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Compounds of Two-coordinated Phosphorus

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A systematic account is given of the available literature data on phosphorus(III) compounds with multiple bonds. The methods of synthesis, the physicochemical properties, and the chemical properties of phosphamethinecyanines, phosphorins, (phosphabenzenes), 1,2,3-diazaphospholes (phosphadiazoles), and other compounds of two-coordinated compounds are considered. The bibliography includes 100 references

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I. INTRODUCTION

Compounds containing two-coordinated phosphorus were virtually unknown until 1964. It was believed that structures with multiple bonds involving a tervalent phosphorus atom are unstable. The diatomic molecules with one-coordinated phosphorus described previously, namely P_2, PN, and PO, were detected only by spectroscopic methods at high temperatures [1-3]. Methinophosphide (phospha-acetylene, carbophosphil) HC≡P could be isolated in the form of a white solid stable at the temperature of liquid nitrogen, but polymerising above −120°C, [4-6] Apart from methinophosphide, its halogeno-, amino-, and hydroxy-derivatives were described [7]. The author demonstrated the monomeric nature of these derivatives by the fact that the phosphorus signals in the ^{31}P NMR spectra consist of narrow singlets. Evidence confirming the molecular weight adopted is not quoted in the relevant paper.

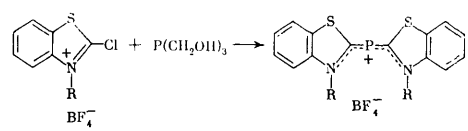
Kirby and Warren [8] compared phosphorus with carbon and nitrogen and adduced a number of causes which explain the greater difficulty of the formation of multiple bonds involving phosphorus(III). The conditions for sufficient overlapping of the orbitals and the formation of π-bonds are apparently more favourable for the $2p$ orbitals of the atoms of Second Period elements, separated by $2p_\sigma$-bonds, than for the more diffuse $3p$ orbitals of the atoms separated by the longer $3p_\sigma$-bonds. Furthermore the repulsion of the filled inner electron shells of the atoms of the Third Period elements constitute an additional obstacle, hindering the decrease of the bond length required for the formation of strong p_π-bonds [9]. Hudson [10] and Mulliken [11] suggest that the relative instability of the π-bonds involving Third Period elements is also caused by the greater energy of their σ-bonds, in particular by the contribution of the $d\sigma$-orbitals.

Nevertheless, a number of acyclic and cyclic compounds containing two-coordinated phosphorus in CPC (phosphamethinecyanines and phosphorins), CPN (diazaphospholes), and NPN [bis(trimethylsilyl)aminotrimethylsilyliminophosphine and triazaphospholes)] fragments have been synthesised recently.

II. ACYCLIC COMPOUNDS

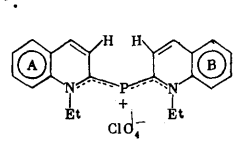
1. PHOSPHAMETHINECYANINES

The first compounds of two-coordinated phosphorus–phosphamethinecyanines–were obtained from *N*-alkylated benzothiazolyl fluoroborates and tris(hydroxymethyl)phosphine in the presence of ethyldi-isopropylamine in dimethylformamide [12]:



Symmetrical and asymmetric phosphamethinecyanines were synthesised analogously from benzothiazolium and quinolinium fluoroborates and perchlorates [12-14]. Instead of tris(hydroxymethyl)phosphine, tris(trimethylsilyl)-phosphine may be used to obtain phosphamethinecyanines.[15] The stability of structures with two-coordinated phosphorus is apparently due to the involvement of the phosphorus atom in conjugation. An X-ray diffraction study of the structure of bis-(*N*-ethyl-2-benzothiazolyl)phosphamethinecyanine showed that the planes of both benzothiazole rings are in the *cis*-positions relative to the phosphorus atom and are rotated relative to one another only by 6°. The C–P–C angle is 104.6°. Both C–P bonds have the same length, amounting to 1.76 Å, i.e. they are longer than the P=C bonds in phosphinylides (1.65–1.68 Å) and shorter than the P–C bonds in triphenylphosphine (1.83 Å).[13]

The replacement of benzothiazole by quinoline in phosphamethinecyanines leads to an appreciable change of molecular geometry, as was to be expected from steric considerations [the close proximity of the hydrogen atoms attached to $C_{(3)}$] [16]:

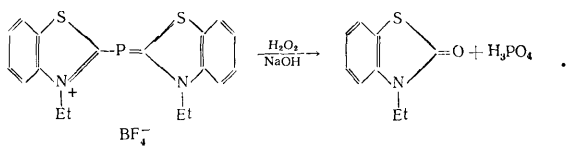


Thus the planes of the quinoline rings A and B are inclined at angles of 40° and 24° relative to the C–P bonds of the cyanine plane. As a result of this, conjugation in the cyanine cation is hindered, which leads to some increase in the length of the C–P bonds, to 1.81 and 1.77 Å, The C–P–C angle in bis-(1-ethyl-2-quinolinyl)-phosphamethinecyanine is 100.4°.

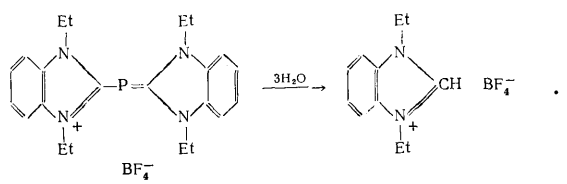
The chemical shift of phosphorus in the ^{31}P NMR spectra is −24.9 p.p.m. for bis-(*N*-ethylbenzothiazolyl)-phosphamethinecyanine and −48.8 p.p.m. for the bis-quinolinyl derivative (relative to 85% H_3PO_4).

The electronic spectra of phosphamethinecyanines resemble those of monomethine- and monoazamethine-cyanines, the position of λ_{max} corresponding to the lower electronegativity of phosphorus compared with carbon and nitrogen [13,14].

The majority of reactions of two-coordinated phosphorus are associated with oxidations involving the phosphorus atom. Phosphamethinecyanines are decomposed by oxidising agents. When treated with 30% hydrogen peroxide in an alkaline solution, the salts of bis-(*N*-alkyl-2-benzothiazolyl)- and bis-(*N*-alkyl-2-quinolinyl)-2-phosphamethinecyanines are smoothly oxidised to 2-benzothiazolone and 2-quinolone derivatives and phosphates. A large number of unidentified radicals are formed at intermediate stages [16]:



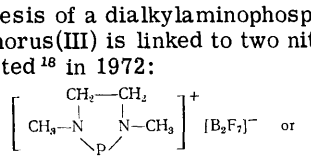
Like methinecyanines, phosphamethinecyanines are protonated by strong acids with formation of colourless dications, which can be reconverted into phosphamethinecyanines by treatment with weak bases [17]. When benzimidazolylphosphamethinecyanine was treated with silver tetrafluoroborate in methanol, colourless crystalline silver complexes, decomposed by an excess of methanol, were isolated. Mercury chloride forms similar complexes with phosphamethinecyanines. Water decomposes phosphamethinecyanines [17]:



2. BIS(TRIMETHYLSILYL)AMINOTRIMETHYLSILYLIMINOPHOSPHINE

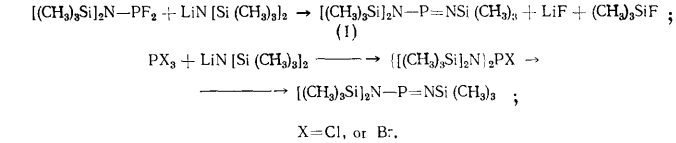
Compounds of two-coordinated phosphorus(III) with a phosphorus–nitrogen multiple bond were unknown until 1972. The reasons for the difficulty of the formation of $p\pi-p\pi$ bonds involving phosphorus(III) were noted above. One need only point out that, whereas the difference between the energies of the σ- and π-bonds for the phosphorus–carbon linkage amounts to 18 kcal mole^{-1}, the difference for the P–N linkage is 23 kcal mole^{-1}.

The synthesis of a dialkylaminophosphonium cation, in which phosphorus(III) is linked to two nitrogen atoms, was briefly reported [18] in 1972:



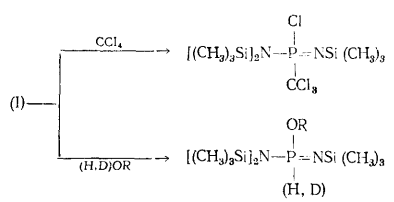
A downfield shift of the ^{31}P signal, which is unusual for organophosphorus compounds was noted in the ^{31}P NMR spectrum of this cation: $\delta_{^{31}P}$ = −274 p.p.m. (in toluene) and −264 p.p.m. (in 1,2-dichloroethane). The magnitude of this shift constituted the only argument justifying the structure adopted.

The first compound with a −P=N group, whose structure was demonstrated rigorously—bis(trimethylsilyl)-aminotrimethylsilyliminophosphine (I)—was obtained by two similar methods [19,20]:

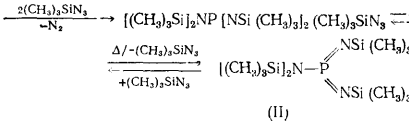


Compound (I) is a yellow-green liquid sensitive to hydrolysis, which is fairly stable in a pure form at temperatures below 0°C and in the absence of light. The composition and structure of the aminoiminophosphine (I) were demonstrated by elemental analysis, mass-spectrometry, and infrared and NMR spectroscopy. The chemical shift of phosphorus is −325.5 p.p.m. This range of chemical shifts had not been reached by any of the phosphorus compounds known hitherto.

The phosphorus atom in bis(trimethylsilyl)aminotrimethylsilyliminophosphine is highly electrophilic, which is manifested in a number of exothermic 1,1-addition reactions [19]:



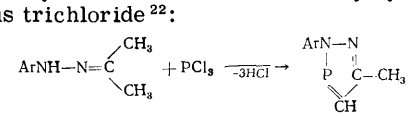
The interaction of bis(trimethylsilyl)aminotrimethylsilyliminophosphine with trimethylsilyl azide leads to phosphine di-imide(II), the first representative of compounds with a three-coordinated phosphorus(V) atom [21]:



III. FIVE-MEMBERED HETEROCYCLES

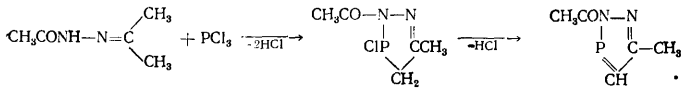
1. DIAZAPHOSPHOLES

The first derivatives of 1,2,3-diazaphospholes were synthesised by the reaction of acetone arylhydrazones with phosphorus trichloride [22]:

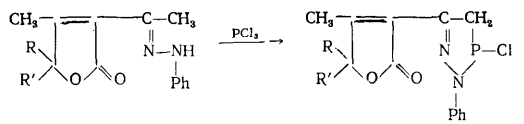


The excess initial phenylhydrazone or triethylamine serves as the hydrogen chloride acceptor. The phenylhydrazones of alkyl methyl ketones and acetaldehyde, β-cyanoethyl-, benzoyl-, and butoxycarbonyl-hydrazones of acetone, and β-cyanoethylhydrazones of acetophenone and *p*-bromoacetophenone react similarly with phosphorus trichloride[22-28].

