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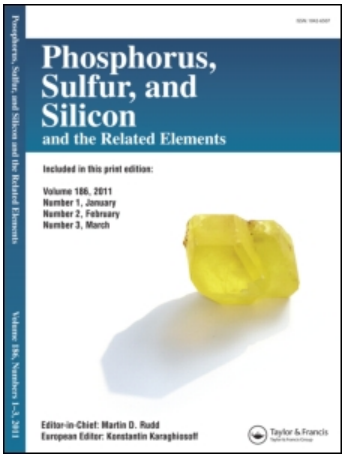

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AROMATIC PHOSPHORUS HETEROCYCLES

G. Márkl[a]
[a] Chemisches Institut der Universitat Regensburg,

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AROMATIC PHOSPHORUS HETEROCYCLES †

G. MÄRKL

Chemisches Institut der Universitat Regensburg

In 1967 we synthesized the first phosphabenzene with tervalent P, coordination number 2, and a $3p_\pi$-$2p_\pi$-P=C-double bond: the 2,4,6-triphenylderivative.[1] One of the challenging problems in synthetic organic chemistry – is it possible to replace in the benzene molecule one of the carbon atoms by a second or third row element, by Si, P, As; is it possible to synthesize – against the classical octet rule – Phospha-, Arsa- or Sila-benzenes, had been solved in principle for the element P. This first synthesis was carried out by reaction of pyrylium salts with $P(CH_2OH)_3$ in refluxing pyridine (Fig. 1).

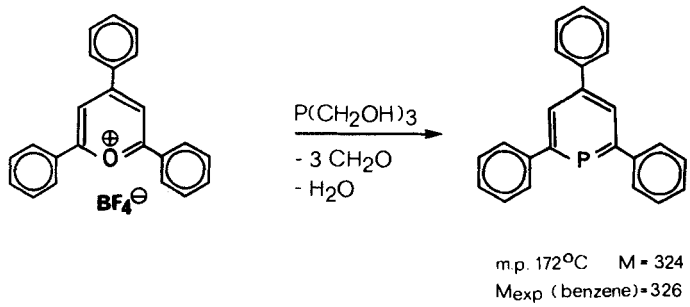

FIGURE 1

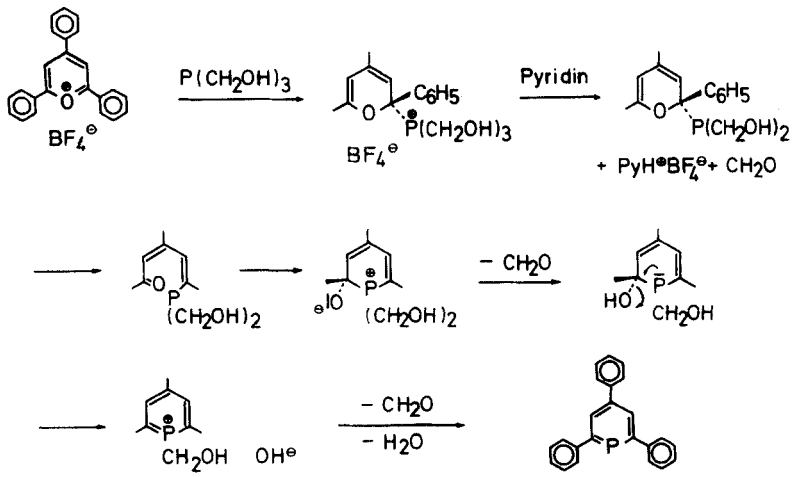

FIGURE 2

$P(CH_2OH)_3$ reacts as a potential PH_3, as a crypto-PH_3, with much larger nucleophilic power than PH_3 itself; the phosphine, as nucleophile, adds to the pyrylium salt in the 2-position and deprotonation of one

† Plenary Lecture. The Vth International Conference of Organic Phosphorus Chemistry, Gdansk, Poland, September 1974.

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CH_2OH-group by the solvent is followed by elimination of formaldehyde. By this intramolecular redox-reaction the phosphonium salt is reduced to the phosphine. Ring closure follows by nucleophilic attack on the carbonyl group. In the final – but important – step the hypothetical phosphabenzene cation has to lose its last mole of formaldehyde faster than nucleophilic attack of OH^- occurs on the cation (in this case, a phosphine oxide would be formed) – the cation is intercepted as stable phosphabenzene (Fig. 2).

Later on, tris (trimethylsilyl) phosphine turned out to be another possible P-precursor, another potential PH_3, which reacts with pyrylium salts at room temperature to give the phosphabenzenes. Silyl-substituted phosphonium salts are unstable, the formation of hexamethyldisiloxane is the driving force for the ring closure (Fig. 3).

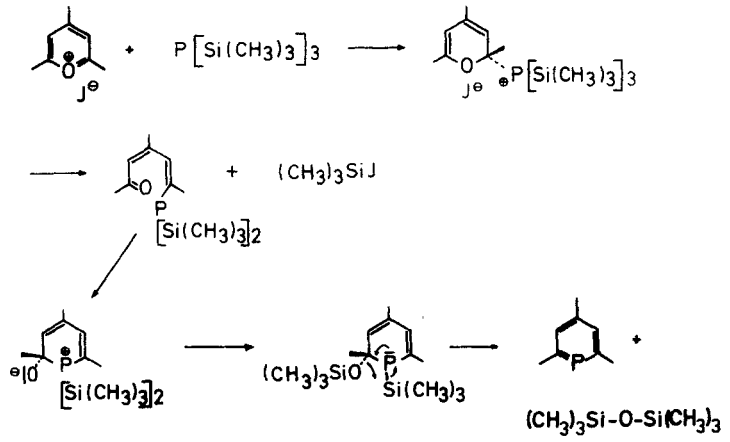

FIGURE 3

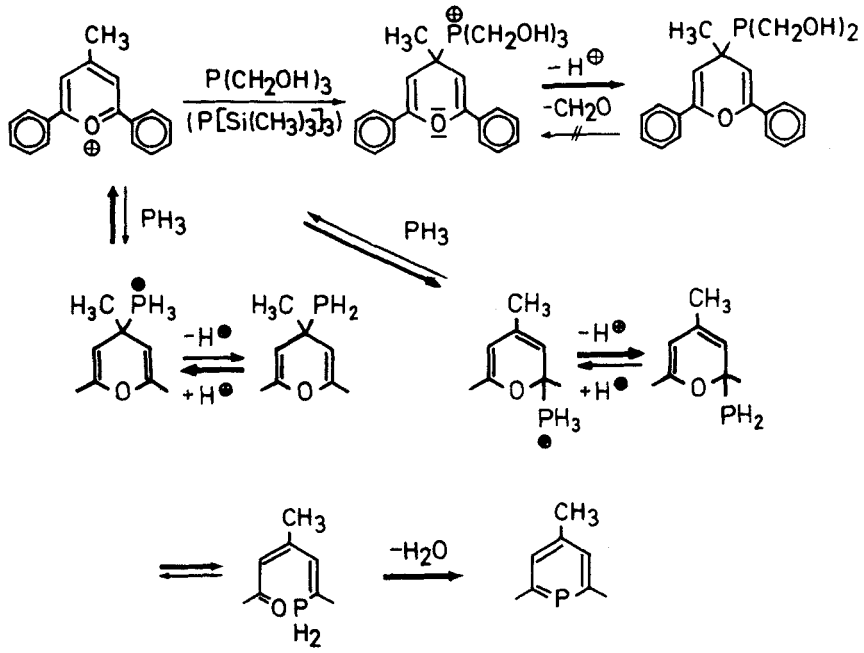

FIGURE 4

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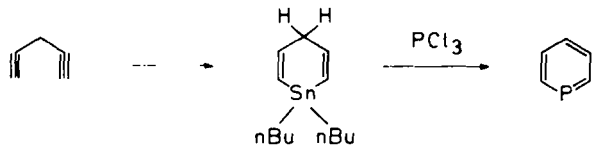
Unfortunately, both the $P(CH_2OH)_3$-method and the $P(SiMe_3)_3$-method are limited to the synthesis of tri- and higher aryl-substituted phosphabenzenes. Simply by replacement of a single aryl substituent by an alkyl group, these syntheses do not work anymore. Our hypothesis was that the reasons for this failure are steric in origin: the trisphosphines are bulky and add at the position of the smallest substituent – for instance in the 4-position; by losing CH_2O or $ClSiMe_3$ this addition becomes irreversible and the phosphabenzene formation impossible (Fig. 4).

Indeed, PH_3 itself – despite its extremely small nucleophilicity – is the best possible P-source for the reaction with pyrylium salts. All steps are H^+-catalyzed and reversible until the ring closure irreversibly forms the phosphabenzenes. Using this trivial method not only triaryl, but also 2,4,6-tri-substituted monoalkyl, dialkyl, and trialkyl substituted phosphabenzenes have been synthesized; 2,4,6-trimethylphosphabenzene is the most simple derivative prepared by this method.[3]

In 1971 A. Ashe published his spectacular synthesis of the unsubstituted phosphabenzene itself: by the simple exchange reaction of 1,1-di-*n*-butyl-1,4-stannabenzene with PBr_3 (Ref. 4) (Fig. 5).



