case, the appropriate 3-phospholene oxide (X) was prepared by methods similar to those of McCormack (11) (reaction of an alkyl or aryl dihalogenophosphine with butadiene). This was followed by an addition of bromine to the phospholene oxide to give the corresponding dibromo phospholane oxide (XI). The syntheses were completed by the reduction of XI with phenyl silane (9) or trichlorosilane (10) followed by dehydrobromination to give the phosphole XII.

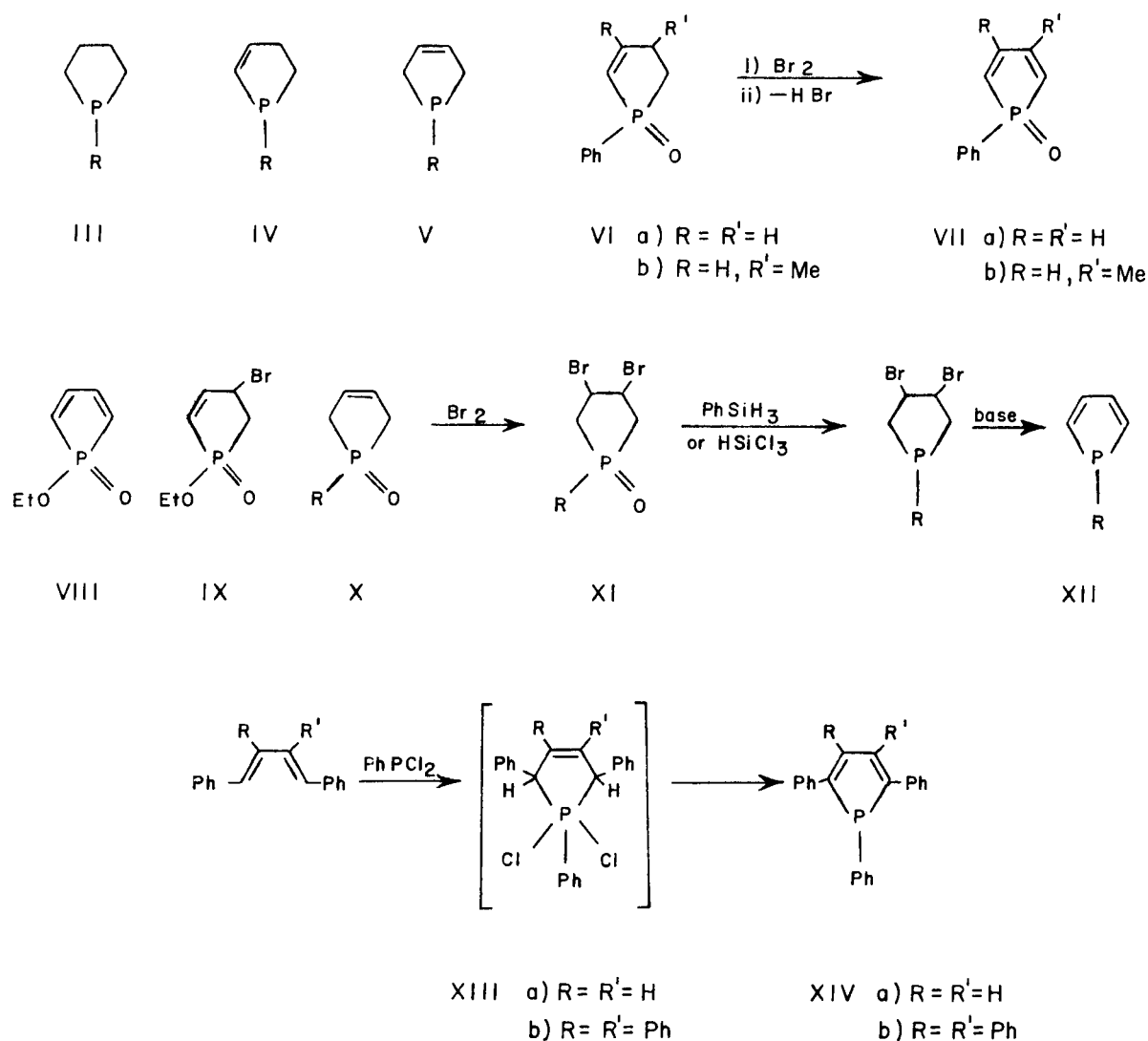
A related synthesis based on the dehydrochlorination of a 3-phospholene type of intermediate is that of Campbell (12,13) in which phenyl dichlorophosphine is heated with 1,4-diphenylbutadiene or 1,2,3,4-tetraphenylbutadiene. The initial reaction is almost certainly the Diels-Alder reaction

of addition of the phosphorus non-bonding electron pair to the diene system [as observed by McCormack (11) in the reaction of phosphorus halides with dienes] to give the intermediate 3-phospholene (XIII). This then spontaneously dehydrohalogenates under the conditions of the reaction to give the corresponding phosphole (XIV) in good yield.

The intermediacy of XIII is also inferred from the fact that phenyldichlorophosphine oxide  $[\text{PhP}(\text{O})\text{Cl}_2]$ , in which the phosphorus lone-pair electrons are not available, will not react with the diene under similar conditions.

Unfortunately, this type of synthesis is apparently not general since attempts to react other conjugated dienes with other dihalogenophosphines were unsuccessful as were attempts (14) to pyrolyse adducts of similar structure to XIII obtained by McCormack's method.

A second approach to phosphole synthesis is one aspect of a general synthesis of heterocyclopentadienes. This



method is the reaction of dihalogenophosphines with 1,4-dithiobutadienes or the reaction of metal phosphides with 1,4-diiodobutadienes (5,15,16). These reactions are based upon the ready availability of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene (XV) by treatment of diphenylacetylene (tolan) with lithium (17). The dilithio compound is either treated directly with a dihalogenophosphine (5,15,16) or is first converted into the 1,4-diiodo compound which is then treated (16) with a suitable metal phosphide such as disodium phenylphosphide ( $\text{PhPNa}_2$ ).

The third approach is related to the second. In this approach (6,16a), the iron carbonyl-diphenylacetylene complex  $\text{Fe}_2(\text{CO})_6(\text{Ph}-\text{C}\equiv\text{C}-\text{Ph})_2$  (XVI) is treated with  $\text{RPhCl}_2$  [ $\text{R}=\text{Ph}$ -(6) or  $\text{PhCH}_2$ -(16a)] to give the corresponding phosphole (1,2,3,4,5-pentaphenylphosphole or 1-benzyl-2,3,4,5-tetraphenylphosphole). The iron carbonyl-tolan complex contains a *cis*-butadienoid system bonded to an iron atom and reacts in similar fashion to XV with phenyl- or benzyldichlorophosphine.

The fourth, and potentially the most general approach to simple phosphole synthesis is due to Märkl (18) and is closely related to pyrrole (19) and thiophene (20) syntheses from conjugated diynes. Bis(hydroxymethyl)phenylphosphine in pyridine and phenylphosphine in benzene containing catalytic quantities of phenyl lithium both react readily with butadiynes to give the corresponding phosphole XVII, usually in good yield.

There is only one other reported synthesis of simple phosphole derivatives. Perveev and Rikhter (21) found that treatment of the acetylenic phosphine XVIII at  $150^\circ$  with an organic base containing a trace of water gives a product to which the structure XIX was tentatively assigned. Satisfactory analytical figures were not obtained and the structure assignment was made mainly on the basis of the infrared spectrum which contained bands indicative of a five-membered cyclic conjugated diene. Oxidation of the compound assumed to be XIXb with hydrogen peroxide yielded a compound which apparently contained two phosphorus atoms. This would appear to rule out the biphosphine structure XIX since hydrogen peroxide normally cleaves P-P bonds (3).

#### Reactions of Simple Phosphole Derivatives.

The reactions of simple phosphole derivatives may occur at the phosphorus atom or on the ring carbon atoms.

The obvious reactions which would be expected to occur at the phosphorus atom are the normal tertiary phosphine reactions such as the formation of oxides, sulfides, selenides, quaternary salts, phosphonium ylids, phosphine dihalides and inorganic complexes. These reactions have not been systematically investigated but reactions at the phosphorus atom of the phosphole system

depend largely upon the availability of the non-bonding electron pair for combination, and the ease with which certain of these reactions occur may throw some light upon the question of the possible aromatic character of the ring system.

Simple phospholes readily form oxides (6,9,12,13,16a), sulfides (6,9,13,16a), selenides (13,16a), *P*-dibromides (13) and quaternary salts (10,13,22). Phosphole oxides are normally prepared by the treatment of phospholes with hydrogen peroxide (9,12,13,16a) but solutions of phospholes having aryl substituents on the ring carbon atom and alkyl substituents (*e.g.* methyl or benzyl) on the phosphorus atom may oxidise spontaneously in air (16a) although Quin (10) does not mention this in connection with 1-methylphosphole (XII,  $\text{R}=\text{Me}$ ) itself. There is one recorded instance (15) of the direct formation of a phosphole oxide by reaction of phenyl dichlorophosphine oxide with the dilithio compound XV.

Sulfides and selenides are usually prepared in high yield from the corresponding phosphole by heating with sulfur or selenium for several hours in a suitable solvent such as benzene (9,13,16a) or xylene (13). Sulfides may also be prepared by heating the phosphole under reflux with sodium polysulfide in 2-ethoxyethanol (6,16a). Unlike the behaviour of  $\text{PhP}(\text{O})\text{Cl}_2$ ,  $\text{PhP}(\text{S})\text{Cl}_2$  reacts (16a) with the dilithio compound (XV) to give largely the corresponding phosphole and only traces of the sulfide.

Phosphole oxides and sulfides (4,8,9) with no aryl substituents on the ring dimerise spontaneously and very rapidly *via* a Diels-Alder reaction to give the adduct XX.

The tendency to dimerise is so great that Westheimer (8) was only able to identify 1-ethoxyphosphole oxide from its ultraviolet spectrum and by trapping it as a Diels-Alder adduct with cyclopentadiene. Phosphole oxides bearing aryl substituents on the ring are quite stable under normal conditions but 1,2,5-triphenylphosphole oxide readily forms a photodimer (13) on brief irradiation with a medium pressure 85 watt mercury lamp. 1,2,5-Triphenylphosphole sulfide also shows some tendency to dimerise (13) on exposure to daylight. This behaviour is not unexpected in view of the tendency of cyclopentadiene to dimerise and, as Märkl (9) has pointed out, thiophene-1,1-dioxide (23) undergoes a similar dimerisation.

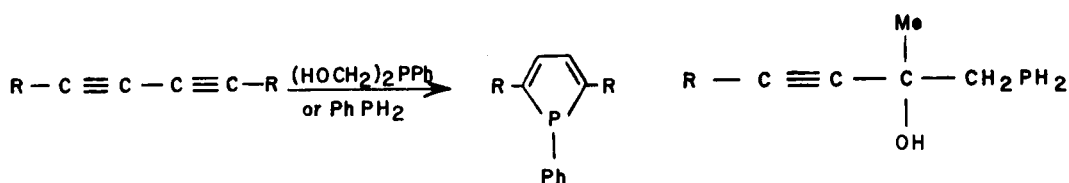
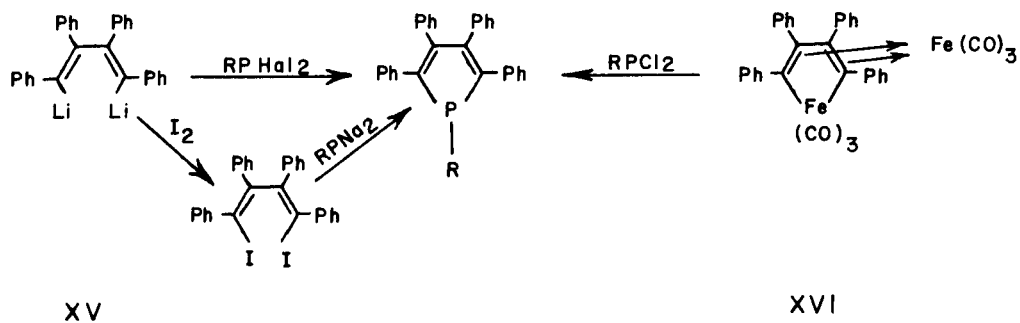
There is only one report (13) of the formation of a simple phosphole *P*-dibromide and this was prepared by heating 1,2,5-triphenylphosphole (XIVa) with bromine in carbon tetrachloride. No attack of bromine on the ring occurred. Exposure of the red solid to air led to rapid and quantitative formation of the phosphole oxide.