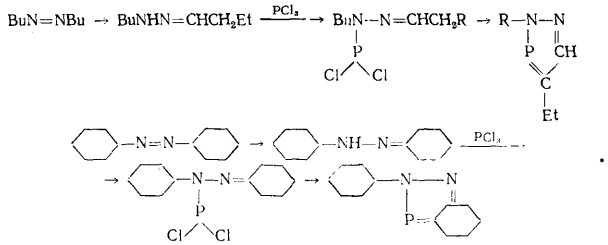
The reaction of phosphorus trichloride with acetone acetylhydrazone under the same conditions leads to 2-acetyl-3-chloro-5-methyl-1,2,3-diazaphospholine, which is converted into 1,2,3-diazaphosphole by additional treatment with triethylamine[24,26-29]:



The formation of 3-chlorodiazaphospholines was also observed when the phenylhydrazones of 2-acetyl-2-but-4-enolides reacted with phosphorus trichloride[30]:



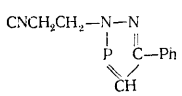
A new method of synthesis of diazophospholes from azo-compounds and phosphorus trichloride was published in 1974. The reaction mechanism involves the isomerisation of the azo-compound to hydrazones[31]:



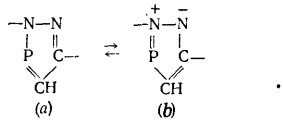
It is interesting to note that, having replaced phosphorus trichloride by arsenic trichloride in the reaction with hydrazones, Märkl obtained a series of arsadiazoles[32,33].

(a) Physicochemical Properties

An X-ray diffraction study of 2-(β-cyanoethyl)-5-phenyldiazaphosphole[34]



showed that the five-membered heterocycle and the benzene ring are planar (the maximum deviation of the atoms from their average planes does not exceed 0.01 Å), the mutual rotation of the planes of the rings is by an angle of only 16.1°, and the $C_{(2)}-C_{(3)}$ bond is coplanar with the planes of both rings, so that the conjugation between the two fragments is unaffected. The P–N and P=C bond lengths are respectively 1.676 and 1.702 Å, i.e. corespond to partial double bond character. The C=N bond length (1.34 Å) is comparable to the value (1.32 Å) found for the diazomethane molecule and the N–N bond length (1.34 Å), although appreciably smaller than the value corresponding to a single bond, is nevertheless characteristic of the bonds between nitrogen atoms of the type =N–N=. Finally, $C_{(1)}-C_{(2)}$ (with a length of 1.41 Å) is a typical linkage with a bond order of 1.5. The observed distribution of bond lengths in the diazaphosphole ring corresponds to partial delocalisation of electrons with structure *a* predominating to some extent:



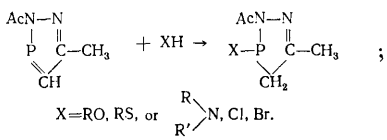
X-Ray diffraction analysis confirmed that 2-(β-cyanoethyl)-5-phenyldiazaphosphole is not dimeric, since the atoms of the closest molecules in the unit cell are separated by a distance greater than the van der Waals radius. The results of the X-ray diffraction study of 2-(β-cyanoethyl)-5-phenyldiazaphosphole are consistent with earlier electron-diffraction data[23,29] for 2-acetyl-5-methyldiazaphosphole and 5-methyl-2-phenyldiazaphosphole.

The ultraviolet spectra of diazaphosphole are similar to those of the corresponding triazoles. There is a bathochromic shift due to the lower electronegativity of phosphorus compared with nitrogen. The wavenumber of the most intense band (1295 cm^{-1}) in the infrared spectra of diazaphospholes was assigned to the pulsating (puckering?) vibration of the ring. The lower value of this wavenumber compared with those of the pulsating vibrations of pyrazoles, triazoles, and oxadiazoles can be explained by the greater mass of the phosphorus atom in the ring[22].

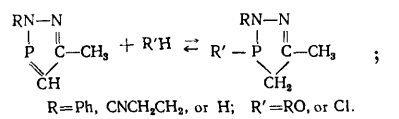
The chemical shift of phosphorus, determined by the method of double phosphorus–proton resonance, is −225 p.p.m. for 2-phenyldiazaphosphole and −238 p.p.m. for 2-acetyldiazaphosphole.

(b) Chemical Properties

A wide variety of compounds with an active hydrogen atom readily add to the multiple bonds of diazaphospholes, which has been investigated in greater detail for 2-acetyl-4-methyldiazaphosphole. The latter reacts readily with alcohols, amines, phenols, mercaptans, nitrogen-containing heterocycles, and hydrogen halides[28]:



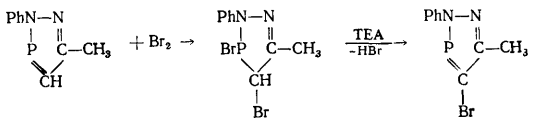
When alcohols and hydrogen chloride add to 2-phenyldiazaphosphole and when alcohols add to 2-(β-cyanoethyl)-diazaphosphole and diazaphospholes unsubstituted in the 2-position, the products are diazaphospholines, which are thermally unstable and are readily reconverted into the initial compounds[35]:



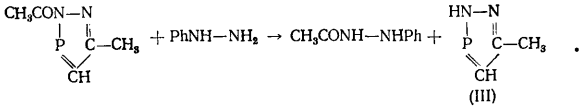
On treatment with an excess of alcohol or alkali, diazaphospholes decompose to hydrazones and phosphites.

Bromine also adds to the C=P bond of 2-phenyldiazaphosphole, giving rise to the unstable 3,4-dibromo-5-methyl-2-phenyldiazaphosphole, the formation of which was confirmed by the PMR method. On treatment of the

reaction mixture containing the above compound with triethylamine (TEA), 4-bromo-5-methyl-2-phenyldiazaphosphole was obtained[35]:



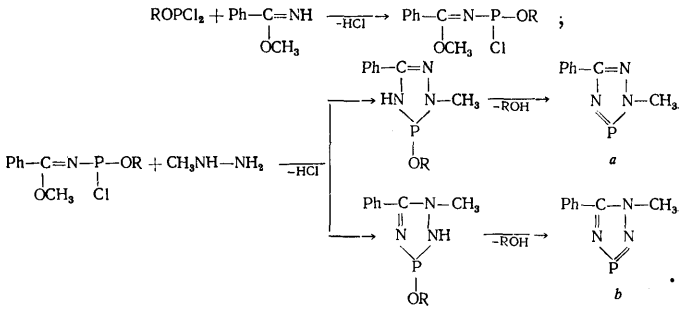
The reaction of 2-acetyl-5-methyldiazaphosphole with phenylhydrazine leads to β-acetylphenylhydrazine and a diazaphosphole unsubstituted in the 2-position: 5-methyldiazaphosphole(III):



The structure of compound (III) was demonstrated by infrared spectroscopy, NMR, and mass spectrometry[35].

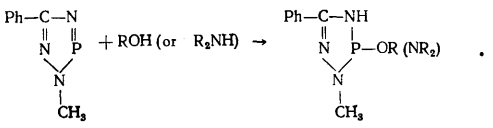
2. TRIAZAPHOSPHOLES

Triazaphospholes were synthesised from *O*-methyl iminobenzoate, phosphorodichloridite, and methylhydrazine[36]:



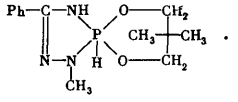
Structure *a* and *b* were attributed on the basis of NMR spectra to the isomeric substances obtained, the ratio of the isomers being 6 : 1. The chemical shifts of the triazaphospholes are −256.1 and −261 p.p.m. respectively.

One of the isomeric triazaphospholes (isomer *a*) is involved in the 3,4-addition reaction with certain alcohols and amines:

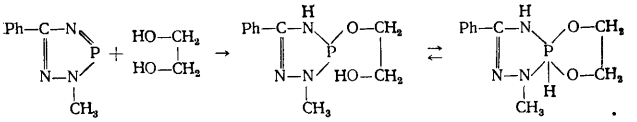


The occurrence of this reaction was inferred[36] from the change in the signals in the ^{31}P NMR spectra. When an attempt is made to vacuum-distill them, the addition products are reconverted into the initial triazaphosphole.

The reaction of triazaphospholes with catechol and pinacone leads to spirophosphoranes:



The reaction with ethylene glycol results in the formation of an equilibrium mixture[36]:



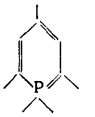
IV. SIX-MEMBERED HETEROCYCLES

1. PHOSPHORINS

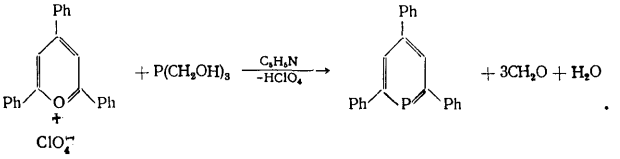
(a) Methods of Preparation

The majority of phosphorin derivatives have been obtained by the reaction of pyrylium salts with phosphines. The general methods for the synthesis of phosphorins also includes the thermolysis of 1-substituted dihydrophosphorins and 1,1-disubstituted phosphorins, the rearrangement of methylenephosphacyclohexadienes, and the reaction of 1,1-dibutyl-1,4-dihydrostannanes with phosphorus tribromide.