Lit : A. Ashe, J. Am. chem. Soc. 93, 3293 (1971)

FIGURE 5

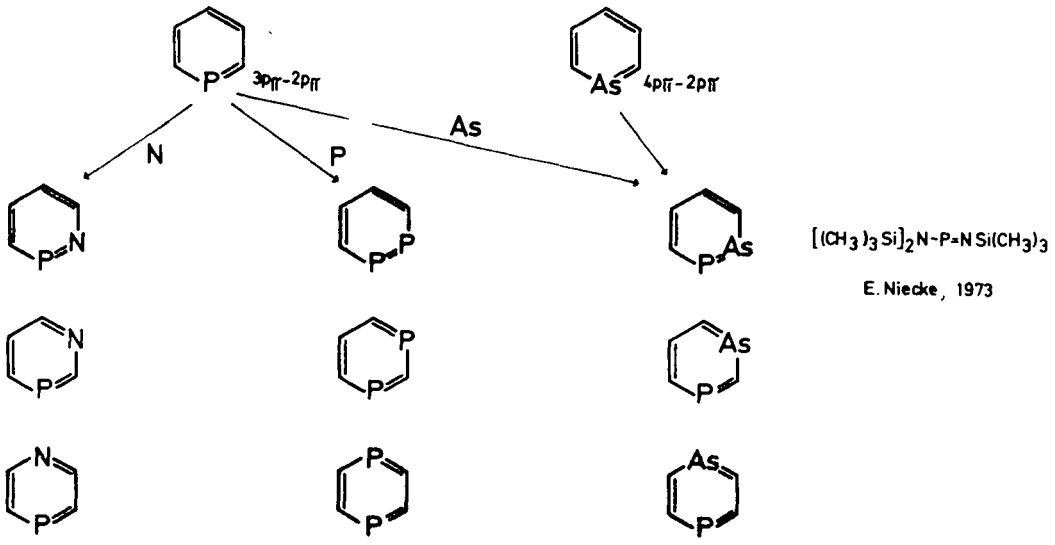


FIGURE 6

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Once the capability of existence of the trisubstituted, as well as the unsubstituted, phosphabenzenes had been proved, the work in this fascinating area of P-chemistry could be continued in various directions:

1) Exploration of new synthetic approaches to the phosphabenzene ring system, especially with respect to new substitution patterns; hitherto we only know the 2,4,6-substituted derivatives and the unsubstituted phosphorine itself.

2) Introduction of further heteroatoms into the ring system, i.e. analogous to the transitions from pyridine to pyridazine, pyrimidine and pyrazine to think about the existence of phospha-aza-, diphospha- and phospha-arsa-benzenes (Fig. 6).

Although the P = C, $3p_\pi$-$2p_\pi$-double bond is reality, there exists no proof about the P = N and the P = P-p_π-p_π-double bonds – with one exception: Niecke[5] very recently synthesized a silyl-substituted phosphazene, $[(CH_3)_3Si]_2N{-}P = NSiMe_3$, as a highly reactive labile compound. However, systems with the second heteroatom in *m*- or *p*-position should be within our present synthetic scope.

3) As the third aspect, synthetic activities should be concerned with the question of the existence of functional groups at the phosphorine ring system. Is it possible to synthesize, for instance, phosphaphenoles, phosphaanilines, phosphabenzaldehyde, or phosphabenzoic acids and what is the chemistry of these molecules? (Fig. 7.)

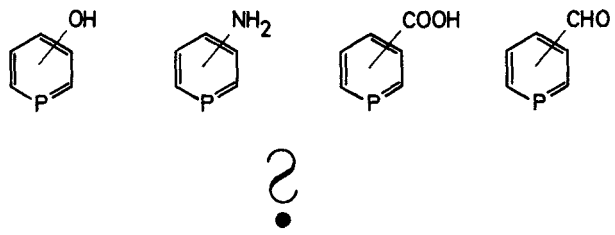
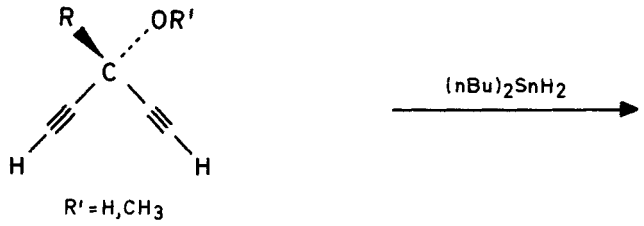


FIGURE 7



R = $-C(CH_3)_3$	yield 61% , b.p. $_{0.01}$ 121°C M.S. : M^+ 386 (< 1%) ; base peak $(M - nBu)^+$ 329 (43%)
	yield 49% , b.p. $_{0.01}$ 160-165°C mol. weight 415 (osm.), M = 412
	yield 68% , b.p. $_{0.01}$ 154-158°C M.S. : M^+ 405 ; base peak $(M - nBu)^+$ 348

FIGURE 8

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4) This question finally brings us to the general problem of phosphabenzene chemistry: what is the bonding situation in this new system and how good is the correlation with its chemistry and physical data?

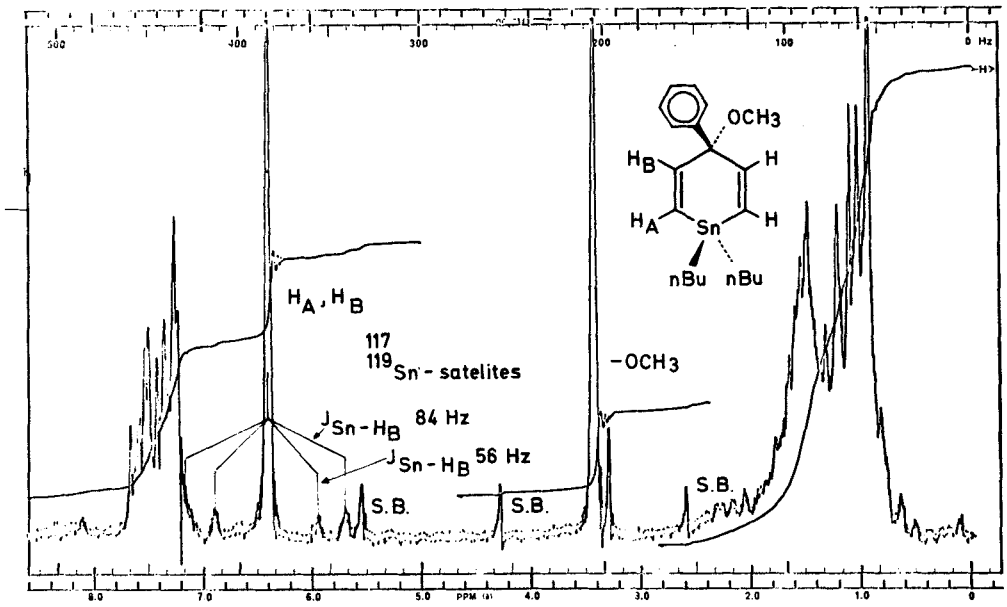

FIGURE 9

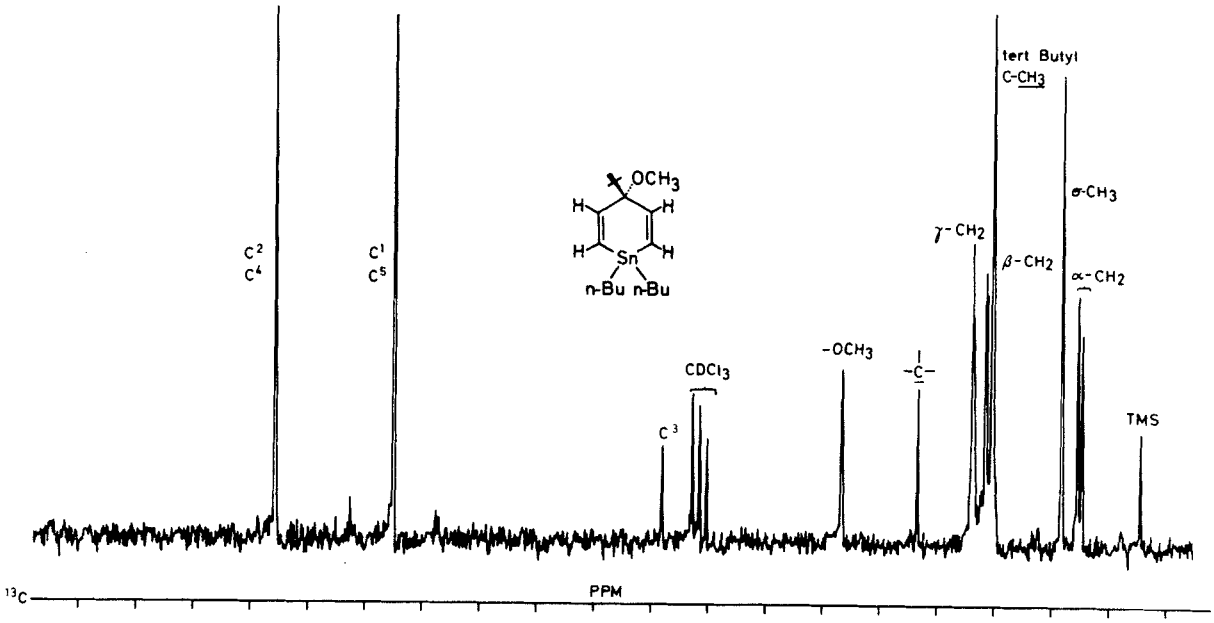

FIGURE 10

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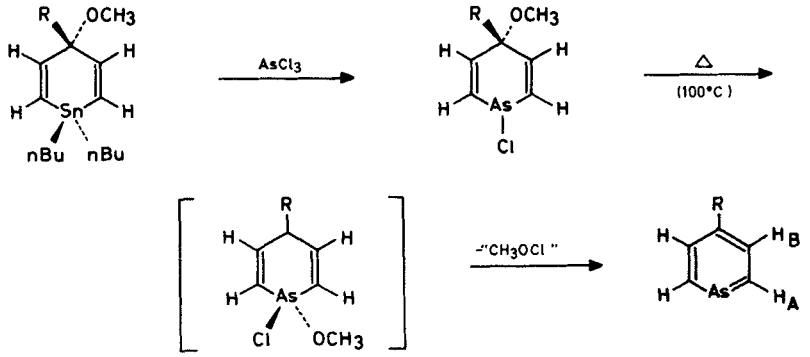
First of all we will discuss point (1), *new synthetic approaches* to the phosphorine system. A very elegant synthesis of phospha – as well as arsabenzenes, alkyl- or arylsubstituted in 4-position[6] – starts out with1,4-dihydrostannabenzenes. The 3-alkyl, aryl-3-methoxy-substituted pentadiines, easily available, react smoothly with di-*n*-butyl-Sn-dihydride to give the corresponding 1,4-dihydrostannabenzenes (Fig. 8): their structure is confirmed by ^{1}H-nmr (Fig. 9) (characteristic: the Sn 117/119-satelites) and ^{13}C-nmr (Fig. 10) which proves the equivalency of C_1/C_6 and C_2/C_5. The exchange reaction with PBr_3 as well as $AsCl_3$ occurs unexpectedly: we immediately isolated the monosubstituted phospha- and arsabenzenes (Fig. 11), colorless, distillable, air-sensitive liquids; structure proof by ir, uv, nmr and ms – these data will be discussed, in part, later.