Phosphole methiodides also form relatively easily (10, 13,22) although Quin (10) observed that 1-methylphosphole (XII,  $\text{R}=\text{Me}$ ) is not extracted from *n*-pentane by 0.5*N* hydrochloric acid. This suggests an unusually low

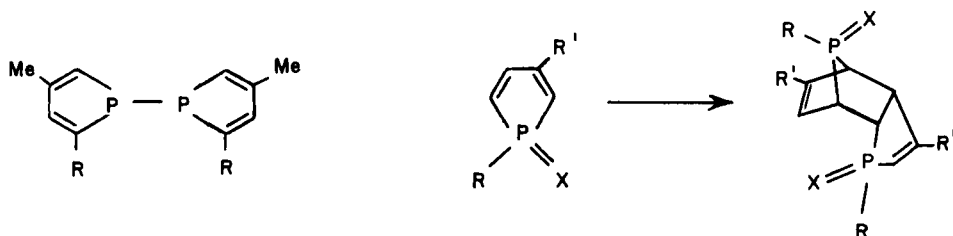
basicity for a tertiary phosphine and may indicate some degree of aromatic character. The alkaline decomposition of the methiodides (XXI) of 1,2,5-triphenyl- and 1,2,3,4,5-pentaphenylphosphole (XIVa and XIVb) has been studied by Bergesen (22). The decompositions were found to follow second-order kinetics (first-order in phosphonium

ion and first-order in hydroxide ion) and the reactions result in cleavage of the five membered rings to give the open chain phosphine oxide XXII.

The activation energies were found to be unusually low (11-12 kcal./mole) compared with those for quaternary phosphonium salts in which Ph is the leaving group (24)

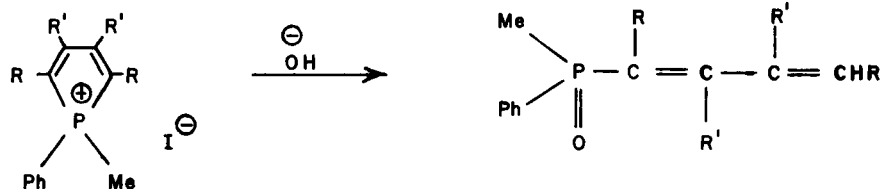


XVII (R = Me, Ph, p-tolyl, p-bromophenyl, 2-naphthyl) XVIII a) R = Me, b) R = Bu



XIX a) R = Me, b) R = Bu

XX R = Ph or OEt, R' = H or Me, X = O or S



XXI a) R = Ph, R' = H, b) R = R' = Ph

XXII a) R = Ph, R' = H, b) R = R' = Ph

(i.e. 35 kcal./mole) and this was attributed to the much greater resonance stabilisation of the intermediate carbanion formed by P-C ring cleavage. Similar decompositions of quaternary salts of dibenzophospholes are less straightforward and will be discussed later.

1,2,5-Triphenylphosphole (XIVa) will also form (13, 25) a phosphonium ylid (XXIII) *via* the quaternary salt XXIV derived from the phosphole and ethyl bromoacetate. The phosphonium ylid XXIII may also be regarded as a phosphafulvene derivative. Hocking (25) corrected the original statement (13) that the ylid XXIII does not undergo the Wittig reaction with cyclohexanone and further investigated the reactivity of XXIII towards a number of carbonyl compounds and the stereochemistry of the products. It was found that in general, the ylid XXIII is somewhat less reactive and less stereoselective than the stable open-chain ylid carbethoxymethylenetriphenylphosphorane ( $\text{Ph}_3\text{P}^{\oplus}-\bar{\text{C}}\text{HCO}_2\text{Et}$ ). Hocking also concluded that XXIII may be of use in Wittig reactions with molecules containing two or more carbonyl groups of different reactivity, e.g. keto-aldehydes.

The ready availability of the phosphorus lone-pair electrons in phospholes is further demonstrated by the formation of phosphole complexes of metal carbonyls (6,16a, 26,27) and metal halides (28). Thus, Braye found (6,16a) that 1,2,3,4,5-pentaphenylphosphole (XIVb) reacts quantitatively with  $\text{Fe}(\text{CO})_5$  to give the phosphole-iron carbonyl complex XXV whereas reaction of XIVb with  $\text{Fe}_3(\text{CO})_{12}$  gives the complexes XXV, XXVI and XXVII. Thus, reactions between 1,2,3,4,5-pentaphenylphosphole and iron carbonyls show characteristics (16a) of both tertiary phosphines and conjugated dienes.

1,2,3,4,5-Pentaphenylphosphole oxide also undergoes complex formation with  $\text{Fe}(\text{CO})_5$  to give the *P*-oxide of the complex XXVI but treatment of the corresponding phosphole sulphide with iron carbonyls results only in complete cleavage of the P-S bond and formation of the complex XXV.

Cookson and his co-workers (26) investigated the reactions of 1,2,5-triphenylphosphole (XIVa) and its oxide with various metal carbonyls such as  $\text{Fe}(\text{CO})_5$ ,  $\text{Fe}_2(\text{CO})_9$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$ , and some morpholine-metal carbonyl complexes. Unlike XIVb, the phosphole XIVa and its oxide both react with  $\text{Fe}(\text{CO})_5$  to give  $\pi$ -complexes analogous to XXVI whereas reaction of XIVa with  $\text{Fe}_2(\text{CO})_9$  gives a normal phosphine complex analogous to XXV. Reaction of the phosphole XIVa with hexacarbonyls of Cr, Mo and W gives, in each case the phosphole-metal carbonyl complex (phosphole) $\text{M}(\text{CO})_5$  (M=Cr, Mo and W). Simple monosubstitution also occurs with  $\text{Ni}(\text{CO})_4$  to give (phosphole) $\text{Ni}(\text{CO})_3$ .

Reactions of the phosphole XIVa with bismorpholine metal tetracarbonyls (of Mo and W) result in displacement

of the morpholine ligand and formation of the complex (phosphole) $_3\text{M}(\text{CO})_4$  (M=Mo and W) i.e. apparent 7-coordination. However, infrared evidence suggests that one of the phosphole molecules is not coordinated directly to the metal atoms although repeated crystallization did not change the ligand-metal carbonyl ratio. Mixed phosphole-morpholine-metal carbonyl complexes were also obtained.

Phosphole and phospholene cobalt carbonyl complexes have been successfully employed as catalysts (27) in hydroformylation reactions of alkenes leading to aldehydes and/or alcohols. Compared with ordinary phosphine complexes, these catalysts reduce the amount of saturated hydrocarbon formed and increase the reaction rate while at the same time substantially increasing the yield of alcohol formed.

All the complexes mentioned above are complexes of zero-valent metals. There is only one reported investigation of the reactions of phospholes with metal halides. Walton (28) found that 1,2,5-triphenylphosphole (XIVa) reacts with halides of Pd, Pt, Hg and Rh to give complexes of the type  $\text{MX}_2, 2\text{TPP}$  (M=Pd, Pt; X=Cl or Br; TPP=the phosphole XIVa),  $\text{HgX}_2, \text{TPP}$  (X = Cl or Br) and  $\text{RhCl}_3, \text{TPP}$ . It was concluded that the stoichiometry indicates that the ligand is only bonded to the metal by the phosphorus atom and that  $\text{HgX}_2, \text{TPP}$  are halogen bridged dimers of type XXVIII. Metal-halogen stretching frequencies were assigned.

It should be noted here that we (29) are currently investigating the reactions of 1,2,5-triphenylphosphole (XIVa) and its oxide, sulfide and selenide with various metal halides such as those of Ta, Nb, Th and U.

In connection with the question of the availability of the non-bonding electron pair in phospholes for chemical reaction, it has been found (30) that 1,2,5-triphenylphosphole (XIVa) reacts as a weak nucleophile with dimethyl acetylenedicarboxylate. However, discussion of this is best deferred to the section on phospholes containing pentacovalent phosphorus.

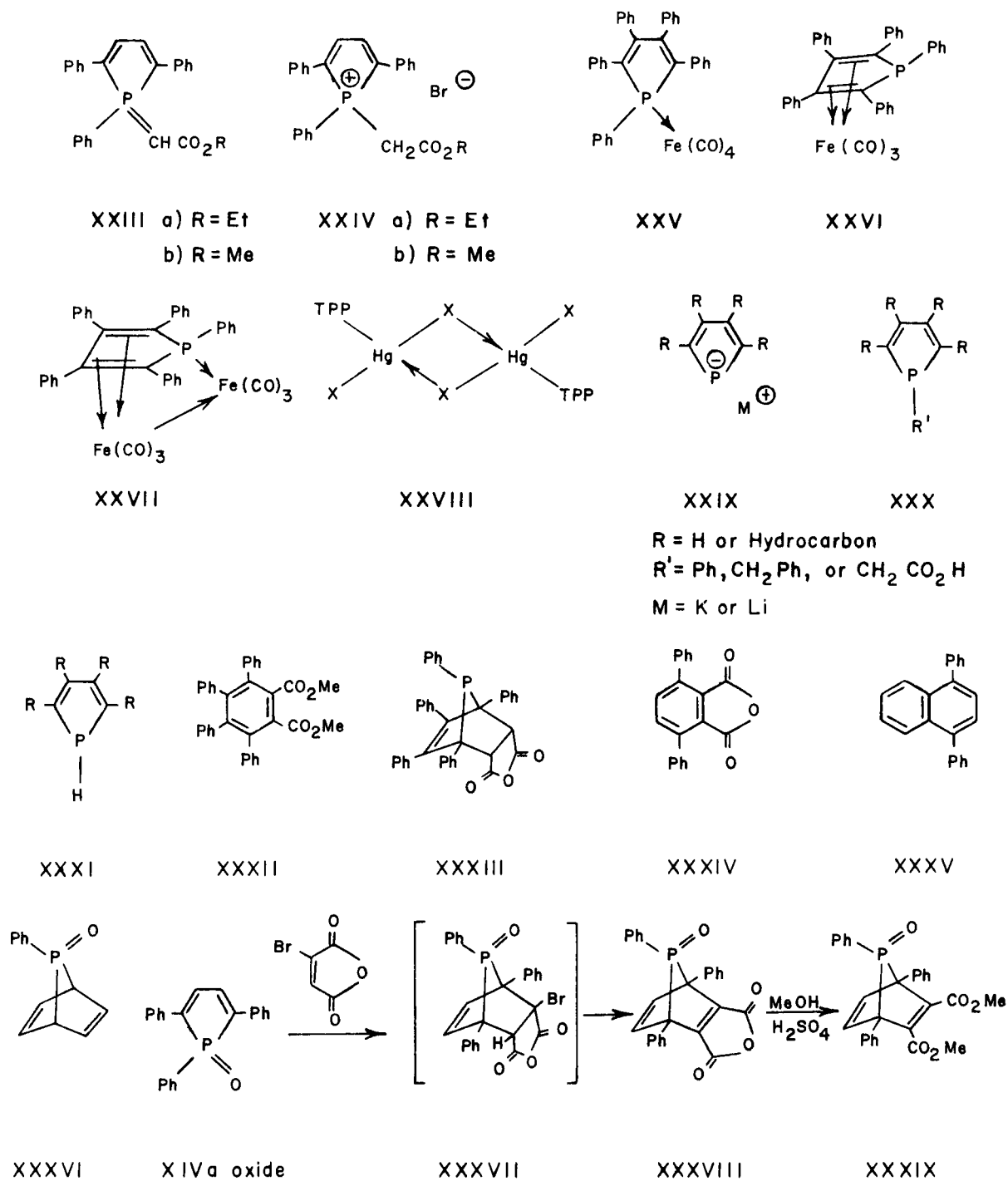
Before leaving reactions at the phosphorus atom of phospholes, there is one further reaction to be discussed which may be of synthetic value. In this reaction, the substituent on the P atom is removed by alkali metals (31,32) to give an alkali metal derivative XXIX of the phosphole XXX. Treatment of compounds of type XXIX with water leads to the formation of phospholes unsubstituted at the phosphorus atom (XXXI). Similar reactions are entered into (31,32) by pyrroles and arsoles. Since phospholes substituted only on the phosphorus atom are now known (9,10,18), this may prove to be a possible route to the as yet unknown parent phosphole (I).