Phosphorin derivatives with a phosphorus(V) atom have been synthesised by Märkl[37,38] from cyclic phosphonium salts and by Price[39] from pyrylium fluoroborates by reaction with phenylphosphine:



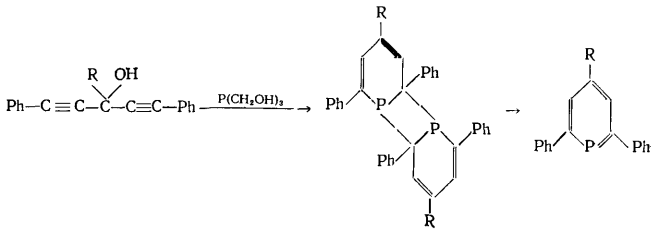
Using tris(hydroxymethyl)phosphine instead of phenylphosphine in the reaction with pyrylium fluoroborate and pyridine as the base and solvent, Märkl synthesised 2,4,6-triphenylphosphorin:



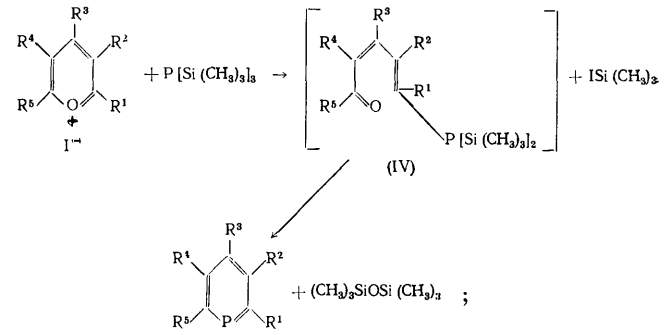
2,4,6-Triphenylphosphorin is a pale-yellow crystalline substance with a melting point of 172–173°, which is readily soluble in organic solvents[40,41]. Tolmachev and Kozlov[42] obtained by the same procedure, involving the reaction of 2,4,6-triarylpyrylium perchlorate with tris-(hydroxymethyl)phosphine, and almost simultaneously with Märkl, a series of arylphosphorins. 4-Indolyl- and 4-pyrrolylpyrylium salts react similarly with tris(hydroxymethyl)phosphine[42,44].

The first phosphorin derivative containing only aliphatic substituents was obtained from 2,4,6-tri-t-butylpyrylium tetrafluoroborate and tris(hydroxymethyl)phosphine[45]. The reaction of tris(hydroxymethyl)phosphine with 1,5-diphenylpenta-1,4-diyn-3-ol gave a phosphorin

dimer, which can be cleaved to the monomeric phosphorin by thermal and photochemical reactions[46]:



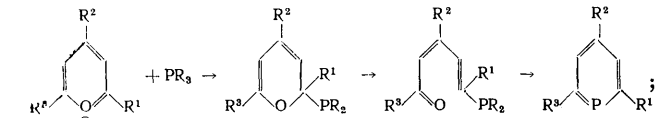
Märkl et al.[15] suggested that tris(trimethylsilyl)phosphine be used to obtain phosphorin derivatives instead of tris(hydroxymethyl)phosphine. In this case there is no need for solvents with basic properties and the yield of substituted phosphorins increases:



$R^1=R^5=$Ph, p-$CH_3C_6H_4$, p-$CH_3OC_6O_4$; $R^2=R^4=$H,Ph; $R^3=$Ph, or p-$CH_3OC_6H_4$.

However, when tris(trimethylsilyl)phosphine is used to synthesise phosphorin derivatives, the second reactants can be only pyrylium iodides. The fluoroborates and perchlorates are unsuitable in view of the weak nucleophilic properties of the anions. The intermediate compound (IV) was not isolated, since spontaneous elimination of hexamethyldisiloxane leads to ring closure with formation of a substituted phosphorin.

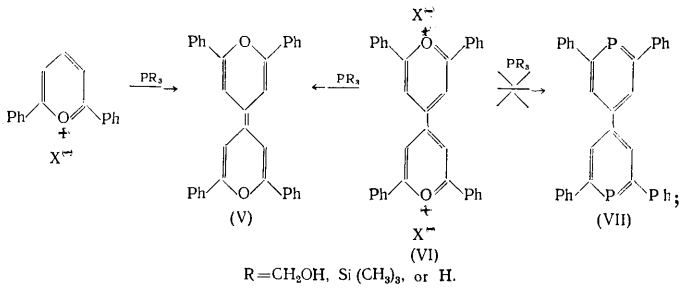
Together with tris(hydroxymethyl)- and tris(trimethylsilyl)-phosphines, unsubstituted phosphine can also be used to synthesise substituted phosphorins. 2,4,6-Trialkylphosphorins, the synthesis of which is hindered by steric factors, have been obtained with the aid of unsubstituted phosphine. The greater the difference between the dimensions of the substituents in the pyrylium salt and of the phosphine molecule, the easier the nucleophilic attack by phosphine on the carbon atom in the 2-position of the pyrylium salt. Subsequently the reaction leads to the formation of a substituted phosphorin:



R=CH_2OH, Si $(CH_3)_3$, or H; R^1, R^2, R^3=CH_3, or Ph.

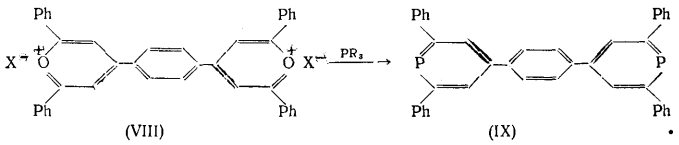
The use of unsubstituted phosphine, whose molecule is much smaller than those of tris(hydroxymethyl)- and tris(trimethylsilyl)-phosphines, extended the scope of the method for the synthesis of phosphorin derivatives. The reaction with unsubstituted phosphine is carried out under the conditions of acid catalysis at 120–130°C.[47]

The method of synthesis of phosphorin derivatives by the reaction of pyrylium salts with phosphines is unsuitable for salts without a substituent in the 4-position. In this case the $C_{(4)}$ atom is involved in the reaction and 2,2′,6,6′-tetraphenyldipyrylene (V) is formed[48,49]:



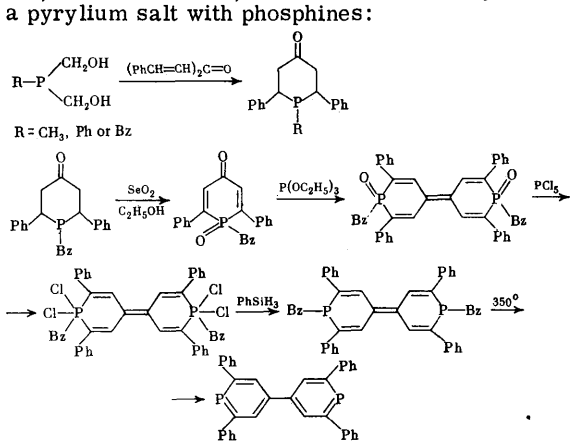
R=CH_2OH, Si $(CH_3)_3$, or H.

On reaction with tris(hydroxymethyl)phosphine, tris-(trimethylsilyl)phosphine, and unsubstituted phosphine, the bispyrylium salt (VI) is reduced to the dipyrylene (V) and does not give rise to the diphosphapyrylene (VII). On the other hand, the pyrylium salt (VIII) reacts under analogous conditions to form the phosphorin derivatives (IX) in a low yield (up to 15%):

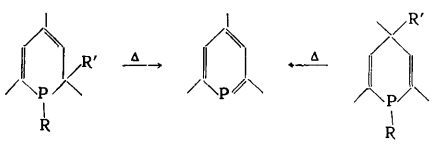


The authors[48,49] attribute this finding to the difference between the redox potentials of compounds (VI) and (VIII).

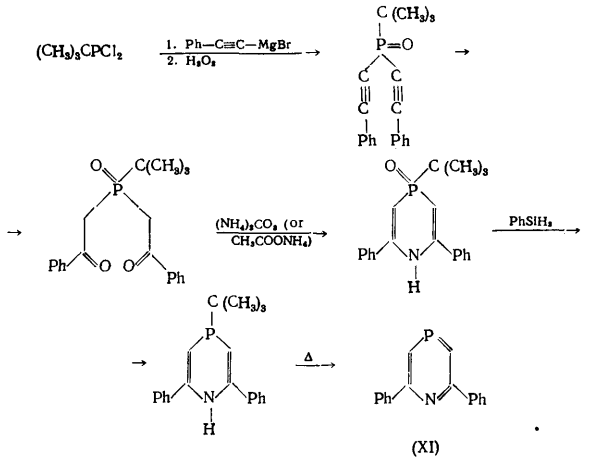
Thermolysis of 1-substituted dihydrophosphorins and 1,1-disubstituted phosphorins. Märkl et al.[49] proposed the following cycle of reactions for the synthesis of diphosphapyrylene (VII), which, as stated above, cannot be obtained by the reaction of a pyrylium salt with phosphines:



The thermolysis of 1,1′-dibenzyl-1,1′-diphospha-4,4′-pyrylene (X) is the first example of the synthesis of phosphorins with a two-coordinated phosphorus atom from 1-substituted dihydrophosphorins[49]. The reaction is general, which Märkl and coworkers showed in relation to the thermolysis of a series of 1-substituted 1,4- and 1,2-dihydrophosphorins:

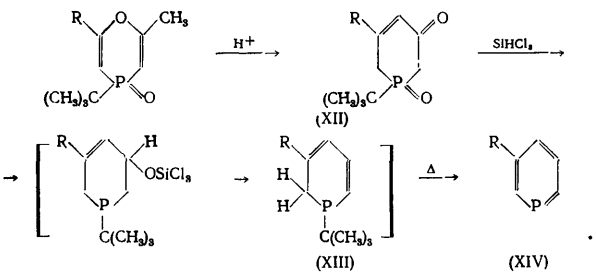


This procedure made it possible to synthesise a wide variety of substituted phosphorins, many of which had been unknown previously[49-52]. Thus a heterocyclic compound containing a nitrogen atom in the six-membered ring together with a two-coordinated phosphorus atom—2,6-diphenyl-1,4-azaphosphorin or phosphapyridine (XI)—was obtained by Märkl and Matthes[50] by means of a scheme based on the thermolysis of 1-substituted 1,4-dihydrophosphorins:



(XI)

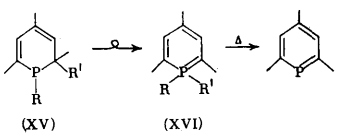
3-Arylphosphorins (XIV), which cannot be synthesised by the reaction of pyrylium salts with phosphines, can be obtained[53] from the readily available 1-t-butyl-3-R-phosphacyclohex-3-ene-1,5-diones (XII) [54]:



(XII) (XIII) (XIV)

The resulting 1-t-butyl-3-R-1,2-dihydrophosphorin (XIII) apparently undergoes thermolysis in the last stage of the reaction.