R = $-C(CH_3)_3$ yield 52% ; M^+ 196 , rel. Int. 50% , $[M-C(CH_3)_3]^+$ 139, 66%
λ_{max} 221 nm (ε 15 600) , 275 nm (15 200)
H_A 0.2 τ , J_{AB} 12 Hz ; H_B 1.9 τ

yield 29 % ; M^+ 222 , rel. Int. 100 %
λ_{max} 223 nm (ε 13 200) , 288 nm (15 900)
H_A 0.3 τ , J_{AB} 11 Hz ; H_B 2.2 τ

yield 26 % ; M^+ 216 , rel. Int. 100 %
λ_{max} 226 nm (22 300) , 302 nm (31 200)
H_A 0.2 τ, J_{AB} 12 Hz ; H_B 1.9 τ

FIGURE 11

This synthesis works by the formal elimination of CH_3OCl with positive halogen. If we intercept the positive halogen by the addition of triphenylphosphine, the yields can be increased up to 50-60 per cent.

An entirely new route – in addition to pyrylium salts and exchange reactions of Sn-heterocycles – starts out with the phosphonia-pyranes; this system was published originally by Simalty[7] in Paris and Aguiar[8] in the USA. *Bis*-(propinyl)-*t*-butylphosphine[9] reacts smoothly with bromomethylketones; the phosphonium salt intermediate cyclizes spontaneously to give the pyrane. Degradation of the phosphonium salt with aqueous alkali to the phosphine oxide is followed by refluxing of the oxide in conc. aqueous HCl – under these reaction conditions the expected diketone cyclizes immediately by an intramolecular aldol reaction to the 1-oxa-phosphacyclohexene-3-one-5 (Fig. 12). This system is a highly reactive one with at least 5 reactive positions; its chemistry is just being studied (Fig. 13).

One entirely unexpected result is of interest in this connection: If we reduce the phosphineoxide with $SiHCl_3$ and distill the expected phosphine, we end up with phosphabenzenes, substituted in the 3-position in fairly good yield (50-70%).[10] Obviously the C = O group must also be attacked, i.e. reduced, by $SiHCl_3$; the resulting cyclohexadiene (by elimination of silanol?) thermolyzes by elimination of isobutene to the phosphorine. These thermolysis reactions will be discussed later. This new synthesis is rather important. Phosphorines with substituents in the 3-position cannot be synthesized otherwise since, for instance, the

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corresponding Sn-heterocycles are not available.

Let us summarize: our synthetic possibilities till now permit the preparation of 2,4,6-tri-, 4-mono- and 3-mono-substituted derivatives in addition to the unsubstituted phosphorine (Fig. 14). Since further phosphorine syntheses result from phosphorine chemistry itself, we will stop the chemical engineering at this point and discuss the structural and spectroscopic features and partly also the chemistry of the phosphorine system.

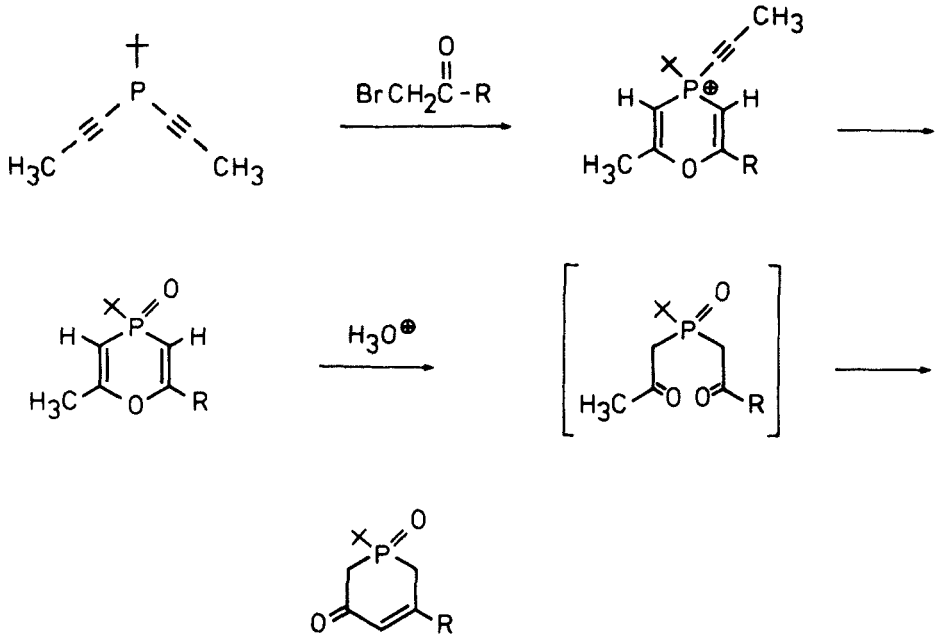

FIGURE 12

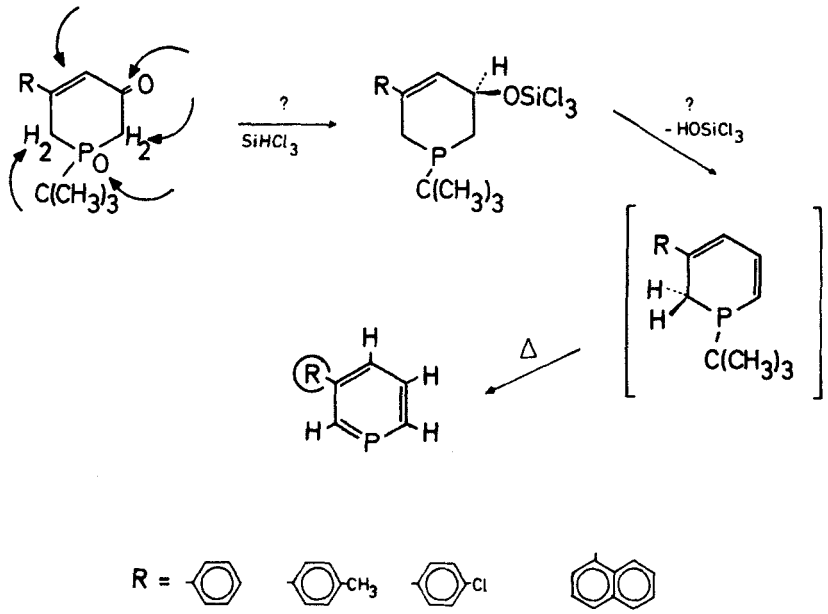

FIGURE 13

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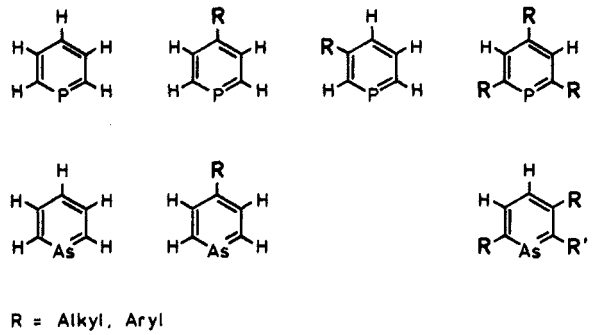
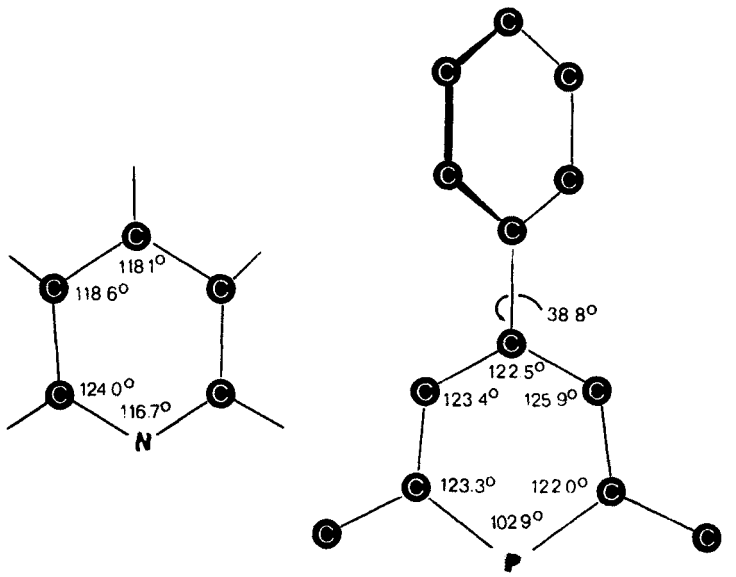


FIGURE 14



Pyridine 2.6-Dimethyl-4-phenyl-phosphabenzene

FIGURE 15

The *x-ray analysis of 2,6-dimethyl-4-phenyl-phosphabenzene*[11] (Fig. 15) confirms the complete π-bond-delocalization of an aromatic system; the ring system is planar; the C-P-C angle of 103°C is about 4° larger than in ordinary tertiary phosphines. The P–C-distances are equal, 1.74 Å; the C–C-distances are also nearly equal, 1.39 Å. If we plot the P–C-distances against the bond order we get in agreement with the π-delocalization, a P–C-value of nearly exactly 1.5 (Fig. 16).