Almost all of the reactions of phosphole derivatives so far studied occur at the hetero-atom. However, there are a few interesting reactions known (apart from the dimeri-

sations of simple phosphole oxides and sulfides already mentioned) which occur at the ring carbon atoms. Thus, under very severe conditions, 1,2,3,4,5-pentaphenylphosphole (XIVb) reacts with dimethyl acetylenedicarboxylate in a Diels-Alder reaction to give (6,16a) the adduct XXXII in which the phosphorus containing fragment has been eliminated. On the other hand, reaction of XIVb with

maleic anhydride under similar conditions (16a) gives the normal adduct XXXIII. Similar reactions were observed (13) for 1,2,5-triphenylphosphole (XIVa) except that with maleic anhydride, the phosphorus fragment is eliminated under the conditions of the reaction and the fully aromatic product XXXIV is obtained.

Phosphole oxides undergo Diels-Alder reactions much



more easily as shown by the trapping (8) of 1-ethoxyphosphole oxide as its adduct with cyclopentadiene. 1,2,5-Triphenylphosphole oxide reacts in hot benzene with dimethyl acetylenedicarboxylate (13), maleic anhydride (13) and acrylonitrile (13,26) to give the expected adduct except that in the case of dimethyl acetylenedicarboxylate the phosphorus containing fragment is again eliminated even under these mild conditions. Recent work (33, 34) has shown that 1,2,5-triphenylphosphole oxide reacts with benzyne to give the adduct XXXV, *i.e.*, the phosphorus fragment is again lost. It therefore seems, that in Diels-Alder reactions of phosphole oxides (and phospholes) with acetylenic linkages (6,13,16a,33,34), the expected 7-phosphabicyclo[2.2.1]heptadiene 7-oxide (XXXVI) type of intermediate tends to aromatise under the conditions of the reaction by elimination of the phosphorus fragment whereas this elimination does not necessarily occur in reactions involving an ethylenic linkage (13) as the dienophile. However, Schmidt (34) has devised an alternative route to compounds of type XXXVI using Diels-Alder reactions of phosphole oxides. This synthesis is shown in the sequence; oxide of XIVa  $\rightarrow$  XXXVII  $\rightarrow$  XXXVIII  $\rightarrow$  XXXIX. Attempts to reduce the phosphine oxide XXXIX to the corresponding phosphine led only to elimination of the phosphorus fragment.

1,2,5-Triphenylphosphole oxide reacts (13) with methyl (or ethyl) diazoacetate and diazomethane to give a variety of products depending upon the reaction conditions. Thus, treatment of the phosphole with methyl diazoacetate in boiling dioxan leads to formation of a compound to which the structure XL has been assigned although the alternative structure XLIIa has not yet been completely excluded. On the other hand, treatment of the phosphole with the diazo ester in the cold either in dioxan or without solvent, results in the formation of the pyrazoline XLII which can be converted into XL by heating under reflux in diglyme in the presence of traces of copper. The hydrazone type structure XLII was assigned in preference to the tautomeric azo-structure XLIII on the basis of infrared evidence.

If the reaction of the phosphole itself with diazoacetic ester is carried out in boiling dioxan containing a trace of copper, the product is the dihydrophthalic ester XLIV which is presumably formed by decomposition of the diazo ester to give dimethyl fumarate which then enters into a Diels-Alder reaction with the phosphole.

1,2,5-Triphenylphosphole oxide reacts quantitatively with diazomethane at  $-20^{\circ}$  over a period of several days to give the pyrazoline XLV which can also be converted by treatment with traces of copper in boiling diglyme into XLIIb. This cyclopropane derivative is of some interest in that it undergoes pyrolytic and photochemical ring enlargement reactions which are currently under investigation

(33). The same phosphole oxide reacts photochemically with diazomethane (13) to give XLIIb directly.

#### Aromatic Character of Simple Phospholes.

It is clear that, superficially, the molecular and electronic structure of phosphole (I) is very similar to that of pyrrole which is regarded as having aromatic character through delocalisation of the hetero-atom non-bonding electron pair. However, although the possible aromatic character of phosphole has occupied chemists for a decade, there has not yet been a satisfactory answer to the question. The chemical behaviour of substituted phospholes indicates that the ring system has little aromatic character at least in the sense that the behaviour of the phosphole system in certain reactions does not parallel that of the common heterocyclopentadienes (particularly pyrrole) and benzene. For example, as already mentioned, phospholes (unlike pyrroles) readily form oxides, sulfides, selenides, and quaternary salts and also undergo the Diels-Alder reaction and form phosphine type complexes with various inorganic species although it has been observed (30) that the Diels-Alder reactions occur under conditions considerably more drastic than is required for furan derivatives. On the other hand, Quin (10) found that 1-methylphosphole is considerably less basic than would be expected for a normal tertiary phosphine and apparently shares the reluctance of pyrroles to protonate under acidic conditions (35).

This apparently non-aromatic behaviour in the chemical sense can perhaps be misleading since, as Brown (36) has pointed out, oxide and quaternary salt formation for pyrrole and an aromatic model of phosphole would involve going from a planar to a tetrahedral arrangement about the hetero-atom and the difference in energy between the two arrangements is very much greater for a nitrogen atom than for phosphorus. Furthermore, Millar (37) has concluded from thermochemical measurements that the dissociation energy for the P=O bond of 1,2,3,4,5-pentaphenylphosphole oxide is about 100 kcal./mole which is very much less than for other phosphine oxides [e.g. triphenylphosphine oxide (38) = 126 kcal./mole; trimethylphosphine oxide (39) = 139 kcal./mole] and has suggested that the lower dissociation energy might be a measure of the conjugation energy of the phosphole system relative to its oxide. In support of this, Brown (36) has calculated that the planar configuration of phosphole (I) would have a substantial conjugation energy which is close to that of pyrrole.

Supporting, though not conclusive, evidence for some degree of aromatic character is provided by N.M.R. measurements. Thus, Märkl (18) states that the chemical shifts of the phosphole ring protons and of the methyl groups in 2,5-dimethyl-1-phenylphosphole are very similar

to those in 2,5-dimethylfuran, 1,2,5-trimethylpyrrole and 2,5-dimethylthiophene and concludes from this that the phosphole ring may possess some aromatic character. Märkl (9) has also studied the N.M.R. spectrum of 1-phenylphosphole and has shown that the phosphole ring protons resonate within the normal aromatic range and that the spectrum is very similar to that of *N*-phenylpyrrole. This is supported by Quin (10) who has noted striking similarities between the N.M.R., U.V. and mass spectra of 1-methylphosphole and *N*-methylpyrrole. It would be interesting to apply to the phosphole system Elvidge's method (40) for the estimation of relative aromatic character in furans, thiophenes and pyrroles by N.M.R. studies and calculations on their 2-methyl derivatives.

Other techniques which might be expected to throw some light on the problem are dipole moment and X-ray crystallographic studies on the phosphole system. We are at present applying both of these techniques (41) to 1,2,5-triphenylphosphole (XIVa). Dipole moment studies give inconclusive results in that the phosphole XIVa gives values of 1.45D and 1.08D in *p*-xylene and dioxan, respectively. These values are very close to that (42) of triphenylphosphine (1.4D in benzene) and comparisons between *P*-alkyl phospholes and alkylphosphines would be more profitable. Preliminary X-ray studies show that the phosphole XIVa crystallizes in the monoclinic system and that the unit cell is large. It is hoped that a complete crystal structure will be determined.

#### Simple Phospholes Containing Pentavalent Phosphorus.

There have been several reports (30,43,44,45) of simple phospholes (or reduced simple phospholes) containing pentavalent phosphorus but later structure revisions have reduced the number of such systems which remain unchallenged to two, only one of which is stable at room temperature while the other may have considerable zwitterionic character.

The first such report came from Johnson and Tebby (43) who investigated the reaction of triphenylphosphine with dimethyl acetylenedicarboxylate in ether at  $-50^{\circ}$ . It was found that an unstable yellow adduct was formed for which structures XLVI and XLVII were postulated with XLVI preferred. These conclusions were supported by Hendrickson (44) who obtained similar results although structure XLVII was preferred on the basis of N.M.R. studies on very fresh samples of the adduct which show only two methoxy signals rather than the three or four required by XLVI. Hendrickson also reported (44a) that triphenylarsine undergoes a similar reaction with the acetylenic ester to give the corresponding arsenic heterocycle XLVIII but the structure and elemental composition of this adduct were later revised (44b) to XLIX.

Both Johnson (43) and Hendrickson (44) found that the adduct XLVII (or XLVI) rearranges rapidly at room temperature to give a stable yellow adduct insoluble in methanol which, on the basis of chemical evidence (peracetic acid oxidation to give diphenylphosphinic acid and benzoic acid), was assigned the open chain structure L. However, more recent work by Tebby (46) has shown that there are in fact two rearrangement products one of which is methanol soluble. Furthermore, the structure of the methanol insoluble rearrangement product has been shown (46) to have a cyclic structure which will be discussed more fully in the next section.

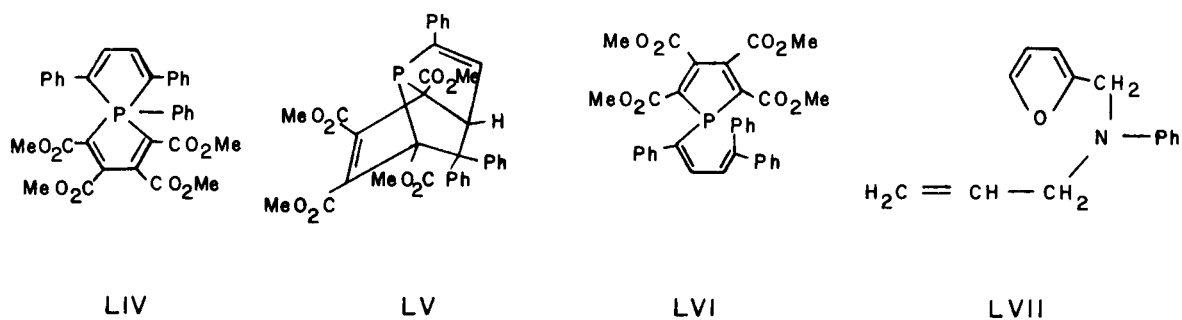
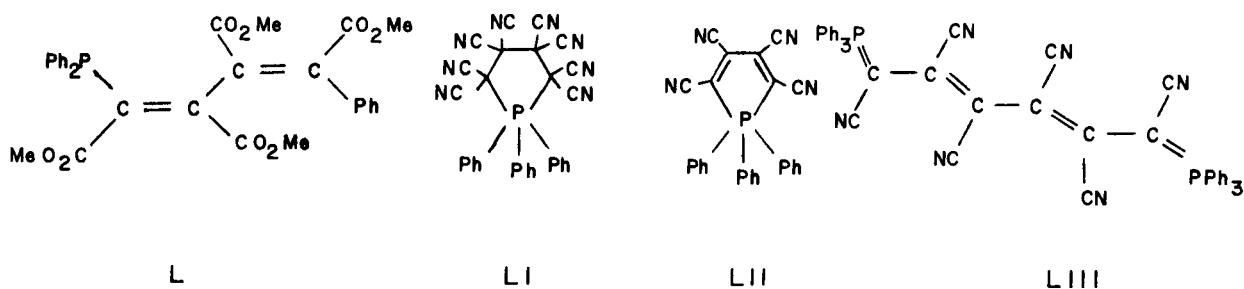
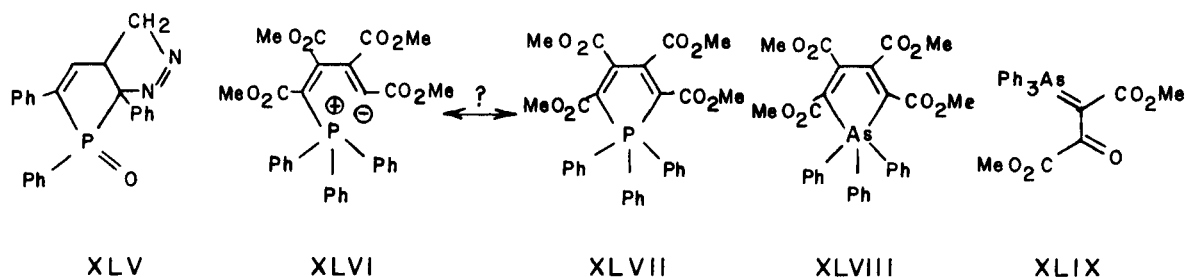
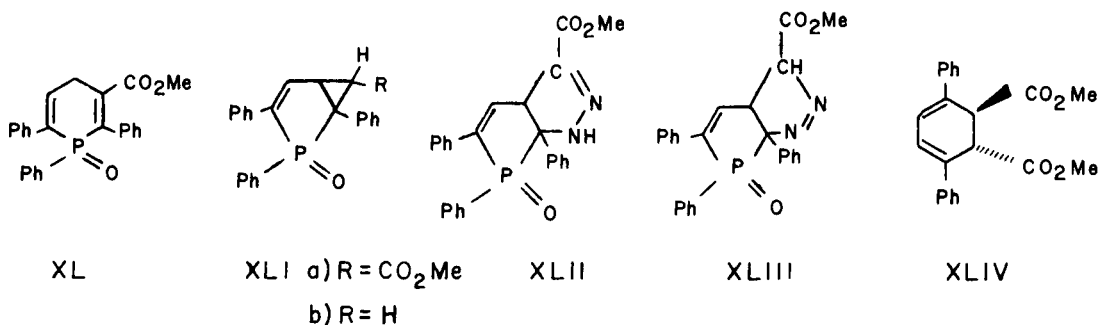
The above experiments led Reddy and Weis (45) to carry out reactions of triphenylphosphine with tetracyanoethylene and dicyanoacetylene to give compounds which were assigned structures LI and LII respectively on chemical and  $^{31}\text{P}$  N.M.R. evidence.