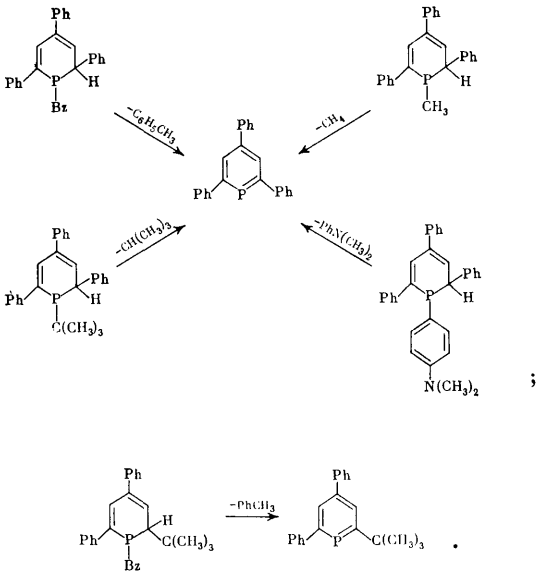
Märkl and Merz[51] showed that the thermolysis of 1-substituted 1,2-dihydrophosphorins involves the migration of the substituent from the 2-position and the formation of 1,1-disubstituted phosphorins in the first stage:



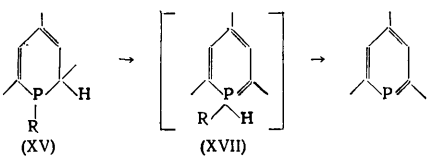
(XV) (XVI)

A similar rearrangement of 1-substituted 1,2-dihydrophosphorins (XV) to 1,1-disubstituted phosphorins (XVI) is the first example of the transformation of tertiary phosphines into phosphinoalkylenes and can be accounted for solely by the stabilisation of the phosphorin system as a result of conjugation. The conditions for the rearrangement depend on the substituents R and R′. Thus the temperature of the rearrangement is 220° for R = C_6H_5 and R′ = $CH_2C_6H_5$, 180°C for R = R′ = $CH_2C_6H_5$, 220°C for R = C_6H_5 and R′ = $CH_2CH{=}CH_2$, and 25°C for R = $CH_2C_6H_5$ and R′ = $C(C_6H_5)_3$.

1-Alkyl- and 1-aryl(2*H*)-dihydrophosphorins are cleaved similarly to phosphorins:



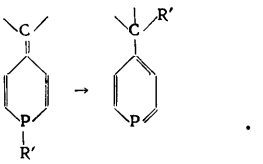
According to the authors[51], the mechanism of this reaction when the latter involves compounds (XV, R′ = H) also consists of the conversion of 1-alkyl(aryl)-2*H*-dihydrophosphorins into 1-alkyl(aryl)-1*H*-phosphorins with subsequent synchronous 1,1-elimination:



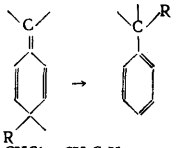
(XV) (XVII)

The authors draw an analogy between this process and the spontaneous N–H → P–H isomerisation of cyclophosphazadienes to cyclotriphosphazenes[55]. Since the formation of 1-R-1*H*-phosphorins (XVII) has not been demonstrated unambiguously hitherto, one cannot rule out the possibility of 1,2-elimination.

Rearrangement of methylenephosphacyclohexadienes to phosphorins. Continuing the investigation of the thermal behaviour of phosphorus-containing heterocycles, Märkl and Fischer[56] found yet another method for the synthesis of phosphorin derivatives substituted in the 4-position. This involves the rearrangement of methylenephosphacyclohexadienes to phosphorins:

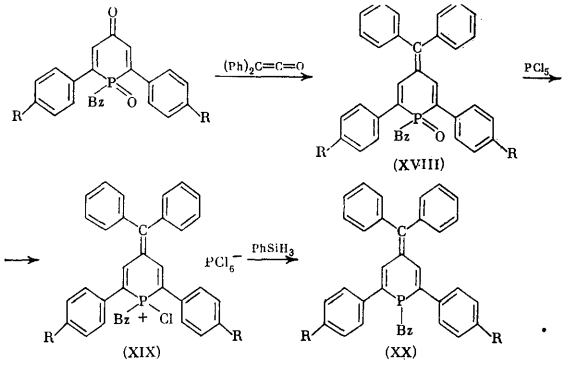


A similar rearrangement of carbocyclic compounds has been known for a long time[57]:

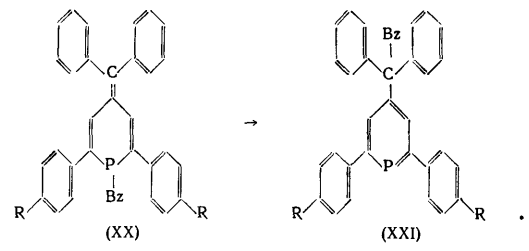


R=CCl_3, $CHCl_2$, $CH_2C_6H_5$, or $CH_2CH{=}CH_2$.

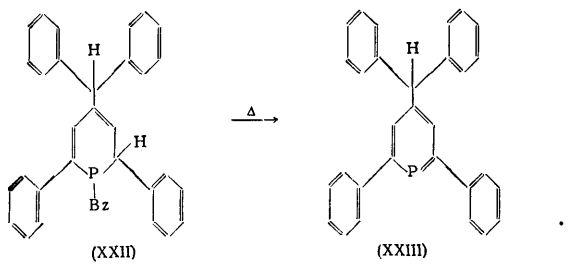
Märkl and Fischer[56] studied the thermolysis of 1-benzyl-4-methylene-1-phosphacyclohexa-2,5-diene (XX), synthesised via the following scheme:



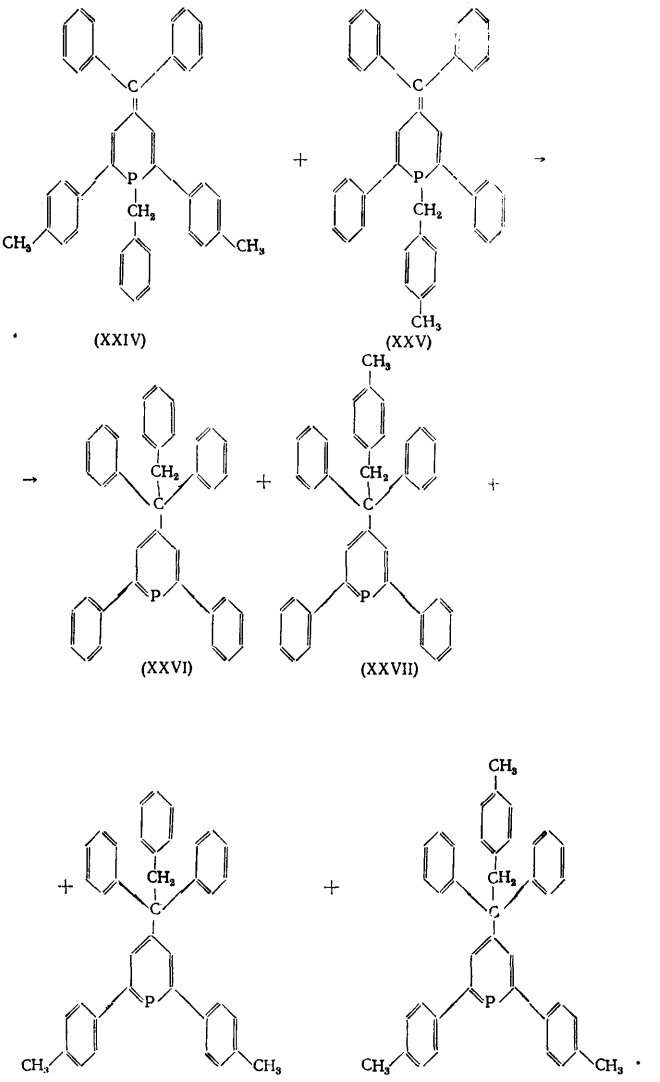
At the melting point (250°C), the resulting methylenephosphacyclohexadiene (XX) undergoes the above rearrangement. This leads to the quantitative formation of a phosphorin derivative (XXI) with a two-coordinated phosphorus atom:



It is interesting to note that the reaction of the oxide (XVIII) in which R = H with phosphorus pentachloride unexpectedly does not lead to the dark-red hexachlorophosphate (XIX) and gives rise instead to yellow hygroscopic salt of unknown structure, whose reduction with phenylsilane gives the 1,2-dihydrophosphorin derivative (XXII). The latter undergoes thermolysis, like the dihydrophosphorin described above, with elimination of toluene and the formation of the phosphorin (XXIII)[56]:



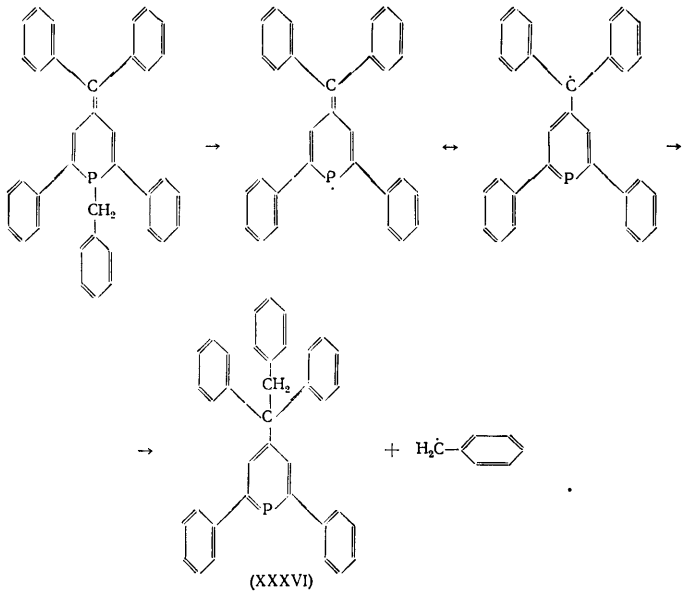
A mass-spectrometric study[58] of the thermolysis products of a mixture of 1-benzyl-4-diphenylmethylene-2,6-di-*p*-tolyl-1-phosphacyclohexa-2,5-diene (XXIV) and 2,6-diphenyl-4-diphenylmethylene-1-*p*-xylylphosphacyclohexa-2,5-diene (XXV) revealed the presence of four reaction products, which supports an intermolecular mechanism of the rearrangement:



The rearrangement probably has a radical mechanism. This hypothesis is based on the analogies, in the first place, with tertiary phosphines, for which thermal heterolytic dissociation of the P–C bond is unknown, and, in the second place, with 1,1-dibenzylphosphorins, the thermolysis of which results in the formation of bibenzyl, which demonstrates the formation of benzyl radicals. The radical mechanism of the rearrangement has been confirmed by experimental data.