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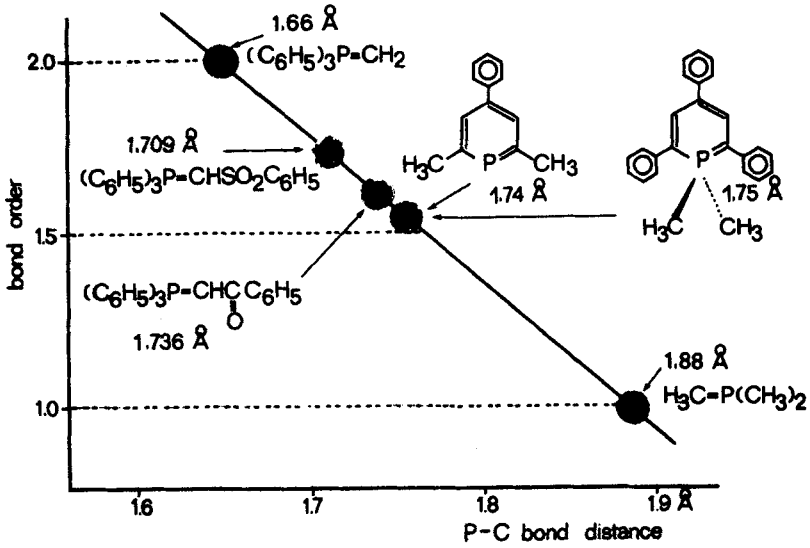

FIGURE 16

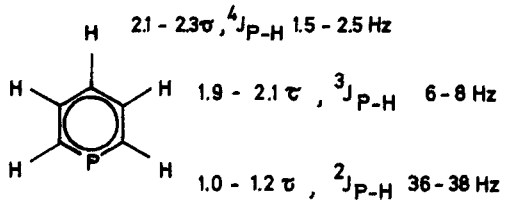

FIGURE 17

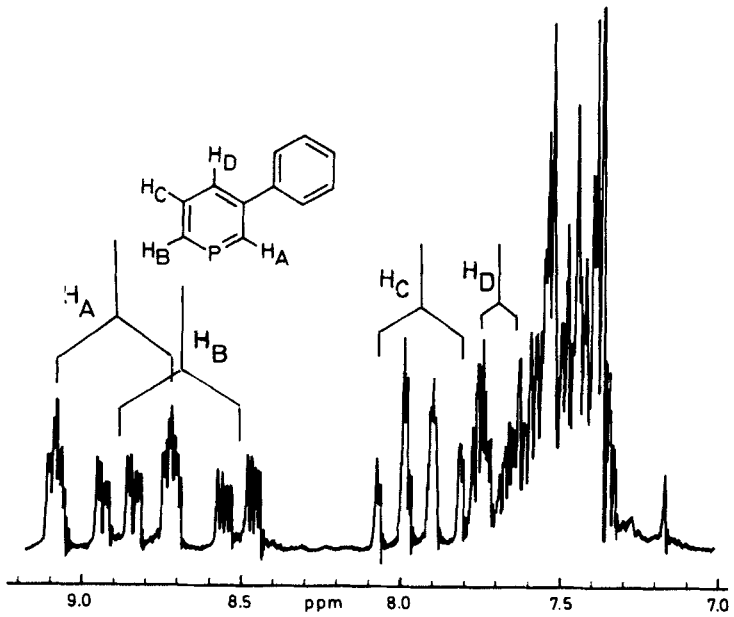

FIGURE 18

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The equivalency of the 2,6- and 3,5-positions as a result of the π-bond delocalization also becomes obvious by ^{1}H-nmr-spectroscopy. In the 2,4,6-triphenyl derivatives the β-hydrogens appear as one doublet, $^3J_{PH}$-coupling 6 Hz, at fairly low field, 1.9 τ, indicating the aromatic ring current. The α-hydrogens – for instance, clearly recognizable in the 3,4,6-triphenyl derivative – because of anisotropic effects of the P-atom are shifted much further downfield to 1.0-1.2 τ and the $^2J_{PH}$ coupling becomes as large as 36-38 Hz.

In the 100 MHz ^{1}H-nmr of 3-phenylphosphabenzene, the α-, β- and γ-hydrogens are clearly separated; the signals are split further by H/H couplings (Fig. 18).

The ^{31}P-nmr signals – for simple phosphines usually between 0 and 60 ppm – appear extremely far downfield: for the 2,4,6-triphenyl derivative at −178 ppm, for 3-phenyl-phosphorine at −209 ppm, thus indicating the unusual electronic situation at the P-atom. The phosphorines as well as the arsenines are the first neutral 6-membered heterocyclic systems where the heteroatom has *d*-orbitals available. Does this have any consequences? It seems that this is still an open question.

The PE spectra indicate that the first atomic ionization energy IE_π is much lower for the phosphorine (9.1 eV) compared to the pyridine (9.8 eV). From the PE spectra and corresponding calculations we learn that the sequence of the highest occupied molecular orbitals is completely inverted from pyridine to phosphorine and arsenine; the π_1-MO with b_1-symmetry is the HOMO, whereas in pyridine the lone-pair $n_N/\sigma(a_1)$ is the HOMO (Fig. 19).

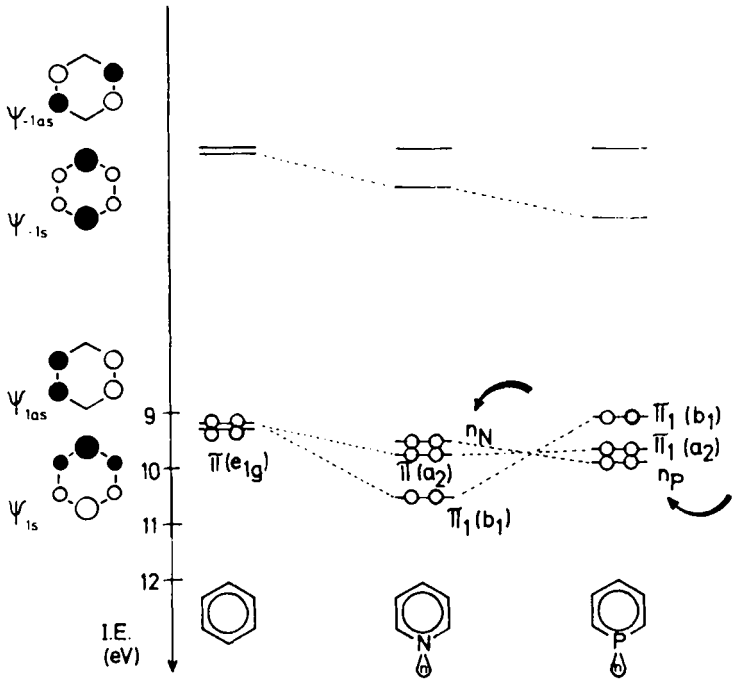

FIGURE 19

Heilbronner and coworkers[12] obtained these results by an *ab initio* calculation; the π-orbital correlations can be rationalized by first-order perturbation. According to these calculations, inclusion of 3*d*-orbitals into the basis set is unimportant to understanding structure and bonding in phosphabenzene. Schweig[13] (he measured the PE spectra of 2,4,6-tri-*t*-butylphosphorine and 9-phosphafluorene) interprets the PE spectra by the same MO sequences, but he did CNDO/2 calculations *with inclusion of 3d-orbitals* (Fig. 20).

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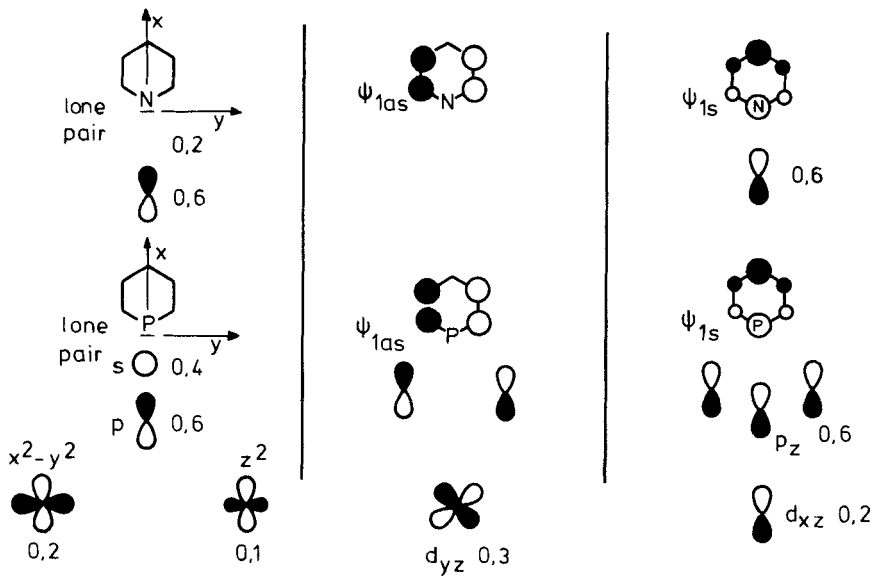

FIGURE 20

In the $a_2(\pi)$ MO, with a node at the heteroatom, the d_{yz}-orbital overlaps with the $2p_z$-orbitals at C_2 and C_6 lowering the energy of the MO. In the $b_1(\pi)$ MO the overlap between the $3p_z$-orbital at the P-atom and the C_2, C_6 $2p_z$-orbitals constitute the major contribution to ring conjugation; since this $3p_\pi$-$2p_\pi$ overlap is less favored, the π-MO is drastically increased despite d_{xz} participation and becomes the HOMO: the result is an inversion of the π-MO-sequence from pyridine to phosphorine and arsenine.

The *electrochemical results* are interesting. The $E_{1/2}^{Red}$-values are far less negative for the phosphorines and arsenines compared to the pyridines and benzenes; for 2,4,6-triphenylphosphabenzene we observe a reversible, one-electron transition at -1.72 (a second one at -2.33 V) compared to -2.2 and < -2.2 V for pyridine and benzene respectively. Since the halfwave reduction potentials are correlated with the LUMO, this must be a result of lowering the energy of the LUMO. These positive shifts of the $E_{1/2}^{Red}$-values indicate the remarkable electron acceptor character of the phosphorines and arsenines and the experiments confirm these conclusions: *phosphabenzenes (as well as arsabenzenes) are strongly electrophilic, but obviously not nucleophilic.*

This fact already answers the question: is the chemistry of the phospha- and arsabenzenes comparable to that of pyridine? Initial experiments indicate that the relationships are extremely poor.