Again, Tebby (47) has cast doubt upon the structure assignment of the triphenylphosphine - tetracyanoethylene adduct by pointing out that a structure containing a pentavalent phosphorus atom is unlikely since recent studies (48) indicate that a phosphorus atom with five covalent P-C bonds normally shows  $^{31}\text{P}$  resonance in the  $+80$  -  $+100$  p.p.m. range (relative to 85%  $\text{H}_3\text{PO}_4$ ) whereas the adduct in question shows  $^{31}\text{P}$  resonance at  $-22$  p.p.m. relative to the same standard. It was also conclusively shown by Tebby (47) that the triphenylphosphine - dicyanoacetylene adduct has structure LIII rather than LII.

The reports of the reaction of triphenylphosphine with acetylenic compounds prompted Hughes and Uaboonkul (30) to further investigate the reaction of 1,2,5-triphenylphosphole (XIVa) with dimethyl acetylenedicarboxylate under mild conditions to see if the phosphole behaves as a diene or a tertiary phosphine or both. It was found that a room temperature reaction in the presence of a large excess of the ester and in the absence of a solvent gives three products. One product (9% yield) was identified as dimethyl 3,6-diphenylphthalate which is presumably formed *via* a Diels-Alder reaction and elimination of the phosphorus fragment. The second and major product (37% yield) was shown to be a 1:2 adduct of the phosphole with the ester to which the spiran structure LIV was assigned. This assignment is a little unsatisfactory since it was made by elimination of several other possible structures on chemical and spectroscopic evidence and it would therefore be desirable to have a  $^{31}\text{P}$  N.M.R. spectrum to confirm the presence of a pentavalent phosphorus atom. The third product (2.5% yield) was shown to be a 1:4 adduct of the phosphole with the ester but was not identified.

The spiran LIV is stable for long periods at room temperature but on warming in chloroform, a rearrangement occurs to give a colourless tertiary phosphine to which the





structure LV has been assigned. The assignment was made on chemical and spectroscopic evidence and it was postulated that phenyl migration similar to that suggested by Johnson (43) first occurs to give the phosphole derivative LVI as a transient intermediate which then undergoes an intramolecular Diels-Alder reaction to give LV. Such an intramolecular reaction would be similar to that undergone (49) by the furan LVII.

2*H*- and 3*H*-Phosph(V)oles.

Simple 2*H*- and 3*H*-phosph(V)oles are cyclic phosphonium ylids and have only been reported very recently. Thus, the 3*H*-phosph(V)ole LVIII is prepared (50) by reaction of diphenylvinylphosphine with dimethyl acetylenedicarboxylate. If the reaction is carried out in the presence of an excess of the ester, further reaction of LVIII occurs to give the interesting bicyclic ylid LIX isolated as its hydrolysis product LX. On the other hand, if the reaction is carried out such that unreacted phosphine

is always present, work-up of the solution of LVIII yields the hydrolysis product LXI of the more stable but still highly reactive tautomer LXII which is a 2*H*-phosph(V)ole derivative.

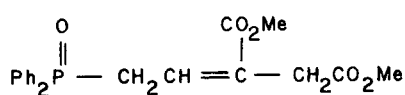
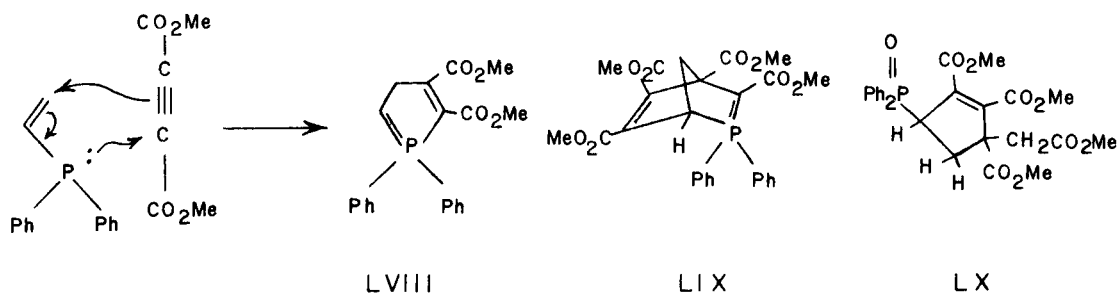
The ylid LXII has been trapped (51) in a Wittig reaction with *p*-nitrobenzaldehyde.

More recently, Tebby (46) has shown that the methanol insoluble room temperature rearrangement product of compound XLVI or XLVII is in fact the stable 2*H*-phosph(V)ole LXIIIa rather than L. This has been demonstrated quite clearly by chemical and spectroscopic techniques and it was also shown that the reaction between tri-*p*-tolylphosphine and dimethyl acetylenedicarboxylate produces a similar 2*H*-phosph(V)ole LXIIIb. We have found independently (51) that cyclopropyldiphenylphosphine also reacts with the ester to give a similar structure LXIIIc.

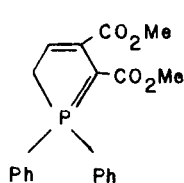
Only one other series of 3*H*-phosph(V)oles is known. The benzo-derivative LXIV (the only benzophosphole so far reported) is prepared by a long route (52) of which the final stage is the dehydrohalogenation of the cyclic phosphonium salt LXV with potassium *tert*-butoxide. The cyclic ylid LXIV behaves normally and reacts with aldehydes to give Wittig reaction products. Formation of the five membered ring of LXV is *via* an interesting intramolecular nucleophilic attack of the phosphonium ylid portion of the molecule LXVI on the alkyl halide portion.

Certain other 3*H*-phosph(V)oles have been postulated as transient intermediates in various reactions leading to the formation of dibenzophosphole derivatives. This will be discussed more fully in the next section.

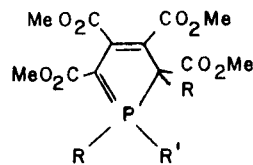
Dibenzophospholes (9-Phosphafluorenes): Synthetic Approaches.



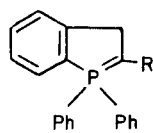
LXI



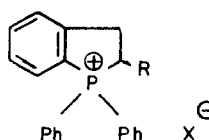
LXII



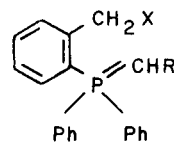
LXIII a) R = R' = Ph  
b) R = R' = *p*-tolyl  
c) R = Ph, R' = cyclopropyl



LXIV



LXV



LXVI

R = H, Ph or CO<sub>2</sub>Me, X = Br or I

As with simple phospholes, several routes to dibenzophospholes are known but again, reactions of general synthetic value are few. On the other hand, unlike the case of simple phospholes, numerous dibenzophospholes containing pentavalent and even six-coordinate phosphorus are known.

The first dibenzophosphole was prepared by Wittig in 1953 (1) by four methods although yields in all cases were poor. The first of these methods was the pyrolysis of pentaphenylphosphorane under nitrogen and the other products of the reaction are benzene, biphenyl, triphenylphosphine and an unidentified residue. The second method involved the preparation of 2,2'-dilithiobiphenyl (LXVII) followed by treatment with phenyldichlorophosphine (PhPCl<sub>2</sub>). In this case, the dibenzophosphole II was isolated as the oxide, presumably through atmospheric oxidation during work-up. The third method was the treatment of triphenylphosphine with phenyl sodium to give the dibenzophosphole II in 10% yield. This last reaction is of some interest since *o*-hydrogen abstraction in the triphenyl phosphine probably occurs (2). Later experiments of this type by Wittig (53) increased the yield of II to 15%.

The fourth method was the treatment of tetraphenylphosphonium bromide with methyl lithium over a period of three or four months. Several products including the dibenzophosphole II (37% yield) are formed. This reaction presumably proceeds *via* the intermediate 3*H*-phosphole derivative LXVIII which, under the conditions of the reaction, eliminates benzene to give II.

The pyrolysis and other reactions of pentaphenylphosphorane have also been investigated by Razuvaev (54) who has shown that, depending upon the reaction conditions, the yield of the dibenzophosphole II can be as high as 60%. The reaction follows a free-radical path and the best conditions for maximum yield of II are agitation of the phosphorane in pyridine at room temperature for 150 hours (54a).

Wittig (55) and Millar (37) later modified the reaction of 2,2'-dilithiobiphenyl and its substituted derivatives with phenyl dichlorophosphine (and certain derivatives) to give much higher yields (*ca.* 50%) of II and derivatives of II with substituents such as -NMe<sub>2</sub> on the rings.

Further work has been carried out on *o*-hydrogen abstraction in tetraphenylphosphonium compounds using organolithium compounds such as lithium piperidide (56) and lithium diethylamide (57,58) and it has been shown that good yields of the dibenzophosphole II (up to 60%) can be obtained by this method. The extreme preference for *o*-hydrogen abstraction under these conditions is shown by the reaction of the *tert*-butyltriphenylphosphonium ion (LXIX) with lithium piperidide (56). The major product of the reaction is still the dibenzophosphole II although it

might be expected that the hydrogens of the *tert*-butyl group would be relatively easily abstracted.

Compound II (and its oxide) has also been obtained by Wittig (59) *via* the intermediate LXVIII by an entirely different route. In this reaction, nucleophilic attack of triphenylphosphine upon benzyne occurs to give initially LXVIII followed by elimination of benzene. Generation of the benzyne by treatment of *o*-bromofluorobenzene with magnesium in the presence of triphenylphosphine gives a poor yield (< 20%) of II whereas generation of the benzyne by treatment of the bromofluorobenzene with butyllithium (followed by an aqueous work-up) gives only the oxide of II in very low yield (6%). The precursor (LXX) of the intermediate LXVIII was trapped with triphenylboron as the adduct LXXI.

Zbiral (60) using benzyne and substituted benzynes has studied the scope of the above reaction and has greatly improved the yields of II and its derivatives. Thus, II is obtained in 40% yield from benzyne and triphenylphosphine and 4-methoxy-9-phenyl-9-phosphafluorene LXXII is obtained in 50% yield using 1-methoxy-2-benzyne. The intermediacy of compounds of type LXVIII and LXXIII was discussed.