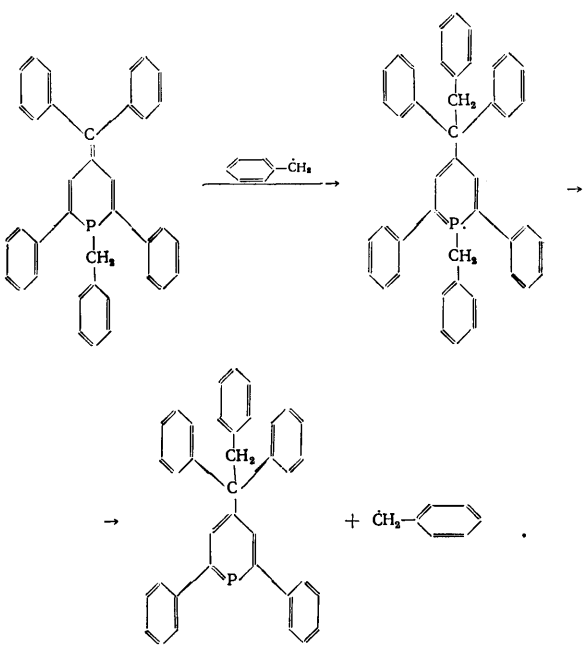
The benzyl radicals formed from Hg $(CH_2C_6H_5)_2$ are capable of becoming involved in the rearrangement of methylene phosphacyclohexadiene. Thus the rearrangement of 1-*p*-xylyl-1-phosphacyclohexadiene (XXV) in the presence of $Hg(CH_2C_6H_5)_2$ entails the formation of the benzylphosphorin (XXVI) together with the xylylphosphorin

(XXVII). The probable mechanism of this rearrangement is as follows[58]:

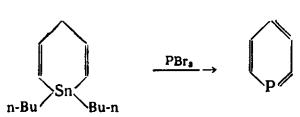


(XXXVI)

According to the authors, the benzyl radical formed reacts immediately with 1-benzyl-1-phosphacyclohexadiene, by analogy with the carbocyclic "semibenzene–benzene" rearrangement, which has been thoroughly investigated:

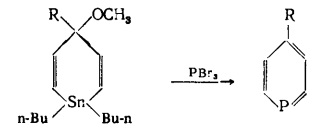


The reaction of phosphorus tribromide with 1,1-dibutyl-1,4-dihydrostannanes. The hitherto unknown unsubstituted phosphorin was synthesised by the reaction of phosphorus tribromide with 1,1-dibutyl-1,4-dihydrostannane[59]:

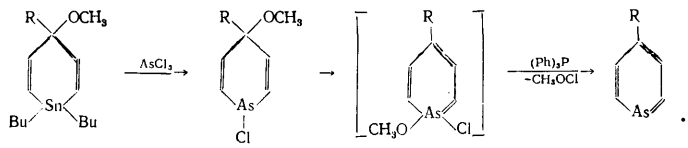


Unsubstituted phosphorin is a colourless liquid, unstable in air, with the characteristic smell of phosphine[59]. In this compound, the properties of the ring are not masked by the effect of substituents, which were to some extent responsible for the interest in its synthesis.

The above method was used by Märkl and Kneidl[60] to obtain previously unknown 4-monosubstituted phosphorins from 4-substituted 4-methoxy-1,4-dihydrostannanes:



The mechanism of the reaction was examined in relation to the synthesis of arsenic compounds–arsenines, obtained when phosphorus tribromide is replaced by arsenic trichloride:



(b) Physicochemical Properties

The ultraviolet, infrared, and PMR spectra of unsubstituted phosphorin are similar to those of pyridine[59]. The magnetic anisotropy of the heteroatom is manifested by a downfield shift of the signals of α-protons in the PMR spectrum and an upfield shift of the signals of the protons attached to $C_{(3)}$ and $C_{(4)}$. The 1515 and 1395 cm^{-1} lines in the infrared spectrum of phosphorin have been assigned to the ring vibrations. λ_{max} = 213 μm (ϵ = 19 000) and 246 μm (ϵ = 8500) as well as a shoulder at 290 μm (ϵ = 250) have been noted in the ultraviolet spectrum of phosphorin, i.e. there is a bathochromic shift relative to pyridine and benzene, which is associated with the fact that phosphorus is less electronegative than nitrogen and carbon.

An X-ray diffraction study of 2,6-dimethyl-4-phenylphosphorin showed that the molecule has 2(C_2) symmetry, the symmetry axis passing through the phosphorus atom and the most remote carbon atom of the phenyl substituent. Both six-membered rings are planar within the limits of the accuracy of the X-ray diffraction analysis. The dihedral angle between the rings is 38.8°C, i.e. approaches the angle of 42° found for biphenyl. The C–P–C angle is 103° and may be compared with the values found for triphenylphosphine (103°) and phosphamethinecyanines. Since the phosphorin ring is planar, the remaining P–C–C and C–C–C angles are greater than 120°. A similar increase of the angles occurs also in the pyridine molecule. The P–C bond length is 1.75 Å, i.e. is comparable to the 1.76 Å bond length found for bis-(*N*-ethyl-2-benzothiazolyl)phosphamethinecyanine. The C–C bond lengths are virtually the same as in benzene[61,62].

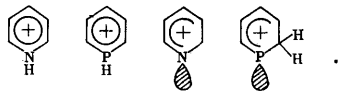
In the ultraviolet spectra of substituted phosphorins, λ_{max} is in the range 258–299 μm and there is also a bathochromic shift relative to the analogous pyridines and aromatic hydrocarbons. The chemical shift $\delta_{^{31}P}$ in the NMR spectra is −178.2 p.p.m. for 2,4,6-triphenylphosphorin and −178.5 p.p.m. for 2,4,6-tri-t-butylphosphorin

(relative to 85% H_3PO_4).[40,63] Such a large downfield displacement of the signal is explained by the effect of the magnetic anisotropy of the $-P=C\langle$ multiple bond.

The introduction of nitrogen into a system containing a two-coordinated phosphorus atom leads, as expected, to a downfield shift of the ^{31}P signals. Thus $\delta_{31P} = -245.4$ p.p.m. for 2,6-diphenyl-1,4-azaphosphorin (XI).[50]

NMR, ultraviolet spectroscopic, and X-ray diffraction data led to the conclusion that phosphorins are aromatic. This has bene confirmed by calculations of the electronic structures of phosphorins by the CNDO/2 method, which showed that the main contribution to π-bonding comes from the $3p_z$ orbital of phosphorus together with an appreciable contribution of the d_π orbitals[64-66].

The CNDO/2 method also made it possible to estimate the basicity of phosphorin[65]. By analogy with pyridine, basic properties might have been expected for phosphorin, but calculations disproved this hypothesis. The calculated proton affinities of pyridine and phosphorin are 328 and 232 kcal mole^{-1} respectively. Since the true experimental proton affinities of these molecules are unknown, Oehling and Schweig[65] obtained "experimental" values of 213 kcal mole^{-1} for pyridine and 192 kcal mole^{-1} for phosphorin by comparing the experimental and theoretical proton affinities of NH_3 and PH_3. The difference between the proton affinities of 21 kcal mole^{-1} corresponds to a difference of 15 units between the pK_a values. Thus it is found that the basicity of two-coordinated phosphorus(III) in phosphorin is just as low as that of the perchlorate and iodide anions ($pK_a = -9$ for $HClO_4$ and $pK_a = -8$ for HI). However, the low pK_a predicted for the phosphorinium ion protonated at the phosphorus atom [the ion (XXVII)] does not imply that phosphorin cannot be more easily protonated at other atomic centres. Indeed primary [preliminary] calculations have shown that protonation in the 2-position is much more preferable for phosphorin [the ion (XXVIII)]:



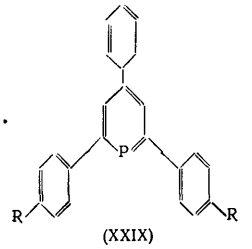
(XXVII) (XXVIII)

Data obtained from the photoelectronic spectra of substituted phosphorins permitted certain conclusions[89]. As was to be expected, phosphorins ionise more readily than the corresponding pyridines, but, the energies of the molecular orbitals of pyridines and phosphorins differ little. The authors suggest that the difference between the energies of molecular orbitals in the pyridine and phosphorin series is probably associated with the contribution of the atomic orbitals of the heteroatom and the neighbouring carbon atoms. The highest occupied molecular orbital (HOMO) of phosphorin is a molecular π-orbital, while in pyridine it is the orbital of the free electron pair of the nitrogen atom. The free electron pair of the phosphorus atom has a greater amount of *s* character than that of the nitrogen atom in pyridine. The electron pair of phosphorus occupies a more diffuse orbital than that of nitrogen. The sequence of π-orbitals in the phosphorin system differs from that in pyridine.

Molecular π-orbitals with a non-zero coefficient at the heteroatom have a higher energy than the molecular π-orbitals with a node at the heteroatom[64-68].

(c) Chemical Properties

Oxidation. The oxidation of 2,4,6-triphenylphosphorin (XXIXa) by various phenoxy-radicals proceeds via a radical mechanism[69], which is confirmed by the ESR spectrum where the constant for the hyperfine interaction of the unpaired electron with the nucleus of the phosphorus atom $a_p = 23.2$ G.

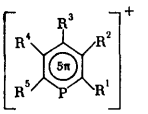


(*a*) R=H; (*b*) R=OCH_3

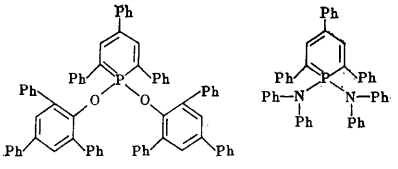
(XXIX)

The spectrum is independent of the structure of the oxidant, which leads to the conclusion that there is no linkage between the phenoxy-group and the phosphorus-containing group.