Alkylations of the phospha- or arsabenzenes to pyridinium salt-like phospha- and arsabenzene cations are not possible even with strongly alkylating oxonium salts; the tervalent P (as well as As) of coordination number 2 obviously has lost its phosphine character and we may seriously ask: what has happened to the lone electron pair at the P-atom? It is not unexpected, therefore, again contrary to pyridine, that the phosphorines and arsenines have no basic character. Schweig[14] calculated a pKa for the protonated phosphorine of -10; compared to the pKa of pyridine (+5) it is an extremely strong acid; the pKa of O for the sp^2 carbon atoms indicate these to be more basic than phosphorus itself. *Phospha-arsabenzenes are not nucleophilic, but strongly electrophilic.*

Dimroth showed that 2,4,6-triphenylphosphorine reacts with K/Na alloy in THF and adds, stepwise, one electron to give the blue-green radical anion and one further electron to give the diamagnetic deep red anion. It must be diamagnetic since the LUMO is not degenerate (Fig. 21). The strong electrophilic character of the phosphorines is also revealed by reaction with nucleophiles[15] (Fig. 22).

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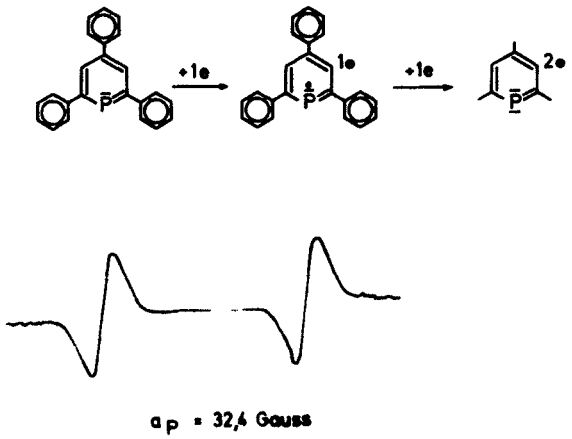

FIGURE 21

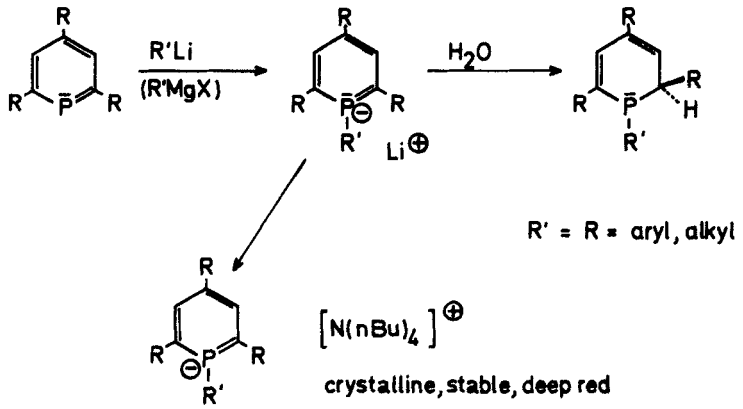

FIGURE 22

Metallorganic compounds, for example phenyl-Li, R-MgX in THF react immediately to give deep blue or green solutions; in contrast to the pyridines, the carbanion adds, by valence shell expansion, to the P-atom, and we get the 1-phenyl or, more generally, the 1-R-phospha-benzene-anions which can be isolated as tetrabutylammonium salts. 1-Substituted 1,2-dihydrophosphabenzenes are formed after hydrolysis. We can see the general application of this unusual reaction in Figure 23.

The reaction of these anions with $FeCl_2$ is very interesting;[16] by analogy with the ferrocene synthesis we get, as a new class, the corresponding Fe-complexes as brownish red, lustrous needles. ^{31}P-nmr, ^{1}H-nmr, and ms confirm the structure, but for final structure proof x-ray analysis is certainly necessary (Fig. 24).

The phosphabenzene-anions are very useful, reactive intermediates: by alkylation with alkyl halides we isolate deep red, stable, crystalline compounds: the 1,1-disubstituted phosphabenzenes.[17] This means we have succeeded in transforming the unsubstituted phosphabenzene with tervalent P of coordination number 2 *via* the 1-R-phosphabenzene anions into the 1,1-disubstituted derivatives with pentavalent P, coordination number 4, and a formal $3d_{\pi}$-$2p_{\pi}$, P=C-double bond (Fig. 25).

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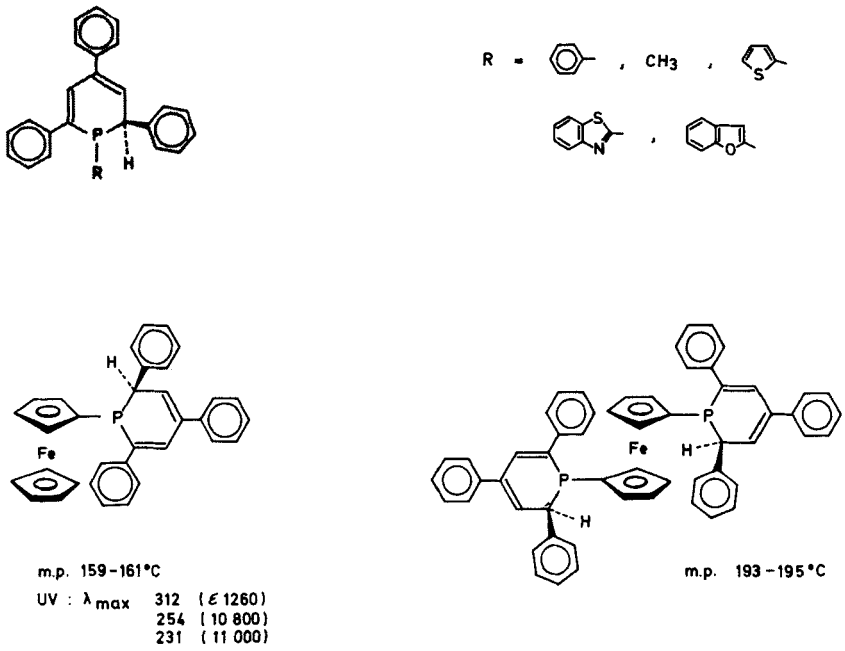

FIGURE 23

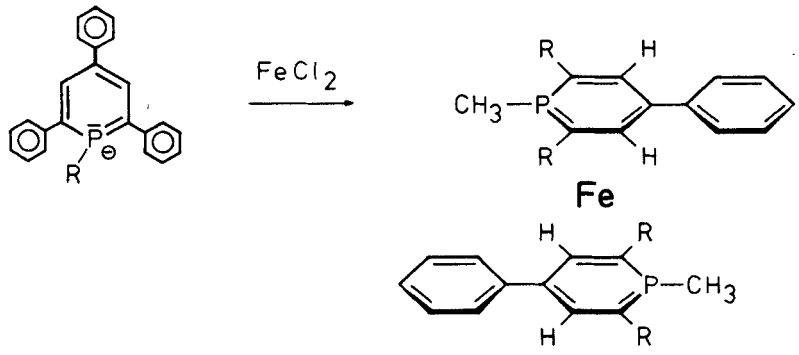

FIGURE 24

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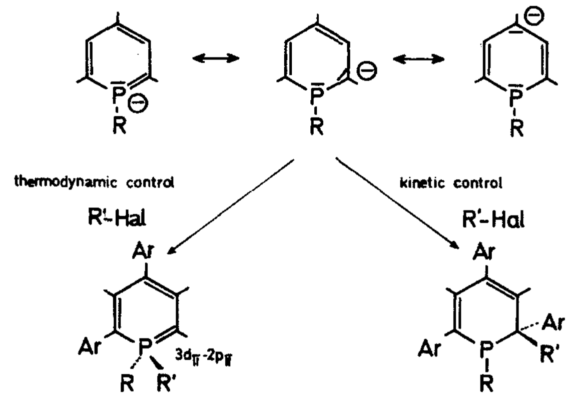

FIGURE 25

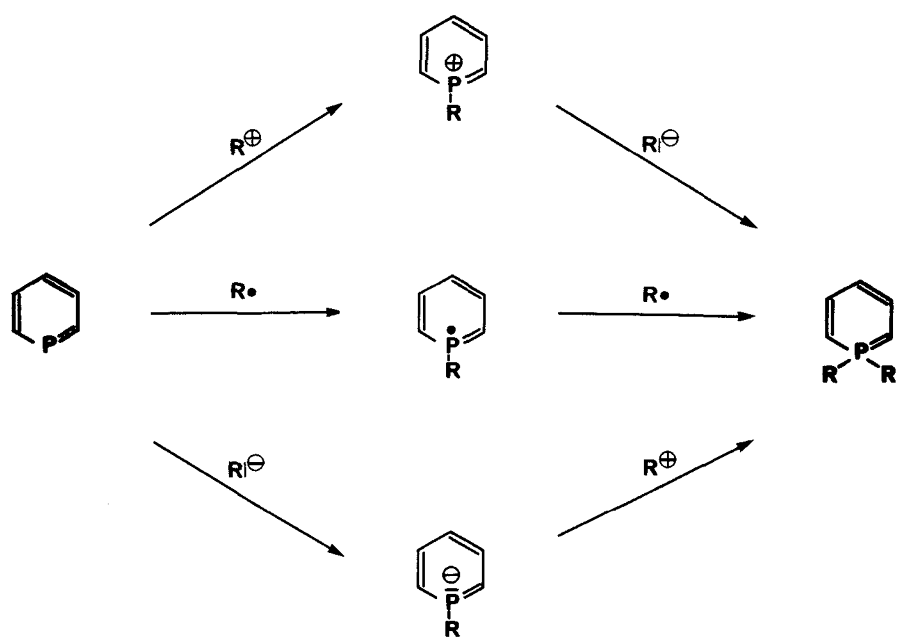

FIGURE 26

In these alkylation reactions, the anions prove to have ambident character: kinetically controlled alkylation occurs at the C-atom in the 2,6-position; alkylation at the P-atom forms the thermodynamically stable 1,1-disubstituted phosphorines. These transformations of phosphabenzenes with tervalent P, coordination number 4, are not only possible *via* anionic, but also by radical[18] and cationic 1-R-phosphabenzene intermediates.[19] (Fig. 26.) The x-ray analysis of the 1,1-dimethyl-2,4,6-triphenylphosphabenzene[20] indicates one surprising feature: its geometry is nearly identical with that of the phosphabenzenes which are unsubstituted at the P-atom. Without discussing the bonding situation – here we need *d*-orbitals anyhow – we also find a delocalized, planar 6π-system in this case (Fig. 27).