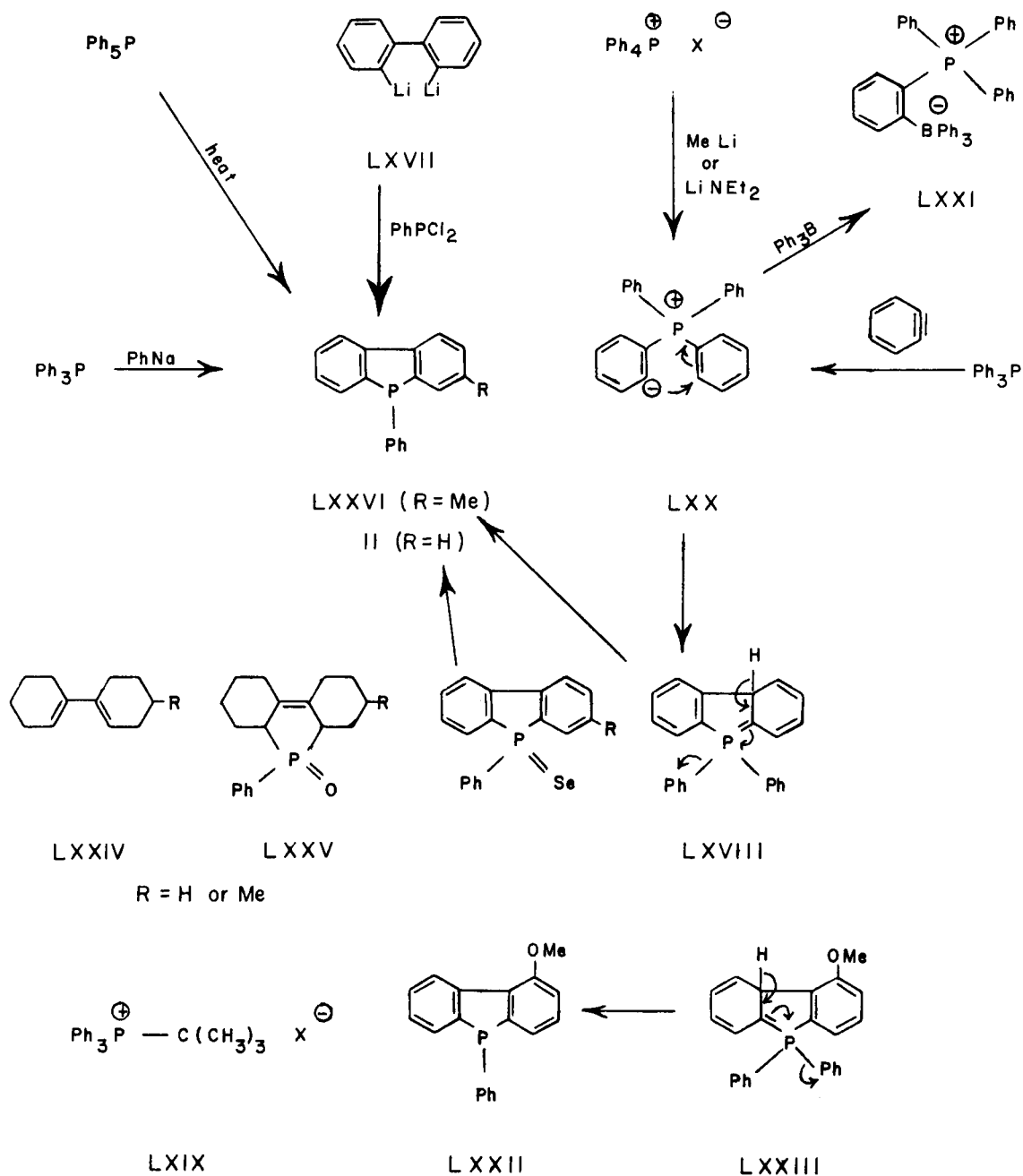
Somewhat more conventional approaches to the dibenzophosphole system are those of Campbell (13,61). One of these approaches (13) is based upon McCormack's synthesis (11) of 3-phospholene oxides in that the 1,1'-bicyclohexenyl LXXIV is treated with phenyl dichlorophosphine followed by water to give the phospholene oxide LXXXV. Selenium dehydrogenation of this compound gives the *P*-selenide of the 9-phenyl-9-phosphafluorene LXXXVI (30% yield). Campbell's other approach to the dibenzophosphole system was the cyclization of 2-biphenylphenylphosphinic acids according to the scheme LXXVII (or LXXVIII) → LXXIX → LXXX → LXXXI. Cyclizations were carried out by phosphorus pentachloride in nitrobenzene. Certain of the products could be nitrated to give the corresponding nitro-compounds.

Freedman and his co-workers have also used cyclization reactions of substituted diphenylphosphinic acids (62) and 2-substituted biphenyl derivatives (63) in the synthesis of dibenzophospholes. The dibenzophosphole derivative LXXXII (phosphafluoric acid) was prepared (41% yield) by treatment of 2,2'-dibromodiphenylphosphinic acid (LXXXIII) with methanolic potassium hydroxide in the presence of 1% palladium on calcium carbonate (62a). This is an example of the Busch reaction (64) for the coupling of aryl groups. The reaction was later extended (62b) to the preparation of a number of substituted phosphafluoric acids in yields of 5-57%. The nitro derivative (LXXXIV) of LXXXII was prepared in 93% yield by direct nitration and reduction of this gave the corresponding amino-compound. Other phosphorus and arsenic

heterocycles may be prepared by this method.

Freedman (63) also prepared 9-chloro-9-phosphafluorene LXXXV by cyclodehydrohalogenation of 2-biphenyldichlorophosphine LXXXVI. The biphenyldichlorophosphine was not isolated and was prepared *in situ* by treatment of biphenyl-2-diazonium fluoroborate with phosphorus trichloride in the presence of cuprous bromide. The cyclization was carried out with aluminum powder in ethyl acetate at reflux temperatures to give about 6% yield of LXXXV. Oxidative hydrolysis of LXXXV, as expected, gave LXXXII in over 90% yield.

A recent and novel approach to dibenzophosphole synthesis is that of Millar (65) in which certain diposphine quaternary salts are pyrolysed. The quaternary salts which were pyrolysed were derived from the diposphine LXXXVII by quaternization with methyl iodide, dibromomethane, 1,2-dibromoethane, 1,3-dibromopropane, 1,4-dibromobutane and *o*-xylylenedibromide to give the salts LXXXVIII, LXXXIX and XC. Pyrolysis of these salts gives the dibenzophosphole XCI. Yields were not recorded and the dibenzophosphole components of the pyrolysis residues were identified by vapour phase chromatography or



by conversion into the corresponding methopicroates. Thus, pyrolysis of LXXXVIII and LXXXIXa gives a mixture of XCIa and XCIIb while similar treatment of LXXXIXb, LXXXIXc, LXXXIXd and XC gives XCIIb as the only dibenzophosphole product of the pyrolysis. Similar pyrolytic decompositions of quaternary salts have been observed (65,66) for arsenic compounds of the same type.

Millar has suggested that the reaction is essentially an  $S_Ni$  displacement reaction in a monoquaternized diphosphine to give a quaternary salt of XCI which in turn undergoes a further pyrolytic decomposition to give XCI. This process is illustrated by the formation of XCIIb from LXXXIXb. This type of mechanism would however appear to be doubtful in the case of the pyrolysis of LXXXIXa which does not contain a P-Me group but nevertheless gives XCIa as one of the products. Millar (65) suggests that a free radical mechanism may be operative in this case.

Finally, the dibenzophosphole system has been detected as the ion XCII in the mass spectra of several organophosphorus compounds. Thus,  $Ph_5P_5$  on electron impact (34) shows a fragment at  $m/e$  183 which has been assigned to the ion XCII. The same ion appears in the mass spectra of compounds containing the triphenylphosphonium grouping (67) and, in this case, appears to be derived from the ion  $Ph_2P^+$  by loss of two hydrogen atoms. More recently, Zeeh (68a) has observed the same ion in the mass spectrum of diphenylphosphine while others (68b,68c) have obtained similar results with triphenylphosphine.

#### Reactions of Dibenzophosphole Derivatives.

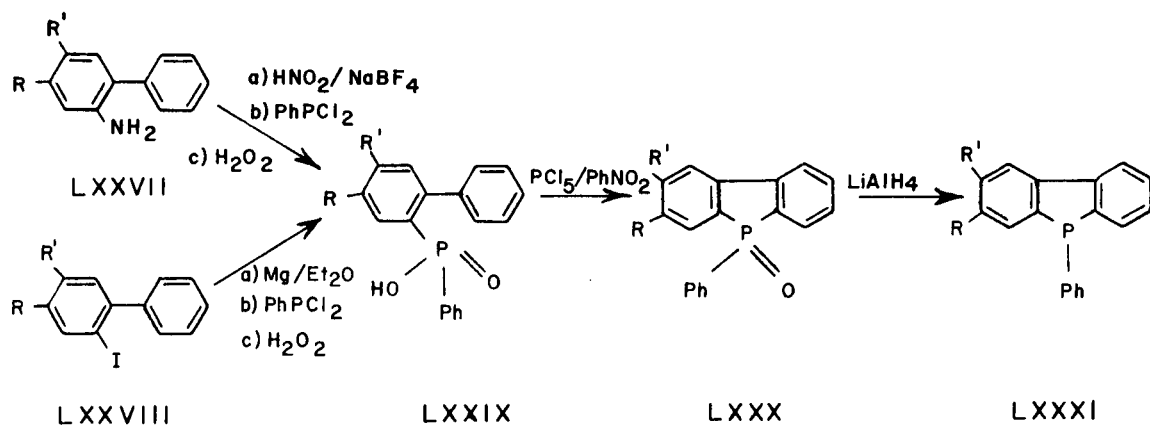
With the exception of the nitrations (61,62b) of the dibenzophosphole system which have already been mentioned, almost all other reported reactions occur at the phosphorus atom. In general, as with simple phospholes, dibenzophospholes undergo the normal tertiary phosphine reactions of oxide, sulfide, selenide and quaternary salt formation. These reactions, as in the case of the simple phospholes show that the non-bonding electron pair of the phosphorus atom is fairly readily available for combination although Millar (37) has found by thermochemical possesses a slightly lower dissociation energy than for normal phosphine oxides. The value obtained was  $126 \pm 9$  kcal./mole which is considerably lower than for trimethylphosphine oxide [ $139 \pm 3$  kcal./mole (39)] and is roughly comparable with that of triphenylphosphine oxide [ $128 \pm 5$  kcal./mole (38)]. Since this value is much higher than for 1,2,3,4,5-pentaphenylphosphole [ $100 \pm 10$  kcal./mole (37)] it would seem that the conjugation of the phosphorus atom with the remainder of the ring system of II is small.

Campbell (61) found that the dibenzophosphole oxide XCIII can be resolved into optical isomers using (+)-1-phenylethylamine and (-)-1-phenylethylamine as resolving

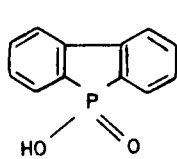
bases. However, reduction of the optically active oxides under mild conditions (lithium aluminum hydride in benzene/di-*n*-butylether) results in the formation of the racemic dibenzophosphole XCIV. As Campbell points out, this indicates that the inversion about the tertiary phosphorus atom is quite rapid which is in agreement with estimates of the optical stability of asymmetric tertiary phosphines (69) although Campbell (70) had previously found that the (+) - and (-)-isomers of the related tertiary phosphine XCV could be prepared by the reduction of the corresponding oxides. One possible explanation for the difference in behaviour of the two systems advanced by Campbell is that the ring containing the phosphorus atom in XCV is part of a skewed system and the optical activity could therefore arise from this rather than asymmetry about the phosphorus atom although Campbell did not favour this explanation. Another possible explanation is that the phosphorus atom in XCIV has significant conjugation with the remainder of the ring system (*i.e.*, the phosphorus containing ring has a tendency towards aromatic character) and the system therefore cannot be regarded as a normal tertiary phosphine.

As already mentioned, dibenzophospholes readily form quaternary salts with alkylhalides (13,57,58,65,71a) and the behaviour of some of these phosphonium salts on hydrolysis is of considerable interest. For example, Millar (65) observed that alkaline hydrolysis of the dibenzophosphole methiodide XCVI (R=Ph or Me) leads exclusively to ring opening of the central ring to give 2-biphenylphosphine oxides of type XCVII. It had previously been observed (71b) that in the alkaline hydrolysis of bromomethyltriphenylphosphonium bromide ( $BrCH_2^+PPh_3 Br^-$ ), phenyl migration to a carbon atom occurs to give benzyl-diphenylphosphine oxide. Millar (71) applied this type of reaction to the dibenzophosphole system using the quaternary salt XCVIII reasoning that the first step in the reaction would be addition of hydroxide ion to give XCIX which would then enter into an intramolecular rearrangement-elimination reaction to give the ring expanded product C. The reaction follows the predicted course giving yields of the ring expanded product in the range 58-71%. Hydrolysis of other quaternary salts XCVI gives either the parent dibenzophosphole or its oxide (when R =  $-CH_2OH$ ,  $-NEt_2$  or  $-CH_2Ph$ ) or ring opening to give biphenylphosphine oxides of type XCVII (when R =  $-CH_2OMe$ ).