2,4,6-Tri-t-butylphenoxy-a and 2,6-di-t-butyl-4-phenylphenoxy-radicals do not oxidise 2,4,6-triphenylphosphorin. Probably either the t-butyl group causes steric hindrance to the reaction or the oxidation-reduction potential of the phenoxy-radical is insufficient. The decrease of the oxidation-reduction potential of compound (XXIX) as a result of the introduction of two *p*-methoxy-groups into the phenyl substituents [compounds (XXIXb)] makes it possible to carry out the oxidation even with lead dioxide. This leads to the formation of the analogous phosphorus-containing radical. According to Dimroth et al.[70], this species has the structure of a radical-cation:

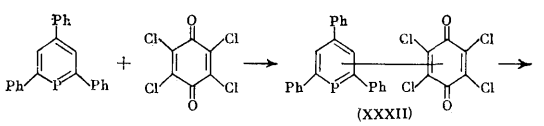


When 2,4,6-triphenylphosphorin reacts with two moles of 2,4,6-triphenylphenoxy-radicals, the product is 2,4,6-triphenyl-1,1-bis-(2,4,6-triphenylphenoxy)phosphorin (XXX). The reaction of tetraphenylhydrazine with 2,4,6-triphenylphosphorin yields 2,4,6-triphenyl-1,1-bis-(diphenylamino)phosphorin (XXXI)[71]:

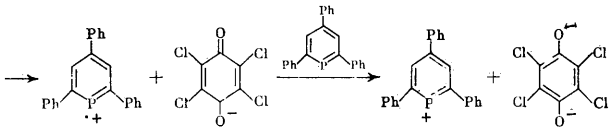


(XXX) (XXXI)

Dimroth and Stade[71,72] investigated the oxidation of triphenylphosphorin by tetrachloro-*p*-benzoquinone. The complex (XXXII) without electron transfer is apparently formed initially, but, when a polar solvent, for example acetonitrile, is added, a doublet with $a_p = 23.2$ G due to the radical-cation (XXXIII) appears in the ESR spectrum:

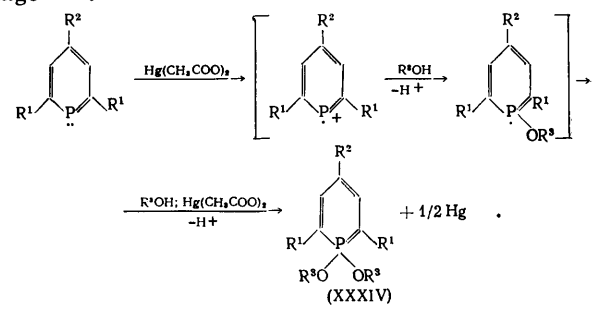


(XXXII)



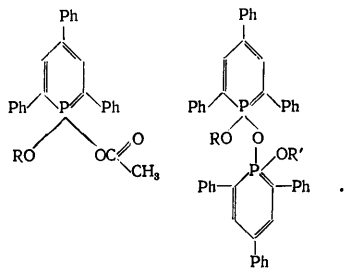
(XXXIII)

When 2,4,6-trisubstituted phosphorins are oxidised by mercury (II) acetate in the presence of an excess of an alcohol of phenol, mercury is liberated and 1,1-dialkoxy- or 1,1-diaryloxy-phosphorins (XXXIV) are formed. The process also probably proceeds via a radical-cation stage [72,73]:

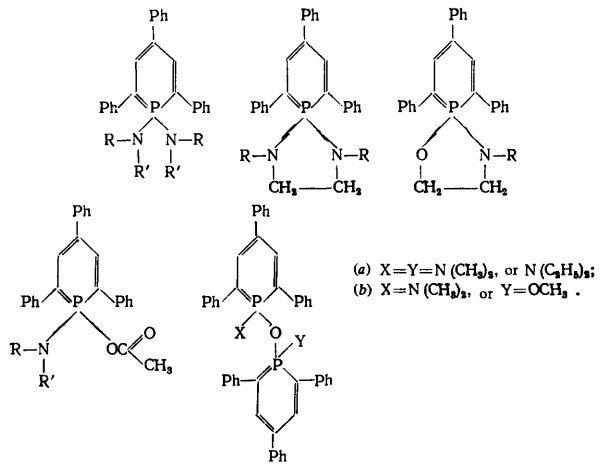


(XXXIV)

A change in the conditions of this reaction leads to the formation of phosphorins belonging to new classes: 1-acetoxy-1-alkoxyphosphorins and substituted bis-(1-alkoxy)hydroxyphosphorins [74]:

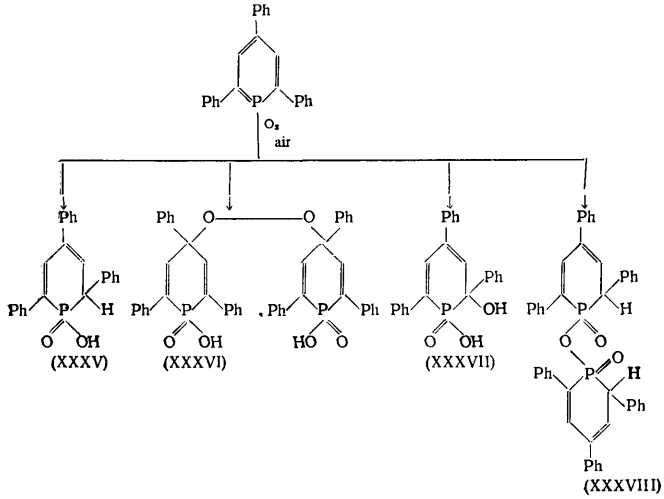


Compounds of the first type described above are formed from trisubstituted phosphorins on oxidation with mercury(II) acetate in dry benzene with one equivalent of alcohol. Those of the second type have been obtained in the presence of 1.5 equivalents of alcohol and one equivalent of water. Depending on the reaction conditions, the following types of compounds have been obtained on oxidation with mercury(II) acetate in the presence of amines [74]:



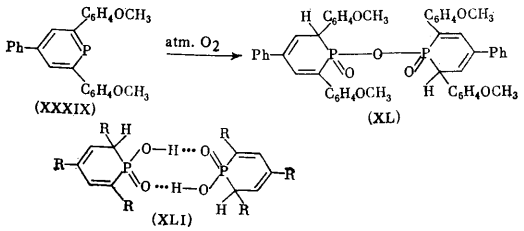
(*a*) X=Y=N(CH$_3$)$_2$, or N(C$_2$H$_5$)$_2$;
(*b*) X=N(CH$_3$)$_2$, or Y=OCH$_3$.

Several 2,4,6-trisubstituted phosphorins have been oxidised by atmospheric oxygen [75,76]. The oxidation of 2,4,6-triphenylphosphorin in benzene solution has been examined in greatest detail [76]; it led to the isolation of compounds (XXXV), (XXXVI), and a substance of unknown structure having the composition $C_{46}H_{36}O_3P_2$. In an earlier investigation [75], the structures of the 2-hydroxyphosphinic acid (XXXVII) and the phosphinic acid anhydride (XXXVIII) were attributed to the products of the oxidation of 2,4,6-triphenylphosphorin by atmospheric oxygen:



(XXXV) (XXXVI) (XXXVII) (XXXVIII).

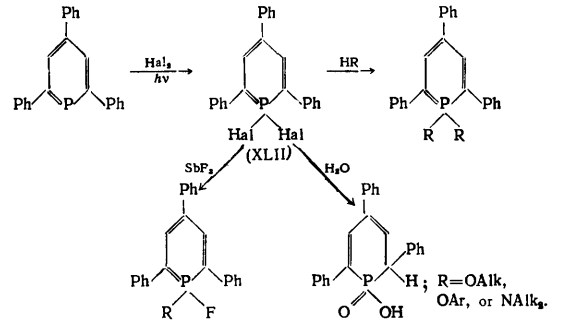
Compound (XL) is formed from 2,6-bis-(4-methoxyphenyl)-4-phenylphosphorin (XXXIX) on oxidation with atmospheric oxygen, while 2,4,6-triphenyl- and 2,4,6-tri-t-butylphosphorins give rise to the dimer (XLI) under the same conditions:



(XXXIX) (XL) (XLI)

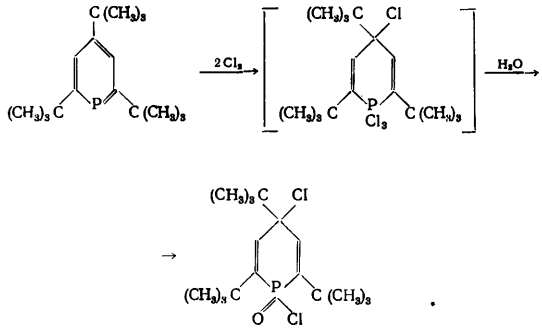
Compounds (XLI) were obtained also on oxidation of 2,4,6-tri-t-butyl- and 2,4,6-triphenyl-phosphorins with hydrogen peroxide in acetone [75,76]. Hydrogen peroxide in ethanol cleaves 2,4,6-tri-t-butylphosphorin, which entails the formation of tri-t-butyl 3,5-di-t-butyl-2-furyl ketone in 30% yield [45].

Kanter and Dimroth [77] oxidised 2,4,6-triphenylphosphorin with bromine and chlorine in the light and obtained 1,1-dihalogenophosphorins (XLII), which readily undergo nucleophilic substitution reactions with water, alcohols, amines, and antimony trifluoride:

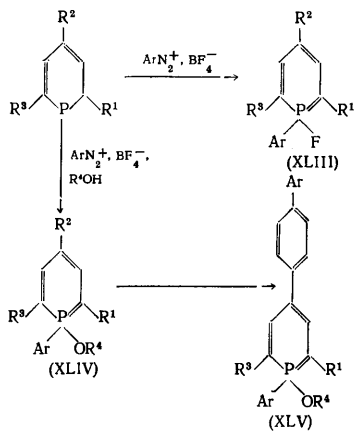


(XLII) R=OAlk, OAr, or NAlk$_2$.

It was shown earlier that 2,4,6-tri-t-butylphosphorin may combine with two moles of chlorine [77]. This involves the formation of 2,4,6-tri-t-butyl-1,1,1,4-tetrachlorophosphorin, which readily hydrolysss and gives rise to a 4-chlorophosphinyl chloride:



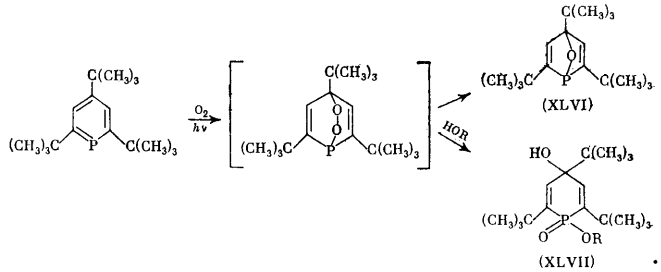
The interaction of trisubstituted phosphorins with aryldiazonium tetrafluoroborates results in the evolution of nitrogen and the formation of 1-aryl-1-fluorophosphorins (XLIII). [78] If the reaction is carried out in the presence of an alcohol, the products are 2,4,6-trisubstituted 1-alkoxy-1-arylphosphorins (XLIV):



The authors [78] suggest that the phosphorin is oxidised initially by the aryldiazonium ion. The oxidation product (a radical cation) then reacts with the aryl radical and the nucleophile (alcohol or F^- ion derived from BF_4^-) to form a 1,1-addition product. In alcohol in the presence of an excess of aryldiazonium tetrafluoroborate, the doubly arylated phosphorin (XLV) is formed together with compound (XLIV). The former can also be obtained directly from compound (XLIV) and the diazonium salt.