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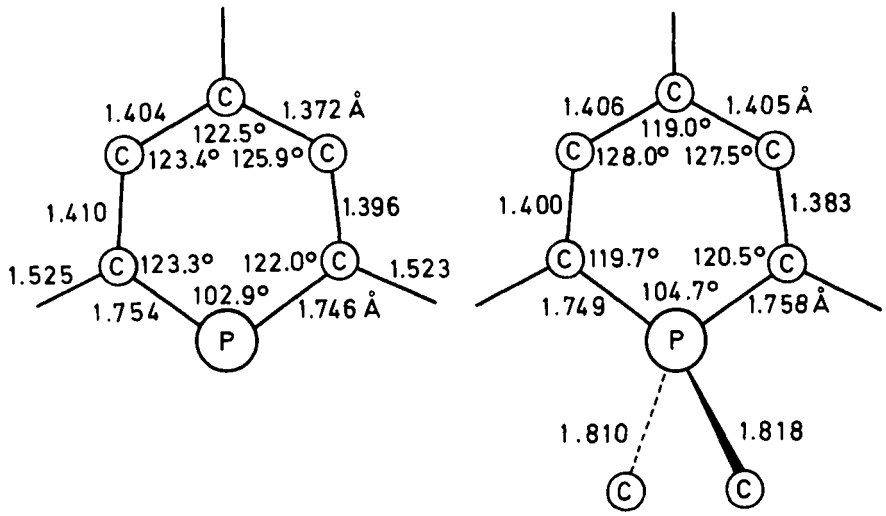

FIGURE 27

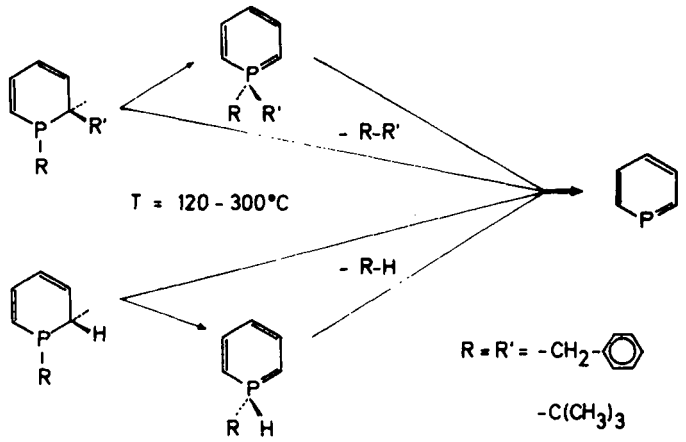

FIGURE 28

This is now the point to come back to the problems of new synthetic approaches to phosphorine systems. If the substituents in the 1,1- or 1,2-position of the phosphabenzenes, respectively 1,2-dihydrophosphabenzenes, are good radical leaving groups, for instance, benzyl or tert-butyl, these derivatives decompose at 200-300°C to give the unsubstituted phosphabenzenes (Fig. 28). For example, 1,2-dibenzylphosphabenzene rearranges at 180°C into the 1,1-dibenzylphosphabenzene which is thermolyzed at 220°C into phosphabenzene and dibenzyl; this chemistry also indicates the sequence of thermodynamic stabilities (Fig. 29).

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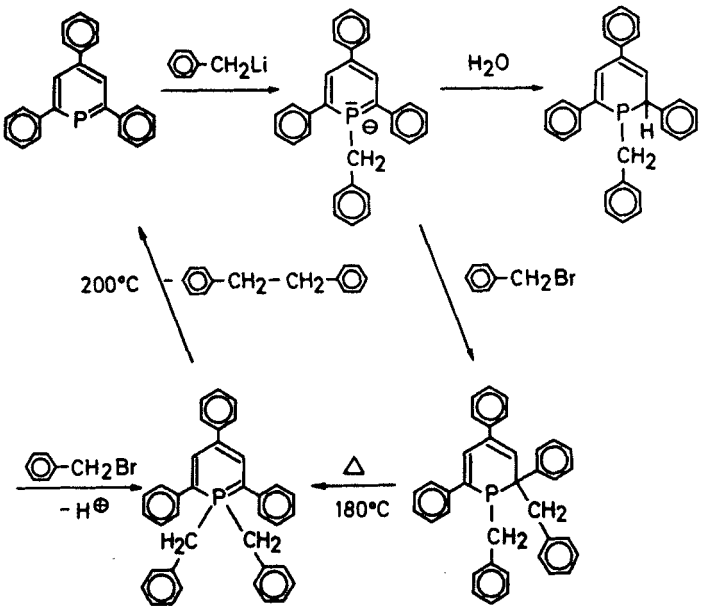

FIGURE 29

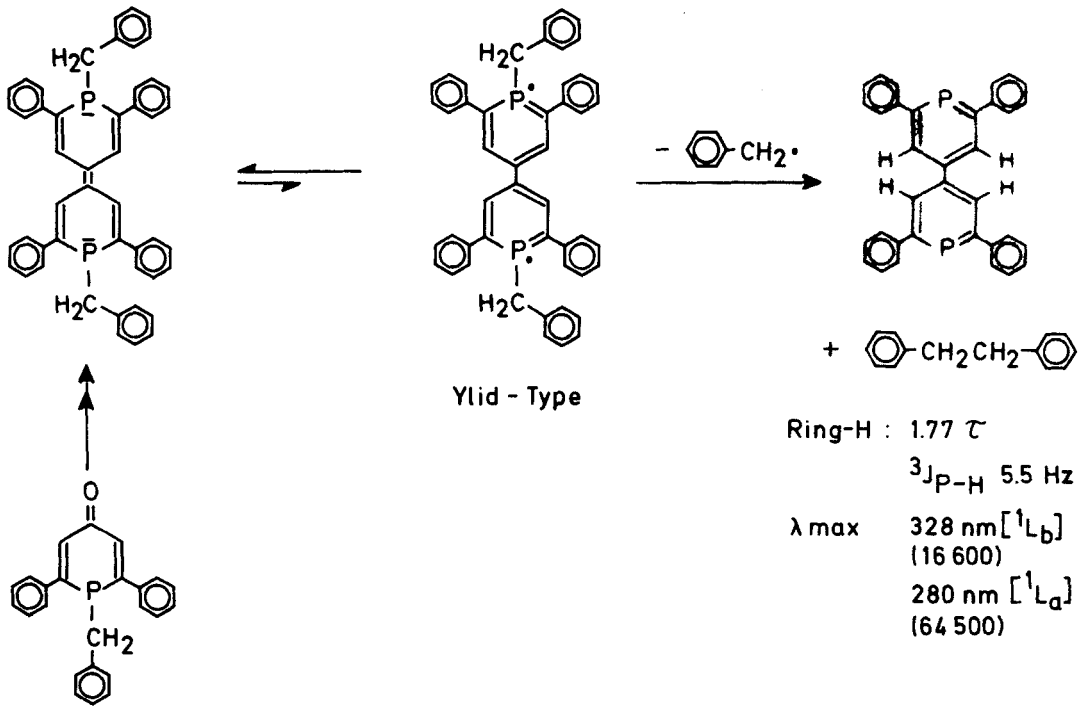

FIGURE 30

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Therefore we have a new synthetic principle in hand: if we are able to synthesize 1,2-di-R-dihydro- or 1,1-di-R-phosphabenzenes with good leaving groups in the 1,2- and 1,1-position respectively, by any means whatever, we are able to build up phosphabenzenes by total-synthesis approach. Some examples demonstrate this new synthetic dimension:

1,1-dibenzyltetraphenyldiphosphadipyrylenes[21] – synthesized *via* four steps starting out with dibenzylacetone – are debenzylated at 320° and we isolate the diphosphadiphenyl derivatives, otherwise not accessible (Fig. 30).

1-benzyl-4-methylenephosphacyclohexadienes[22] – also prepared *via* four steps – rearrange by a 1,5-benzyl shift, similar to the so-called semibenzene-rearrangement, to give the isomeric phosphabenzenes. Cross-experiments prove this rearrangement to be intermolecular and radical (Fig. 31).

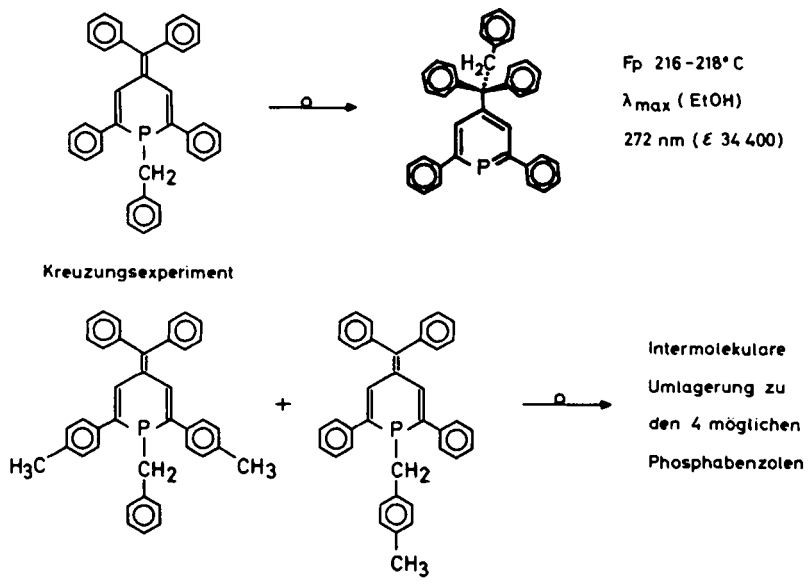

FIGURE 31

1-benzyl-2-phenyl-1,2-dihydrophosphanaphthalene – synthesized in 12 steps starting with o-bromobenzylbromide – thermolyzes at 250° and the first phosphanaphthalene, the 2-phenyl derivative, distills[23] (Fig. 32).