Millar discussed these results in terms of the stereochemistry of the intermediates in the hydrolysis, drawing attention to Trippet's suggestion (72) that in such hydrolyses, one P-C bond of the main ring system in the phosphorane intermediate CI probably occupies an apical position while the other occupies an equatorial position in the trigonal bipyramid. This stereochemistry would be



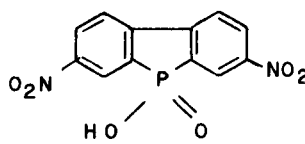
R = H or Me, R' = H or Br



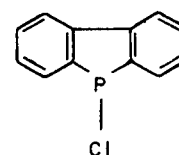
LXXXII



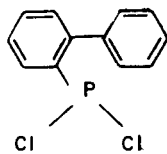
LXXXIII



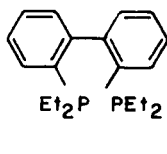
LXXXIV



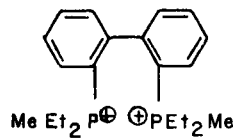
LXXXV



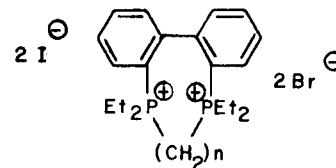
LXXXVI



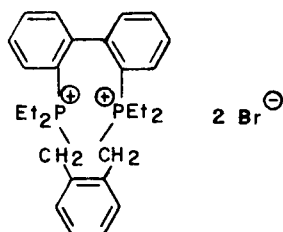
LXXXVII



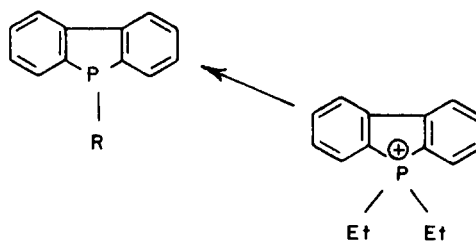
LXXXVIII



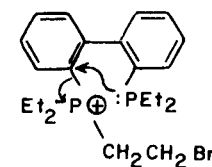
LXXXIX a) n=1  
b) n=2  
c) n=3  
d) n=4



XC



XCI a) R = Me  
b) R = Et



preferred (72) because the  $\text{C}_2\text{P}$  bond angle in four- and

five-membered ring phosphorus heterocycles would be less strained in the apical-equatorial position ( $90^\circ$ ) than in the diequatorial position ( $120^\circ$ ). The final step in the hydrolysis is the cleavage of the apical P—C bond to give a 2-biphenylphosphine oxide. However, as Millar points out (71), this principle does not always operate since certain quaternary salts XCVI ( $\text{R} = -\text{CH}_2\text{OH}$ ,  $-\text{NEt}_2$  or  $-\text{CH}_2\text{Ph}$ ) hydrolyse without cleavage of this bond. This is attributed to the stability of the leaving group  $\text{R}^-$ .

Similar results have been observed (58) for benzyl phosphonium salts of type XCVI and these results have been discussed in terms of Trippet's suggestions. However, the same workers observed that although benzyldiphenylphosphine oxide is cleaved by fusion with sodium hydroxide to give diphenylphosphinic acid, the *P*-benzyl dibenzophosphole oxide CII cleaves under similar conditions to give 2-biphenylbenzylphosphinic acid CIII. This is contrary to Horner's observations (73) in the cleavage of tertiary phosphine oxides which indicate that the leaving group will be that which will form the most stable carbanion. Ezzell and Freedman (58) suggest that in this case the intermediate is not a trigonal bipyramidal structure as in the case of the hydrolysis of phosphonium salts of dibenzophosphole and that formation of such an intermediate (CIV) would be inhibited by coulombic repulsion of the oxygen atom of the P—O bond and the approaching hydroxide ion. Trigonal bipyramidal structures involving both bonds of the main ring system in an equatorial position were dismissed on the grounds of the serious ring strain that would be involved. It was suggested (58) that cleavage of the ring P—C bond occurs as the new P—O bond is formed and that the transition state approximates to a trigonal bipyramid.

Tebby (74) observed that triarylphosphines react with phenylacetylene ( $\text{HC}\equiv\text{CPh}$ ) in the presence of water to give the phosphine oxide CV. Similar reactions of triarylphosphines occur (75) under milder conditions with methyl propiolate ( $\text{HC}\equiv\text{CCO}_2\text{Me}$ ). The mechanism of the reaction was thought to be as shown in the sequence  $\text{Ph}_3\text{P} + \text{HC}\equiv\text{CPh} \rightarrow \text{CVI} \rightarrow \text{CVII} \rightarrow \text{CVIII} \rightarrow \text{CIX} \rightarrow \text{CV}$ . Tebby (75) successfully applied this reaction (using methyl propiolate as the electrophile) to dibenzophospholes of type XCI ( $\text{R} = \text{Me}$ ,  $\text{Ph}$  or  $-\text{CH}_2\text{Ph}$ ) in order to obtain ring expansion of the dibenzophosphole system to 9,10-dihydro-9-phosphaphenanthrene-9-oxides (CX where  $\text{R} = \text{Me}$ ,  $\text{Ph}$  or  $-\text{CH}_2\text{Ph}$ ).

Both Wittig (59) and Zbiral (60) extended their investigations of the reactions of triarylphosphines with benzyne to give the dibenzophosphole system. Thus, Wittig found that the dibenzophosphole II reacts with benzyne

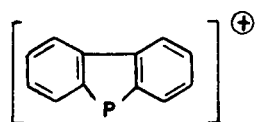
in the presence of  $\text{Ph}_3\text{B}$  to give the compound CXI while Zbiral found that II reacts with 1-methoxy-2-benzyne to give the 2-biphenyldibenzophosphole CXII ( $\text{R}=\text{OMe}$ ) via the 3*H*-phosphole type of intermediate CXIII.

Like simple phospholes containing the Ph—P group (31, 32) and triphenylphosphine (76), the dibenzophosphole 9-phenyl-9-phosphafluorene (II) reacts with alkali metals such as Li, Na, K and Cs (77) to cleave the P—Ph bond. The reaction occurs in two steps, the first of which is P—phenyl cleavage to give the metal phosphide CXIV (and the metal phenide) which can be trapped by treatment with hydrogen peroxide to give the phosphoauric acid LXXXII. No free radical appears to be involved in this preliminary step (E.S.R. measurements).

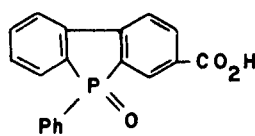
If the phosphide CXIV is allowed to remain in contact with the metal at  $-50^\circ$  the yellow solution becomes red brown and E.S.R. measurements indicate the presence of a radical. Britt and Kaiser (77) suggested that the radical is CXV produced by electron transfer from unreacted metal to CXIV. The E.S.R. spectrum supports this by indicating that there is one phosphorus atom per radical and that the spectrum in general is consistent with CXV. The E.S.R. measurements were complicated by the presence of a second radical which appears to have two phosphorus atoms per radical and which was assigned the anion radical structure CXVI. This suggests that the biphosphine CXVII is a product of the reaction. Traces of this biphosphine in crude form were isolated by addition of pyridine to the reaction mixture followed by cooling to  $-15^\circ$ . The material was not analyzed nor were its IR and UV spectra recorded. However, its melting point ( $232 - 238^\circ$ ) was found to be close to that reported in the literature for CXVII by Mann (78) who obtained this biphosphine as a by-product in the reaction of the phosphine CXVIII with lithium followed by treatment with ethyl dichlorophosphine.

#### Dibenzophospholes Containing Quaternary, Pentavalent and Six-Coordinate Phosphorus.

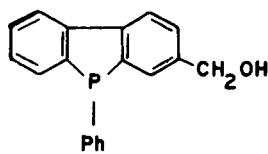
First reports of dibenzophospholes containing pentavalent phosphorus came in 1964 (53,55) from Wittig and his co-workers. Wittig approached the synthesis of these compounds in two ways. In the first of these approaches (55), a triarylphosphinimine is converted into the corresponding immonium bromide by treatment with methyl bromide and the product is treated with aryllithium. Thus, tetraphenylphosphinimine ( $\text{Ph}_3\text{P}=\text{NPh}$ ) on treatment with methyl bromide gives the corresponding salt  $[\text{Ph}_3\text{P}-\text{NMePh}]^+ \text{Br}^-$  which reacts further with phenyllithium to give pentaphenylphosphorane ( $\text{Ph}_5\text{P}$ ). If the intermediate immonium salt is treated with 2,2'-dilithiobiphenyl (LXVII), the corresponding phosphorane



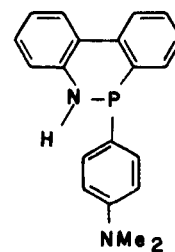
XCII



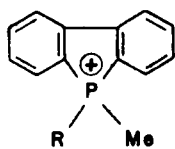
XCIII



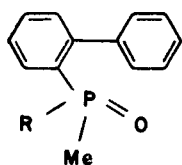
XCIV



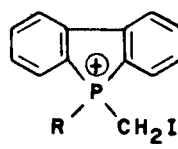
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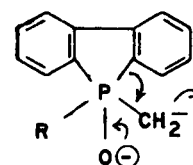
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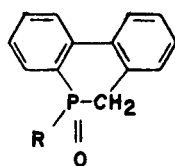
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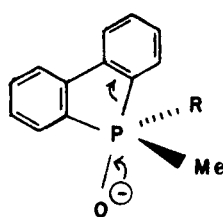
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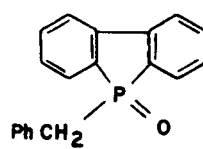
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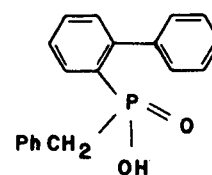
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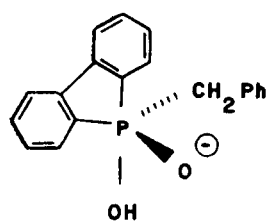
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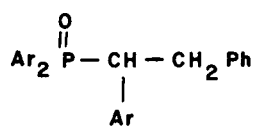
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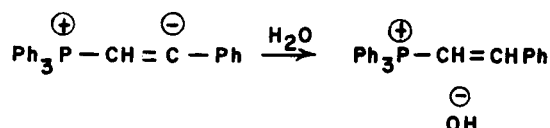
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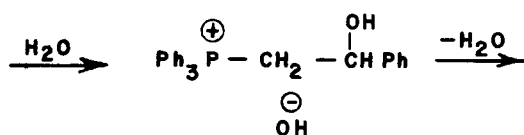