When 2,4,6-tri-t-butylphosphorin was oxidised in dry cyclohexane using a mercury lamp in the presence of eosin as the sensitiser, two crystalline compounds were obtained in 15% yield. The structures (XLVI) and (XLVII) were attributed to them on the basis of the results of elemental analysis and infrared and ultraviolet spectroscopic, NMR, and mass-spectrometric measurements [79].

Compound (XLVII) is also obtained when 2,4,6-tri-t-butylphosphorin is oxidised with a mixture of nitric and phosphoric acids. Photochemical oxidation of 2,4,6-triphenylphosphorin leads to a large number of products which are difficult to separate.



Attempts to use concentrated perchloric and sulphuric acid solutions as oxidants for triphenylphosphorin have been described in the literature. Oxidation did occur under these conditions, but the reaction products could not be isolated [75].

Thus the mode of oxidation of phosphorins depends on the oxidant employed, the reaction conditions, and the nature of the substituents in the phosphorin ring. Depending on these factors, the oxidation either involves the phosphorus atom with formation of 1,1-disubstituted phosphorins, or it involves the 1,2- or 1,4-positions with formation of oxidised derivatives of 1,2- or 1,4-dihydrophosphorins, or the phosphorin ring is disrupted.

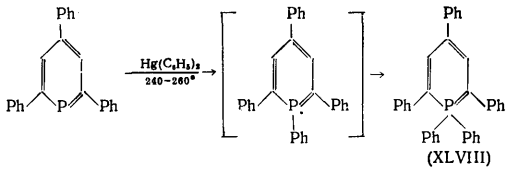
Reduction of phosphorin. Phosphorin derivatives are capable of being reduced to radical-ions [80]. ESR has shown that, when 2,4,6-triphenylphosphorin is reduced with a potassium mirror or a sodium–potassium alloy in tetrahydrofuran, stable radical-anions are formed with a constant for hyperfine interaction of the unpaired electron with the phosphorus nucleus $a_P = 32.4$ G. When a benzene solution of the radical-cation (with $a_P = 23.2$ G), [69] obtained by oxidising triphenylphosphorin, is added to a solution of the radical-anion, the signals of both radicals in the ESR spectra vanish and triphenylphosphorin is reformed.

On being reduced, 2,4,6-triphenylphosphorin can combine with three electrons in succession and the reaction products can likewise give up three electrons in succession. In the absence of air, all three reduction products (radical monoanions, non-radical dianions, and radical-trianions) persist for a long time.

Electrophilic properties of the phosphorin system. As noted above, theoretical calculations by the CNDO/2 method established the presence of weak basic properties in phosphorins. Märkl and coworkers [40] demonstrated experimentally that phosphorins do not exhibit nucleophilic properties. Thus 2,4,6-triphenylphosphorin is not alkylated by methyl iodide or triethyloxonium fluoroborate, reacting instead with nucleophiles and radical reagents.

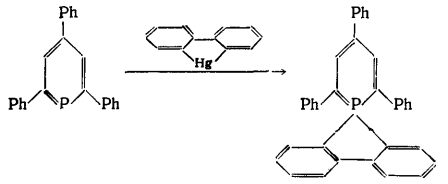
The reaction of triphenylphosphorin with diphenylmercury, involving the formation of 1,1-diarylphosphorins (XLVIII), probably proceeds via a radical mechanism.

Such oxidative arylation probably takes place via the formation of the 1,2,4,6-tetraphenylphosphorinyl radical:

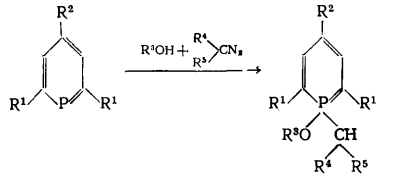


(XLVIII)

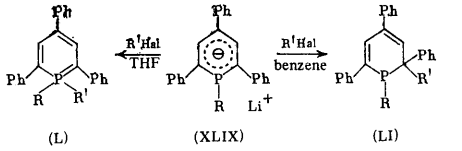
The reaction of diphenylenemercury with 2,4,6-triphenylphosphorin gives a 20% yield of spiro-1,1-diphenylene-2,4,6-triphenylphosphorin[81]:



Trisubstituted phosphorins readily react with diazoalkanes[82] to form 1-alkoxy-1-alkylphosphorins in the presence of alcohols and phenols. It is suggested that the reaction begins with nucleophilic attack by diazoalkanes on the phosphorus atom:

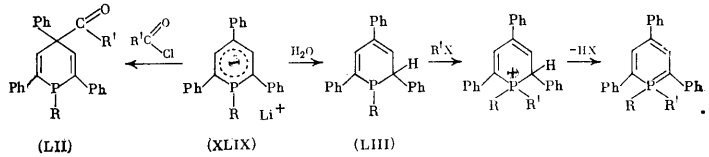


Powerful nucleophiles such as alkyl- and aryl-lithium and organomagnesium compounds react with 2,4,6-triphenylphosphorin even at room temperature[15,83]. The base adds directly to the phosphorus atom with formation of the anion (XLIX), which has ambident properties and has reaction centres in the 1-, 2-, 4-, and 6-positions[84]. In complex-forming solvents such as tetrahydrofuran and 1,2-dimethoxyethane, electrophilic substitution by reaction with alkyl halides takes place preferentially in the 1-position with formation of a 1,1-disubstituted phosphorin (L). In non-polar solvents, for example in benzene, a 2-alkyl-1,2-dihydrophosphorin (LI) is formed:



(L) (XLIX) (LI)

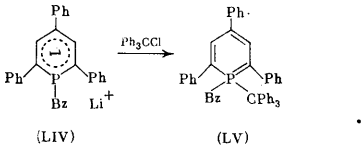
Electrophilic substitution as a result of reaction with acid chlorides takes place in the 4-position and the products are 4-acyl-1,4-dihydrophosphorins (LII). Hydrolysis of the anion (XLIX) leads to 1,2-dihydrophosphorins (LIII):



(LII) (XLIX) (LIII)

The alkylation of the anion (XLIX) by alkyl halides apparently proceeds both via an S_E1 and an S_E2 mechanism. The reaction involving the S_E2 mechanism proceeds via the more nucleophilic centre—the phosphorus atom; when the S_E1 mechanism operates, centres with a higher electron density react, i.e. the carbon atoms in the 2-, 4-, and 6-positions. The reaction mechanism depends not only on the solvent used but also on the nature of the alkyl halide. The reaction with alkyl halides via the S_E2 mechanism leads to the formation of 1,1-disubstituted phosphorins (L, R′ = CH_3 or C_2H_5). In the reactions with alkyl halides forming a stabilised carbonium ion, alkylation takes place in the 2-position and leads to the dihydrophosphorins (LI, R′ = $CH_2C_6H_5$ or CH_2–CH=CH_2).[84]

As noted above[49], 1-substituted 1,2-dihydrophosphorins (LI) are capable of rearranging to 1,1-disubstituted phosphorins (L), while the reverse rearrangement of compounds (L) to (LI) is impossible. This probably accounts for the, at first sight, unexpected formation of the 1,1-disubstituted phosphorin (LV) in the reaction of the anion (LIV) with chlorotriphenylmethane. The structure of the alkyl halide suggested that in this case the reaction should proceed via the S_E1 mechanism with formation of a 1,2-disubstituted 1,2-dihydrophosphorin[84]:

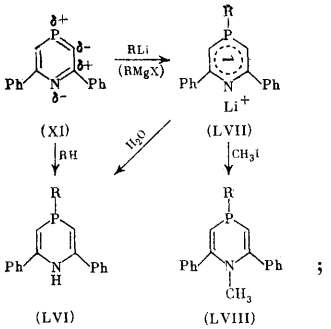


(LIV) (LV)

Presumably the 1,2-dihydrophosphorin formed immediately rearranges to a 1,1-disubstituted phosphorin (LV).

The replacement of carbon by nitrogen in the phosphorin enhances the electrophilic properties of the system[50]. Thus 2,6-diphenyl-1,4-azaphosphorin (XI) reacts readily not only with organometallic compounds but also, in contrast to phosphorins, with weaker nucleophiles such as phenols, alcohols, amines, and mercaptans. In the latter case, addition in the 1,4-positions takes place with formation of the corresponding 1,4-dihydro-derivatives (LVI).

The azaphosphorin (XI) reacts with organometallic compounds to form initially the mesomeric anion (LVII), which then interacts with water and is alkylated, also with formation of the 1,4-dihydro-derivatives (LVI) and (LVIII):

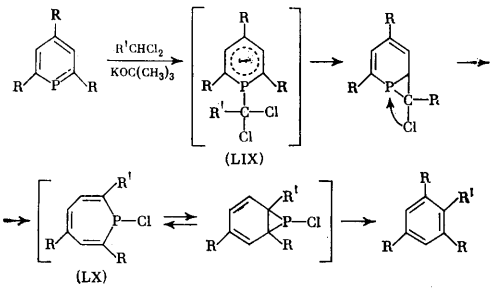


(XI) (LVII) (LVI) (LVIII)

R = R′O, R′S, or R'_2N .

The reactions of phosphorins with carbenes. When 2,4,6-triphenyl-, and 2,4,6-tri-t-butyl-phosphorins react with the halogenomethanes CH_2Cl_2, $CHCl_3$, and $C_6H_5CHCl_2$ in the presence of potassium

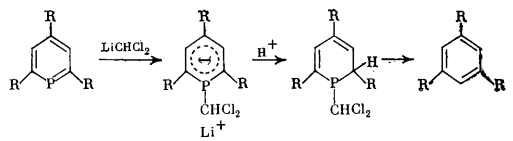
t-butoxide, phosphorus is eliminated and benzene derivatives are formed[85]. On the basis of a series of analogies, the authors suggest the following reaction mechanism:



(LIX)

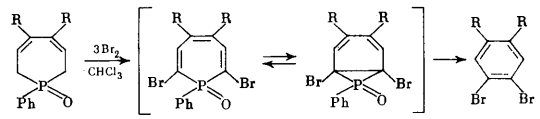
(LX)

The intermediate anion (LIX) is probably formed via a process resembling the reaction of 2,4,6-triphenylphosphorin with dichloromethyl-lithium. The dark-red 1-dichloromethylphosphorin anion (LIX) is formed in tetrahydrofuran at −80°C. Its protonation by glacial acetic acid gives 1-dichloromethyl-2,4,6-triphenyl-1,2-dihydrophosphorin (LXI), which was identified by PMR.[85] This compound is unstable and is readily converted into an aromatic hydrocarbon:



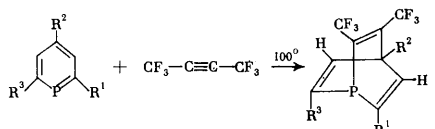
(LIX) (LXI)

As for the reaction of the intermediate phosphepin (LX), the authors found that the reaction of 4,5-dimethoxycarbonyl-1-oxo-1-phenyldihydrophosphepin (LXII) with bromine results in the formation of a 4,5-dibromophthalate ester (LXIII):



(LXII) (LXIII)

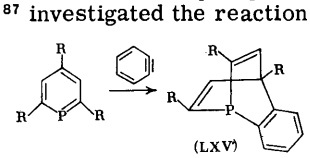
The Diels–Alder reaction in the series of phosphorin derivatives. 2,4,6-Trisubstituted phosphorins are involved in diene synthesis only with highly reactive dienophiles but under milder conditions than aromatic hydrocarbons. For example, hexafluorobutyne reacts[86] with substituted phosphorins at 100°C, while the reactions with benzene and durene take place only at 200°C:



(LXIV)

Apart from hexafluorobutyne, the Diels–Alder reactions of dicyanoacetylene, diethyl acetylenedicarboxylate, and maleic anhydride with phosphorins were investigated[86]. In all cases cycloaddition takes place exclusively in 1,4-positions with formation of 1-phosphabarrelenes (LXIV).