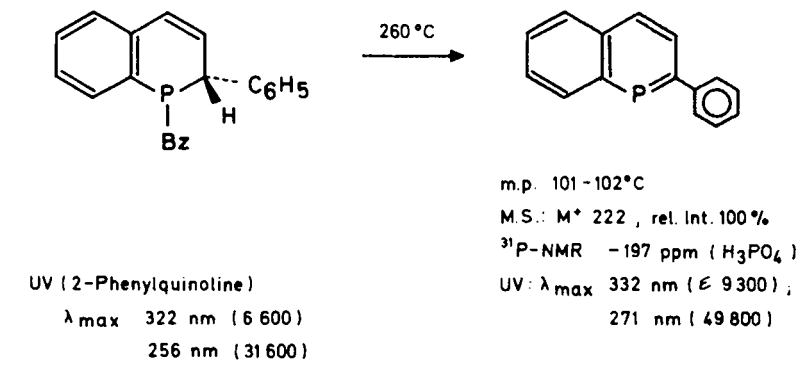

FIGURE 32

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Like naphthalene itself, the x-ray analysis of the phosphanaphthalene[24] shows that the angular P–C and C–C bonds are much longer than those in the monocyclic systems, they have more single bond character (Fig. 33):

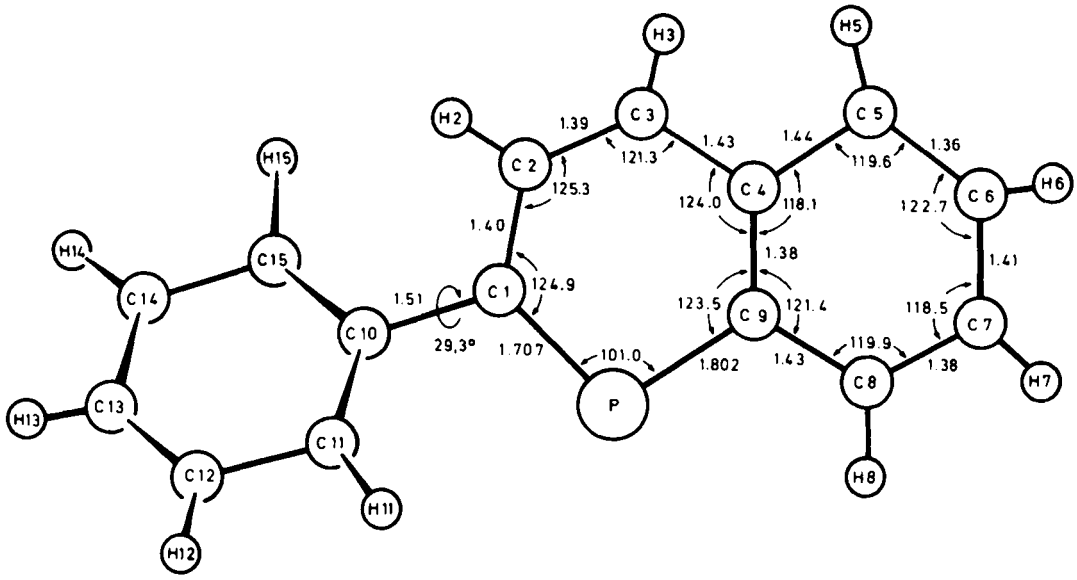

FIGURE 33

This thermolysis reaction scheme now permits us the first synthesis of a phosphabenzene with a second heteroatom of the fifth group in the P-ring, the 1-aza-4-phosphabenzene system:[25] 1-aza-4-phospha-4-*t*-butylcyclohexadienes, prepared in 6 steps starting with the *bis*-alkinyl-*t*-phosphine *via* the diketone, eliminate isobutene and H_2 at 310°C and the 1-aza-4-phosphabenzenes (R = phenyl, *t*-butyl) crystallize after high vacuum distillation at 0.1 Torr (Fig. 34).

Structure proof is provided by ^{1}H-nmr: the α-ring-H are fairly downfield as doublets at 1.36 τ, J_{PH} 36 Hz (Fig. 35).

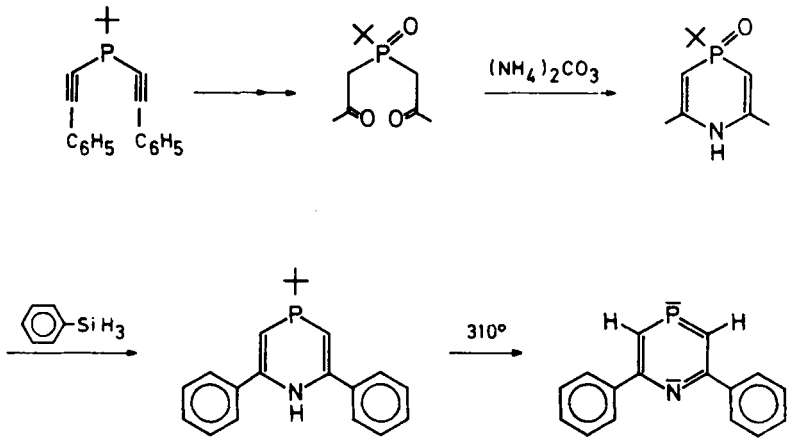

FIGURE 34

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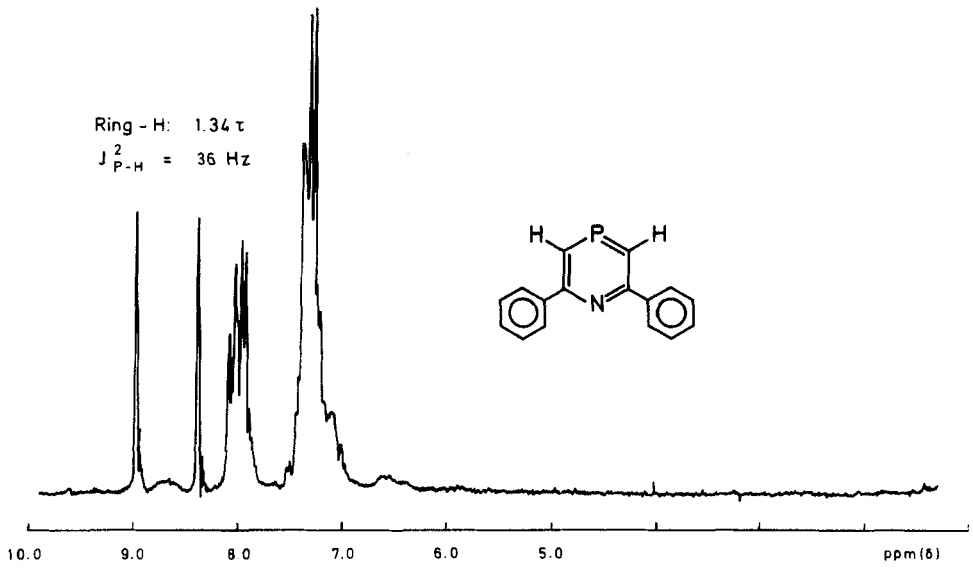

FIGURE 35

Also, the ^{31}P-nmr signal appears at extremely low field, $\delta = -245$ ppm against H_3PO_4.

The chemistry of this new system compared to the chemistry of the phosphabenzenes differs, not in principle, but as a matter of degree. The phosphabenzenes are *strongly* electrophilic, the aza-phosphabenzenes are *extremely* electrophilic due to the electronegativity of nitrogen and the electronegativity difference between N and P (Fig. 36).

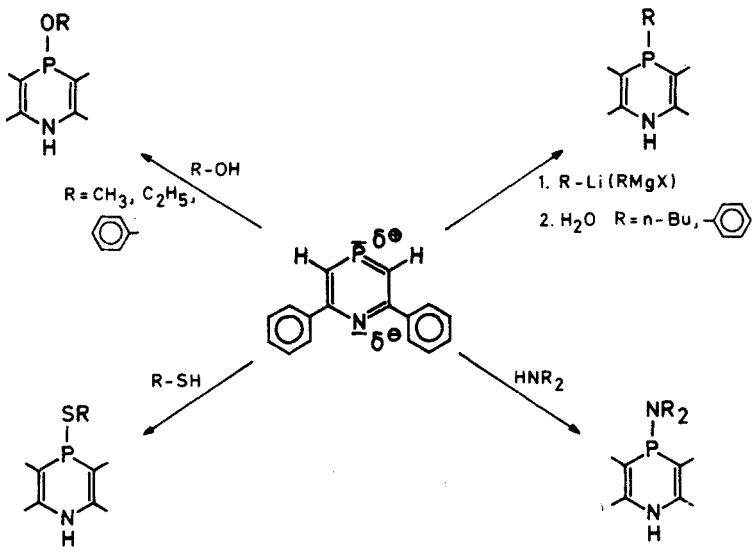

FIGURE 36

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Metallorganic compounds and even weak nucleophiles, alcohols, phenols, thioalcohols, amines and water add vigorously in the 1,4-position to give the 1,4-dihydro system with the nucleophiles at the P-atom. Furthermore, if we replace, in the aza-phosphabenzenes, one C = C double bond by a tervalent N with a free electron pair, we get a new class of heteroatomic systems with tervalent P, coordination number 2, the *phosphadiazoles* (Fig. 37).