CV

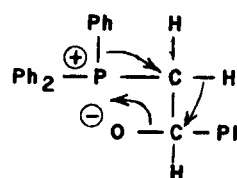


CVI

CVII



CVIII



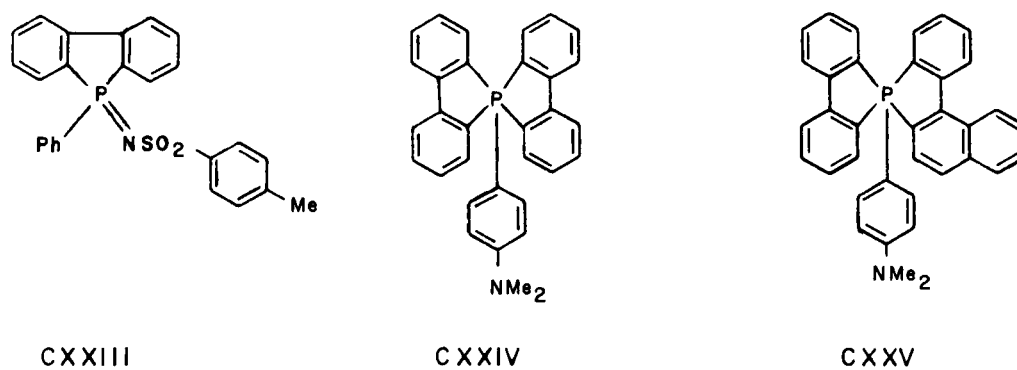
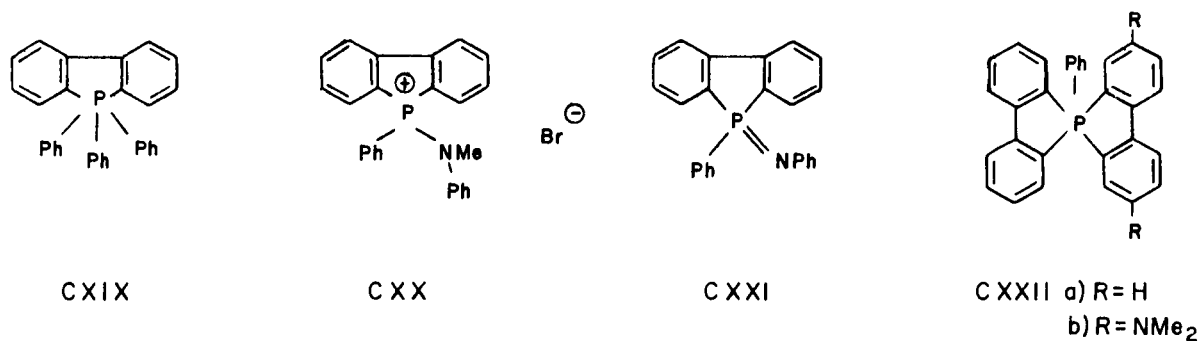
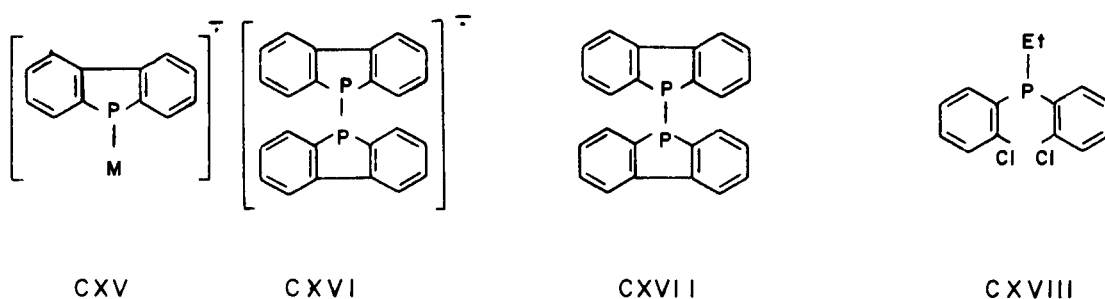
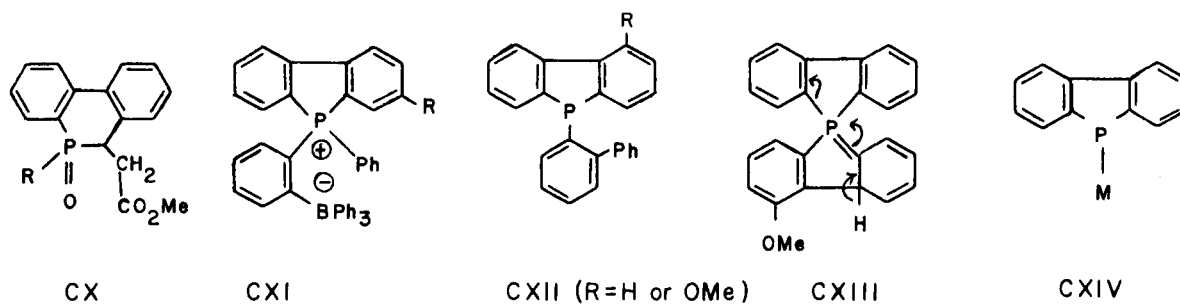
CIX



derivative CXIX is formed. Likewise, a similar immonium salt CXX is formed from the dibenzophosphole II by treatment with phenyl azide (to give CXXI) followed by addition of methyl bromide. This immonium bromide reacts slowly with phenyllithium to give CXIX and with 2,2'-dilithiobiphenyl (LXVII) to give the spirophosphorane CXXIIa in high yield. The spirophosphorane CXXIIb was

prepared by similar methods but attempts (53) to resolve these spirophosphoranes into their optical antipodes were unsuccessful.

In the second approach (53), the key intermediate is a tosylimine of a phosphine (e.g., CXXIII). These tosylimines are prepared from the phosphine or dibenzophosphole (53) by reaction with chloramine-T and have the



advantage that they will react directly with aryllithium compounds to give the corresponding phosphorane. Similar reactions are observed for arsenic and antimony compounds (79). The spiroposphoranes CXXII, CXXIV and CXXV were prepared by this method (53).

Much of the recent work on dibenzophospholes containing quaternary, pentavalent or six-coordinate phosphorus is due to Hellwinkel, who approached the synthesis of such compounds by treating phosphorus pentachloride with 2,2'-dilithiobiphenyl (LXVII) and its substituted derivatives (48,80). The product of this reaction (50% yield) is the "onium-ate" complex bisbiphenylenephosphonium trisbiphenylenephosphate (CXXVI). "-Ate" complexes of various elements have been discussed in detail by Wittig (81).

The complex CXXVI is quite stable at normal temperatures and reacts with sodium iodide to give the phosphonium salt CXXVII ( $X = I$ ) and the phosphate complex CXXVIII. The phosphonium salt CXXVII ( $X = I$ ) may also be prepared in high yield (48) by the reaction of 2,2'-dilithiobiphenyl (LXVII) with triphenylphosphate  $[(PhO)_3PO]$  or triethylphosphate  $[(EtO)_3PO]$  followed by addition of potassium iodide.

The salt CXXVII reacts with butyllithium and methyllithium (48) to give the spiroposphorane CXXIX ( $R = Me$  or  $Bu$ ). The "onium-ate" complex CXXVI also reacts with phenyllithium or methyllithium to give CXXIX ( $R = Ph$  or  $Me$ ) while the salt CXXVII reacts with 2,2'-dilithiobiphenyl to give the complex CXXVI.

Spiroposphonium salts of type CXXVII have also been prepared by Hellwinkel (82) by the pyrolysis of alkyl 2,2'-biphenylene-2'-bromo-2-biphenylphosphonium salts such as CXXX. These salts are prepared (82) by treatment of spiroposphoranes such as CXXIX with bromine. Pyrolysis of the salt CXXX gives the spiroposphonium salt CXXVII ( $X = Br$ ) in yields approaching 80% in some cases together with traces of the dibenzophosphole derivative 9-(2'-bromo-2-biphenyl)-9-phosphafluorene (CXXXI,  $X = Br$ ). The efficiency of the reaction was found to be very dependent upon the nature of  $X$  and  $Y$  with the best results being obtained when  $X$  and  $Y$  are  $Br$  and  $Br$  or  $Br$  and  $I$ , respectively. If  $X = Y = Cl$ , substantial yields of CXXXI are obtained. The nature of  $R$  ( $Me$ ,  $Bu$  or  $-CH_2Ph$ ) does not markedly affect the yield. Dibenzophosphole derivatives of type CXXXI may also be obtained by reduction of the salts CXXX with lithium aluminum hydride.

An alternative route (82) to the spiroposphonium structure CXXVII is *via* treatment of CXXXI with butyl lithium to give the corresponding aryllithium compound which on addition of iodine gives the spiroposphonium salt CXXVII. The reaction is thought to proceed with the phosphoranyl radical CXXXII as an intermediate.

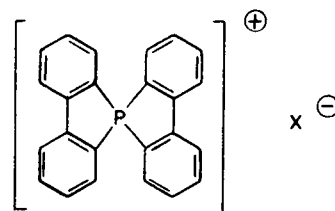
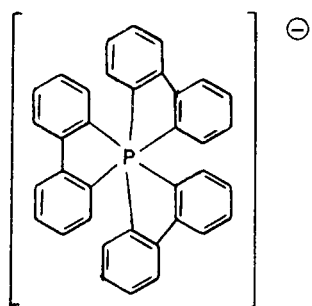
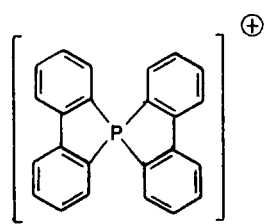
Yet another synthesis of the spiroposphonium salts CXXVII, also due to Hellwinkel (82), is the reaction of the dibenzophosphole CXII ( $R=H$ ) with phosphorus pentachloride in a sealed tube. Yields of 80-90% are obtained and the reaction is thought to proceed with the *P*-dichloro-derivative of the dibenzophosphole as an intermediate.

Until recently, derivatives of the hypothetical parent phosphorane  $PH_5$  containing  $P-H$  bonds were unknown. However, Hellwinkel (83,84) has recently synthesized the spiroposphorane CXXIX in which  $R = H$ . The synthesis was achieved by reduction of spiroposphonium salts such as CXXVII with lithium aluminum hydride in ether (53% yield) or sodium borohydride in ethanol (88% yield). The compound is remarkably stable and can be kept indefinitely under nitrogen in the dark at room temperature and for several days in air, but decomposes at higher temperatures. The behaviour of this compound is remarkable in that it can lose hydrogen as  $H^+$ ,  $H^-$  or atomic hydrogen depending upon the conditions.

Solutions of the spiroposphorane CXXIX ( $R = H$ ) in benzene (from which air has been excluded) rapidly develop a deep violet coloration and show an E.S.R. spectrum consistent with the radical structure CXXXII. Moreover, the loss of the signal due to the  $P-H$  proton in the N.M.R. spectrum indicates that the conversion to the radical is very substantial. The same radical is produced when the spiroposphonium salt CXXVII ( $X = I$ ) is treated with a sodium/potassium alloy in benzene (83). If the  $Na/K$  alloy is allowed to remain in contact with the radical, further electron transfer occurs to give the anion CXXXIII. The same anion is obtained when the phosphorane CXXIX ( $R = H$ ) is treated with strong bases such as potassium *tert*-butoxide (84). This anion rearranges by  $P-C$  bond cleavage to give the carbanion CXXXIV which protonates to give the tertiary phosphine CXII ( $R=H$ ).

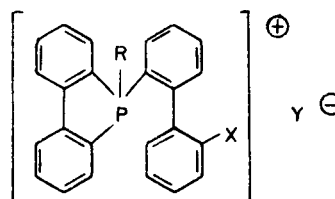
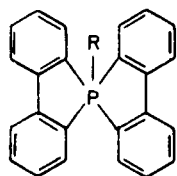
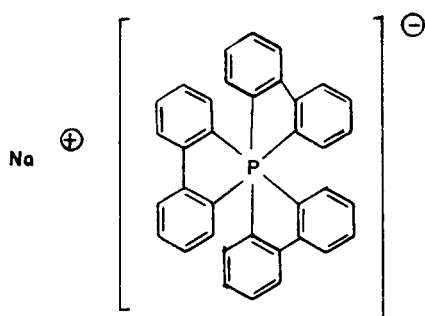
This phosphine is also obtained together with the dimeric structure CXXXV when thiophene-free benzene solutions of the spiroposphorane CXXIX ( $R = H$ ) are allowed to stand for several days. Evaporation of the solution to dryness followed by addition of ethanol leads to the isolation of the phosphine CXII in up to 50% yield and the dimer CXXXV in up to 25% yield. Hellwinkel suggests (84) that the radical structure CXXXVI is a significant contributor to the overall resonance hybrid of the radical CXXXII and that addition of a hydrogen atom to the radical may produce the 2*H*-phosph(V)ole structure CXXXVII which rearranges as shown to give the phosphine CXII ( $R=H$ ).

Treatment of the phosphorane CXXIX ( $R = H$ ) with organo lithium compounds at  $-70^\circ$  leads to formation of intermediate "-ate" complexes such as CXXXVIII which eliminate hydride ion to give the spiroposphorane CXXIX ( $R = Bu$ ) (84). Several other reactions of the spiroposph-



CXXVI

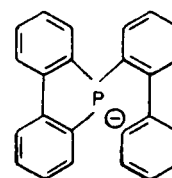
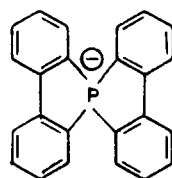
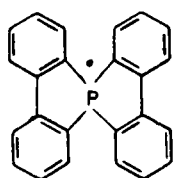
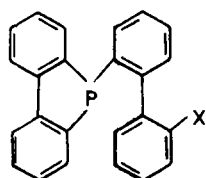
CXXVII



CXXVIII

CXXIX

CXXX

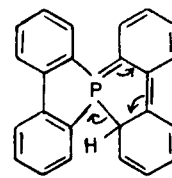
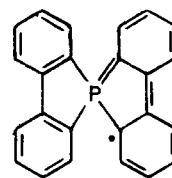
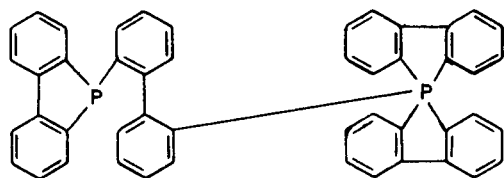


CXXXI (X = Cl or Br)

CXXXII

CXXXIII

CXXXIV



CXXXV

CXXXVI

CXXXVII

phorane have been described (84) including reactions of the system with ethanol, lithium aluminum hydride and ethanolic hydrogen chloride. The phosphorane CXXIX ( $R = H$ ) shows the P-H stretching frequency at the unusually low value of  $2096\text{ cm}^{-1}$ .

Another recent synthesis of spirophosphoranes containing the dibenzophosphole systems is that of Märkl (85) in which 2,4,6-triphenylphosphabenzene (CXXXIX) is heated with 2,2'-biphenylenemercury (CXL) to give the spiran (CXXLI), presumably by radical addition. The interest of this system lies in the possible aromatic character of the phosphorus-containing six-membered ring and the ylid nature of the same ring.