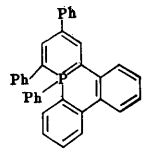
Märkl et al.[87] investigated the reaction of phosphorin with arynes:



(LXV)

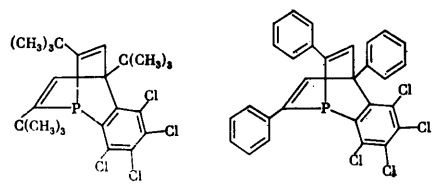
They suggest that the reaction may proceed via the intermediate formation of ambident phosphorin anions.

The reaction of 2,4,6-triphenylphosphorin with dehydrobenzene yields, in addition to the phosphabarrelene (LXV), a 1 : 2 adduct to which the structure (LXVI) was attributed on the basis of spectroscopic data:



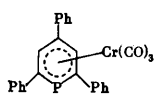
(LXVI)

Pentachlorophenyl-lithium reacts with 2,4,6-tri-t-butyl- and 2,4,6-triphenyl-phosphorins, again forming benzophosphabarrelenes [compounds (LXVII) and (LXVIII)]:



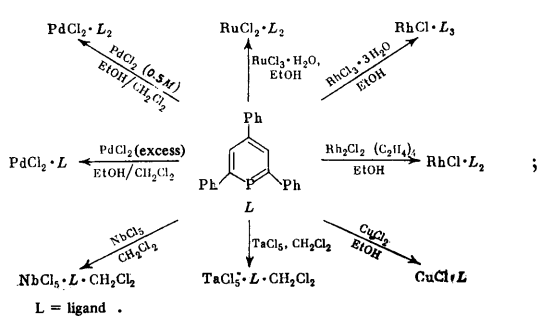
(LXVII) (LXVIII)

Electron-donating properties of phosphorins. In contrast to pyridine derivatives, aryl- and alkyl-phosphorins cannot be protonated by strong acids which are not oxidants, such as, for example, trifluoroacetic acid. However, trisubstituted phosphorins are capable of forming complexes with transition metal salts. For example, 2,4,6-triphenyl- and 2,4,6-tri-t-butylphosphorins react with chromium hexacarbonyl, forming π-complexes. The structure of the π-complex (LXIX) obtained from 2,4,6-triphenylphosphorin was confirmed by X-ray diffratcion analysis[88]:



(LXIX)

In an inert atmosphere, 2,4,6-triphenylphosphorin also forms complexes with transition metal chlorides[89]:

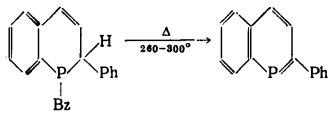


L = ligand .

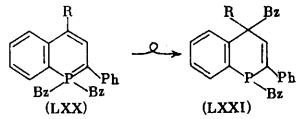
2. COMPOUNDS WITH CONDENSED RINGS

(a) Phosphanaphthalenes

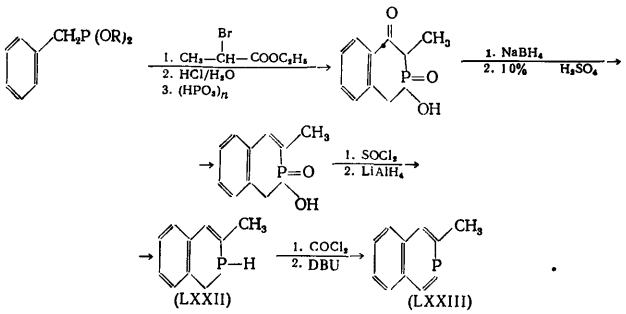
Three phosphanaphthalene derivatives have now been obtained, namely: 2-phenyl-1-phospha- and 3-methyl-2-phospha-naphthalenes as well as unsubstituted 2-phosphanaphthalene. 2-Phenylphosphanaphthalene is obtained similarly to phosphorin, by the thermolysis of 1-substituted dihydro-derivatives [90]:



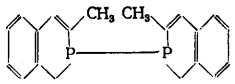
In contrast to phosphorin derivatives, phosphanaphthalenes cannot be obtained by the thermolysis of 1,1-disubstituted phosphanaphthalenes. Thus 1,1-dibenzylphosphanaphthalene (LXX) rearranges at 230–250°C to 1,4-dibenzyl-1,4-dihydrophosphanaphthalene (LXXI) [91]:



3-Methyl-2-phosphanaphthalene (LXXIII) is synthesised by the dehydrochlorination of the appropriate chlorodihydro-derivatives with the aid of 1,5-diazabicyclo[5,4,0]-undec-5-ene (DBU) [92]:



The chlorophosphine formed in the reaction of the secondary phosphine (LXXII) with phosgene is treated with DBU without being isolated. After the separation of the DBU hydrochloride and the vacuum sublimation of the residue, white crystals of compound (LXXIII) are obtained in a low yield. Apart from this product, the dimer



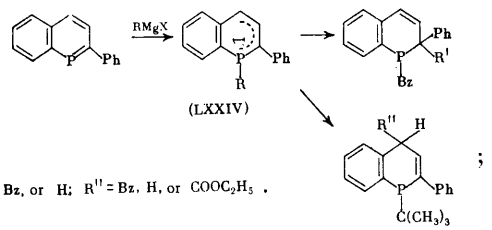
is also formed in the reaction.

The attempt to obtain by this procedure the unsubstituted 2-phosphanaphthalene was not altogether successful, since it could not be isolated in a pure form [92]. The presence of 2-phosphanaphthalene in the reaction mixture was only inferred from ultraviolet spectroscopic data. In another paper [93] devoted to this compound, the method of preparation is not described.

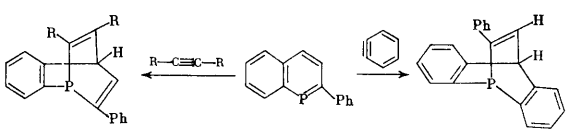
The structure of phosphanaphthalene derivatives has been demonstrated by ultraviolet spectroscopy and NMR. The chemical shift and the spin–spin interaction constants are consistent with the values for phosphorins. A bathochromic shift is observed in the ultraviolet spectra of phosphanaphthalenes relative to the corresponding aromatic hydrocarbons, for example λ_{max} = 332 nm for 2-phenyl-1-phosphanaphthalene compared with 322 nm for 2-phenylquinoline. [92]

The chemical properties of phosphanaphthalenes have been studied comparatively little. When 2-phosphanaphthalene is reduced with metallic potassium in tetrahydrofuran, a radical-anion similar to that obtained in the reduction of phosphorin is formed [93].

2-Phenyl-1-phosphanaphthalene reacts with organomagnesium compounds and gives rise to the anion (LXXIV), which is capable of reacting with dialkyl halides [94]:

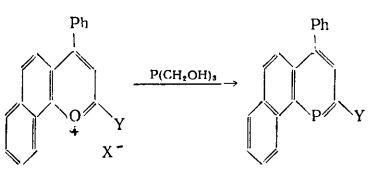


2-Phenyl-1-phosphanaphthalene combines with arynes and alkynes, forming benzo- and dibenzo-phosphabarrelenes [95]:

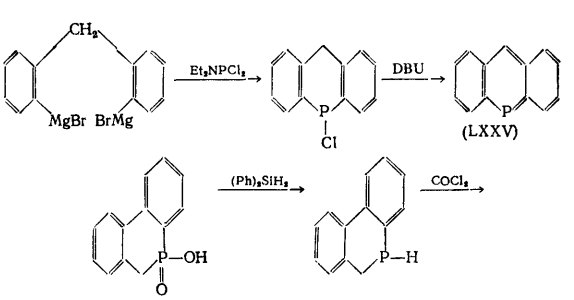


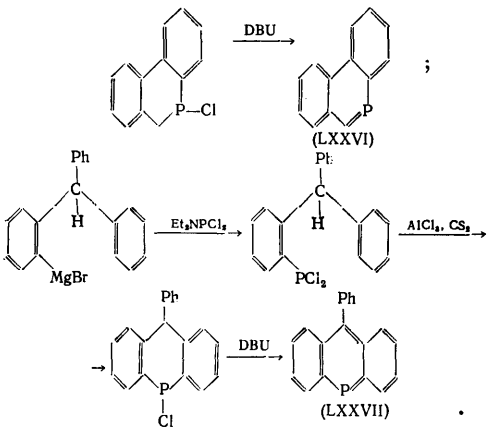
(b) Phospha-anthracenes and Phosphaphenanthrenes

The above derivatives of phosphorin with condensed rings are synthesised, like phosphorin, from substituted pyrylium salts [96,97]:



Dibenzo[*b*, *e*]phosphorin (LXXV), dibenzo[*c*, *e*]phosphorin (LXXVI), and 10-phenyldibenzo[*b*, *e*]phosphorin (LXXVII) can be obtained similarly to 3-methyl-2-phosphanaphthalene [92], by the dehydrochlorination of chlorodihydro-derivatives with the aid of DBU [98–100]:





Compounds (LXXV) and (LXXVI) are unstable and their formation has been demonstrated mainly by spectroscopic methods. Compound (LXXVII) is stable and can be sublimed at 160°C and 10^{-3} mmHg. The PMR and ultraviolet spectra of condensed phosphorins are consistent with those observed for the non-condensed systems [100]. An X-ray diffraction study of 4-aryl-2-t-butyl-5,6-dihydro-1-phosphaphenanthrene showed that the phosphorus-containing ring in this compound is also planar and has the same bond lengths and angles as in substituted phosphorins [97].

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