In addition to the reactions of spirophosphoranes of type CXXIX and the "-ate" complexes of type CXXVI and CXXVIII already mentioned, there are several other reactions of considerable interest. Thus, if the spirophosphoranes CXXIX are heated briefly above their melting point, ring enlargement to a phosphanonetetraene derivative CXLII occurs (48,53,55). Similarly, treatment of these spirophosphoranes with methyl iodide at  $100^\circ$  leads to the formation of the methiodide of CXLII ( $R = Ph$ ) (55). Pyrolysis of 9,9,9-triphenyl-9-phosphafluorene (CXIX) give the terphenyl phosphine CXLIII (55). The spiran ring of CXXIX ( $R = Ph$ ) is also cleaved by acid (53) to give the phosphonium salt CXLIV.

The "-ate" complexes CXXVI and CXXVIII undergo similar ring opening reactions (48). For example, the lithium analogue of CXXVIII pyrolyses to the phosphanonetetraene CXLII ( $R = 2$ -biphenyl). The same "-ate" complex on treatment with acid gives the spirophosphorane CXXIX ( $R = 2$ -biphenyl). Several reactions of this general type have been reported (48,53,55).

#### Stereochemistry of Dibenzophospholes Containing Penta-covalent and Six-Coordinate Phosphorus.

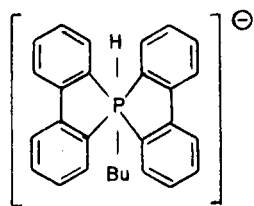
The stereochemistry of spirophosphoranes of type CXXIX was first considered by Wittig (53,55) who assumed that such molecules would have a trigonal bipyramidal structure similar to that of pentaphenylphosphorane (86). Thus, compounds such as CXXIIa and CXXIIb might be expected to be resolvable depending upon the arrangement of the substituents about the phosphorus atom. For example, if in CXXIIa the groups are arranged such that the phenyl group occupies an equatorial position, it follows that in each of the 9-phosphafluorenyl groups one P-C bond would be equatorial while the other would be apical. This would give rise to a dissymmetric structure (CXLV) which should be optically resolvable. On the other hand, if the phenyl group were to occupy an apical position, one of the 9-phosphafluorenyl groups would be diequatorial while the other would be apical-equatorial and the molecule would not be dissymmetric. The same arguments

would apply to CXXIIb except that there would be two arrangements ( $-NMe_2$  on a diequatorial 9-phosphafluorene system and on an apical-equatorial 9-phosphafluorene system) which would be non-dissymmetric. Similar arguments would apply to a square-pyramidal structure of the phosphorane. Presumably, the 9-phosphafluorene systems in the trigonal bipyramidal arrangement would tend to be equivalent with both having apical-equatorial arrangements to minimize the ring strain as outlined by Trippett in his discussion (72) of trigonal bipyramidal intermediates in the hydrolysis of phosphonium salts of dibenzophosphole derivatives.

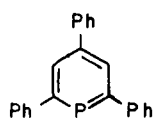
Wittig's attempts to resolve these spirophosphoranes were unsuccessful but Hellwinkel (87) has carried out a stereochemical study using N.M.R. spectroscopy which shows why resolution could not be expected.

This study shows that in penta-*p*-tolylphosphorane, only one methyl signal is observed in the N.M.R. spectrum even at  $-60^\circ$ . This is clear evidence that the phosphorane cannot be regarded as a normal trigonal bipyramid or a normal square pyramid since both structures would show two different methyl signals. Similarly, the spirophosphorane CXLVI ( $R = Ph$  or 2-naphthyl) shows only one signal although this would be consistent with a square-pyramidal arrangement in which both 9-phosphafluorene groups occupy a diequatorial position. When  $R$  is increased in size to 9-anthryl, two distinct methyl signals appear in the N.M.R. spectrum. Hellwinkel (87) interpreted these results to mean that the methyl groups in both the penta-*p*-tolylphosphorane and the spirophosphorane CXLVI ( $R = Ph$  or 2-naphthyl) occupy an average magnetic environment as a result of a rapid transformation between two trigonal bipyramidal forms with a square pyramidal transition state. The process is illustrated in the sequence  $CXLVII \rightleftharpoons CXLVIII \rightleftharpoons CXLIX$ . When the size of  $R$  becomes sufficiently large, the rate of the transformation is reduced until each trigonal bipyramid has a significant lifetime. The process has been termed pseudorotation and the idea has been used (88) to explain the magnetic equivalence of the fluorine atoms in phosphorus pentafluoride even though infrared measurements indicate a definite trigonal bipyramidal structure. The concept of pseudorotation has also been used to explain the chemical behaviour of a number of organophosphorus compounds (89).

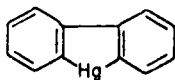
Hellwinkel (90) studied the pseudorotational process in the spirophosphoranes CXLVI ( $R = Me, Et, Ph, -CH_2Ph, 2$ -naphthyl, 1-naphthyl, 2-biphenyl and 9-anthryl) by variable temperature N.M.R. measurements and estimated the free energies of activation for the process. The spirophosphoranes used in this study were prepared by the action of organolithium compounds or Grignard reagents upon the spirophosphonium salt CXXVII.



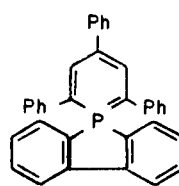
CXXXVIII



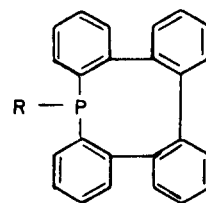
CXXXIX



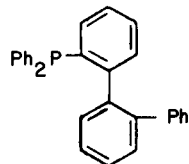
CXL



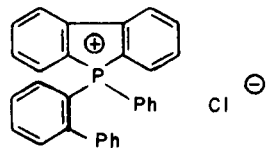
CXLI



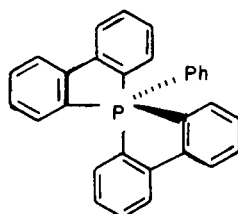
CXLII



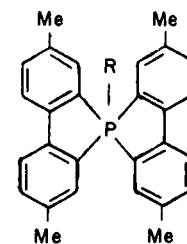
CXLIII



CXLIV



CXLV



CXLVI



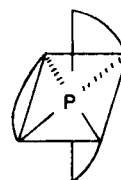
CXLVII



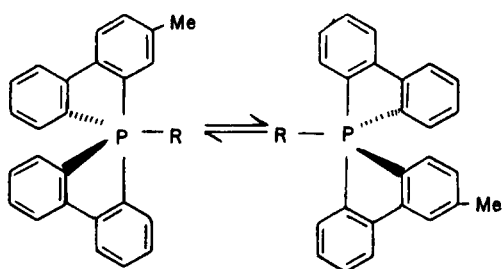
CXLVIII



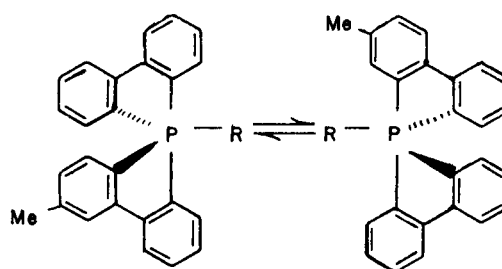
CXLIX



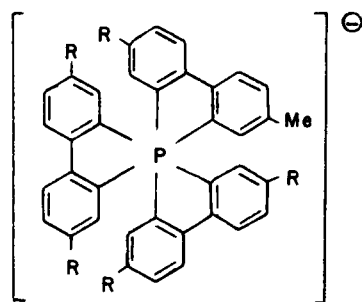
CL



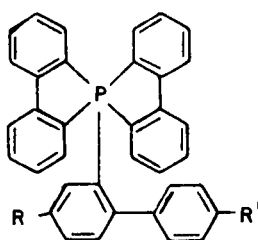
CL I a



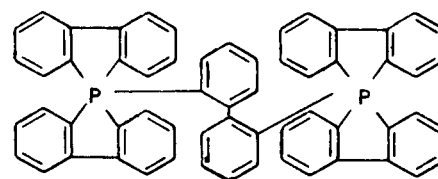
CL I b



CLII a) R = H  
b) R = Me



CLIII a) R = H, R' = Me  
b) R = Me, R' = H



CLIV

In another series of papers, Hellwinkel (91-95) has investigated in considerable detail the stereochemistry of dibenzophospholes containing pentacovalent and six-coordinate phosphorus. The octahedral structure of the lithium analogue of the "ate" complex CXXVIII has been clearly demonstrated (91,92) by its optical resolution into the stereoisomers CL. The resolution may be carried out by addition of *N*-methylbrucinium iodide to a methanolic solution of the "ate" complex followed by fractional crystallisation of the precipitated mixture of methylbrucinium trisbiphenylenephosphates from acetone. The isomeric salts on treatment with potassium iodide in acetone give the stereoisomers CL which have the extraordinarily high specific rotations of  $[\alpha]_{578}^{24} = \pm 1930^\circ$ . Addition of the phosphonium salt CXXVII ( $X = I$ ) to solutions of each of the two isomers CL gives two optically active "onium-ate" complexes of type CXXVI.

It was found (92) that the optically active "onium-ate" complex CXXVI is cleaved by acid to give racemic CXXIX ( $R = 2$ -biphenyl).

In a later paper, Hellwinkel (93) reported the synthesis of the first optically active spirophosphorane CLIIa and CLIIb ( $R = 2$ -biphenyl). This was prepared by acid cleavage of the "ate" complex CLIIa (which in turn was prepared by the tosylimide method). Two other spirophosphoranes CLIII are produced by the acid cleavage of the "ate" complex but were discarded as unsuitable for studies of optical activity. The two enantiomers CLIIa and CLIIb both exist as fluctuating trigonal bipyramids (pseudorotation) with a square pyramidal transition state. Separation of the enantiomeric pair was made easier by a spontaneous cleavage of the racemate and recrystallisation of the mixture from acetone gave alternating crops of *d*-enantiomer and *l*-enantiomer. Several recrystallisations gave pure *d*- and *l*-enantiomers  $[\alpha]_{578}^{24} = \pm 94^\circ \pm 1^\circ$ .

A similar acid cleavage of the optically active "ate" complex CLIIb gives an optically inactive spirophosphorane CXLVI ( $R = 4,4'$ -dimethyl-2-biphenyl) (94). The loss of optical activity was explained as before as being due to pseudorotational processes between trigonal bipyramidal structures.

Finally, Hellwinkel (95) has shown by  $^{32}P$  labelling experiments that the "onium-ate" complex CXXVI does not undergo any syncoordination to the isomeric phosphorane structure CLIV.

#### Acknowledgment.

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#### Note added in proof:

Since the early part of this review was prepared, Quin (96) has published a full account of his studies on 1-methylphosphole (XII, R=Me). A detailed analysis of the proton and  $^{31}\text{P}$  N.M.R. spectra of XII (R=Me) was reported and the small  $^{31}\text{P}$  chemical shift (+8.7 p.p.m. relative to external 85%  $\text{H}_3\text{PO}_4$ ) compared with other unsaturated tertiary phosphines was taken to indicate some delocalization of the lone-pair electrons of the phosphorus atom. The UV spectrum of XII (R=Me) ( $\lambda$  max 286 m $\mu$ , log  $\epsilon$  3.89 in isoctane), is not consistent with a cyclic divinylphosphine and resembles that of *N*-methylpyrrole. Mass spectrometric evidence also supports a pyrrole type electronic structure.

The  $\text{pK}_a$  value of XII (R=Me) was found to be 0.5 which is very much less than is normal for tertiary phosphines ( $\text{pK}_a=7-8$ ) and also lower than the value ( $\text{pK}_a=5.2$ ) calculated (96) for divinylphosphines.

1-Methylphosphole forms a brownish polymeric material on treatment with 6*N* hydrochloric acid and this behaviour is very similar to that of pyrroles. The phosphole oxidizes rapidly in air

and also forms what was assumed to be a *P*-dibromide.

There is therefore strong evidence for a considerable degree of aromatic character in the phosphole system.

A molecular and crystal structure determination of the Diels-Alder dimer of 1-ethoxyphosphole oxide (VIII) has been reported (97) and the structure XX(R=OEt, R'=H and X=O) has been confirmed.

It should also be noted that in spirophosphoranes of type CXXIX, the group R will undergo nucleophilic ligand exchange with organo lithium compounds R'Li so as to replace R by R' (98).

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