These aromatic P-heterocycles are, according to A. F. Vasilev, Mel'nikov and others,[26] surprisingly simple to prepare by reaction of the phenylhydrazones of α-methyleneketones with PCl_3. In the meantime, we were able to show that the scope of the corresponding $AsCl_3$ reaction is even wider, the arsadiazol ring can be constructed even in steroid systems[27] (Fig. 38).

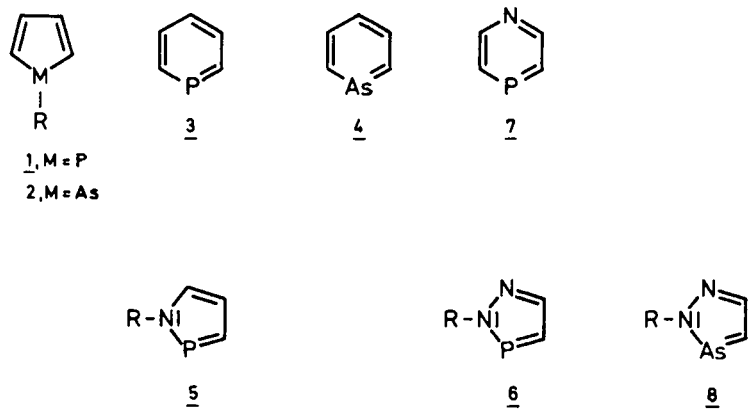

FIGURE 37

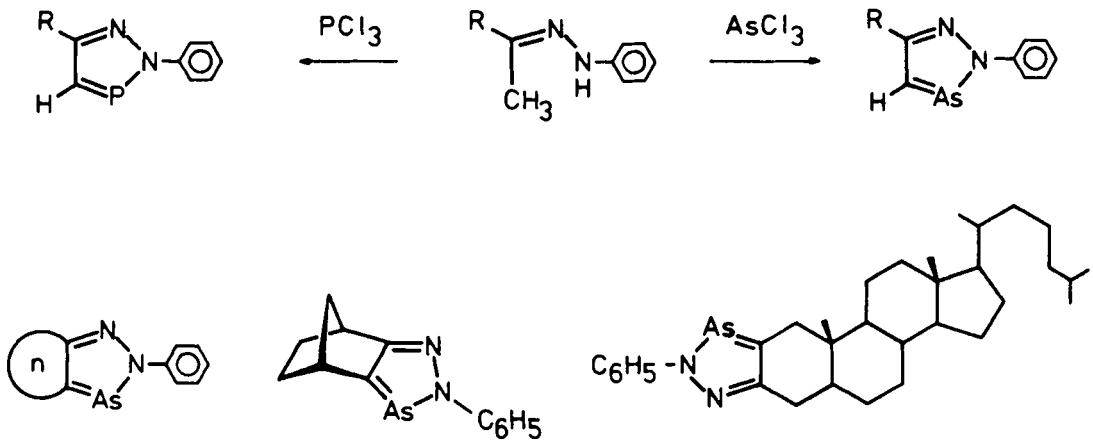

FIGURE 38

The extreme downfield shifts of the ring-H in the ^{1}H-nmr-spectra demonstrate the aromatic character of these systems (Fig. 39).

Returning to the chemistry of azaphosphabenzene, which is dictated by the electronegativity difference between N and P, this chemistry presents a challenge to synthesize the 1,4-diphosphabenzene system: since there is

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no longer an electronegativity difference between the heteroatoms, this system should be much less reactive and more comparable to phosphabenzene itself. There is a trace, but only a trace, of this 1,4-diphosphabenzene system in the literature.

Phosphorines as well as arsenines react analogously to benzenes with highly reactive dienophiles; for instance, with hexafluorobutine, but also dicyanoacetylene, to give the new phospha- and arsabarralenes respectively[28] (Fig. 40).

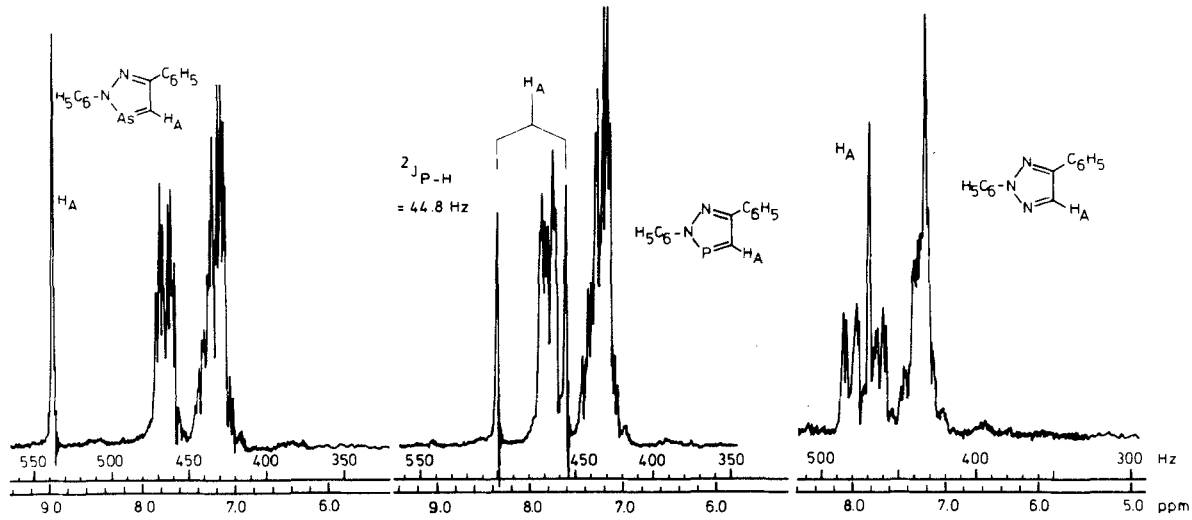
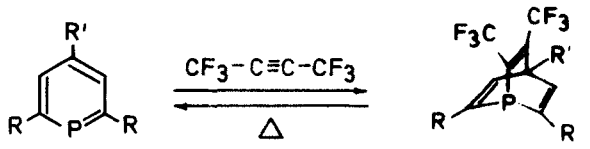


FIGURE 39



R = R' = C_6H_5 ; R = t-Butyl , R' = CH_3 ; R = CH_3 , R' = C_6H_5
R = R' = C_6H_5 ^{31}P = + 65 ppm

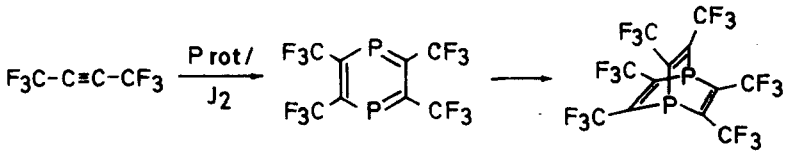


FIGURE 40

In 1961 Krespan[29] had already reported the synthesis of diphosphabarrelenes by reaction of hexafluorobutine with red P. The chemistry of the phosphorines is certainly a good argument for believing the diphosphabenzene to be the intermediate. Experiments attempted to realize a retro Diels-Alder reaction (as shown in Figure 40) failed.

The cycloaddition reactions of primary phosphines to *bis*-ethinylphosphines, provided with good leaving groups in both P-atoms, seemed to be a promising synthetic route to 1,4-diphosphabenzenes (Fig. 41).

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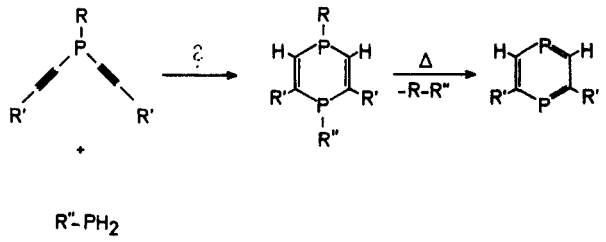

FIGURE 41

Indeed phenylphosphine (phenylarsine) adds quite smoothly to the *bis*-phenylethinyl-*t*-butylphosphine under radical conditions. By ^{13}C-nmr-spectroscopy 5-ring – and not the expected 6-ring – cycloaddition becomes apparent (Fig. 42).

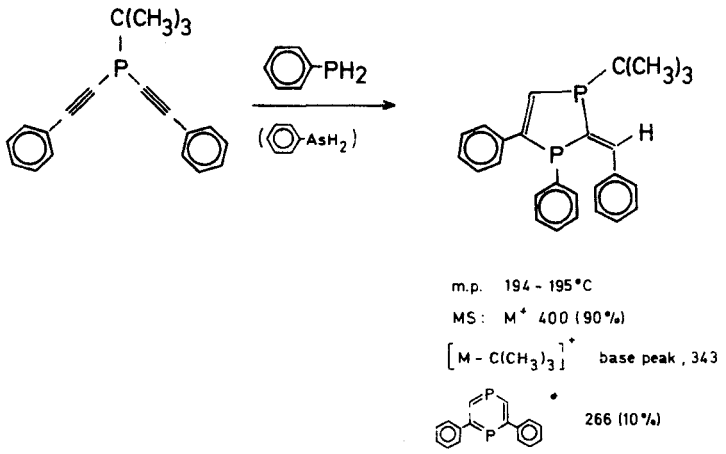

FIGURE 42

The reaction proceeds *via* the most stable radical intermediate in the first step, similar to the 5-ring-cycloadditions of phosphines and arsines to the 1,5-diaryl- as well as 1,5-dialkylpentadiineones,[30] pentadiineoles,[31] and pentadiines themselves (Fig. 43).

Only *bis*-ethinyl-*t*-butylphosphine reacts with $PhPH_2$ and $PhAsH_2$ clearly by 6-ring cycloaddition to give the 1-*t*-butyl-4-phenyl-1,4-dihydro-1,4-diphosphabenzenes and 1-phospha-4-arsabenzenes respectively[9] (Fig. 44).

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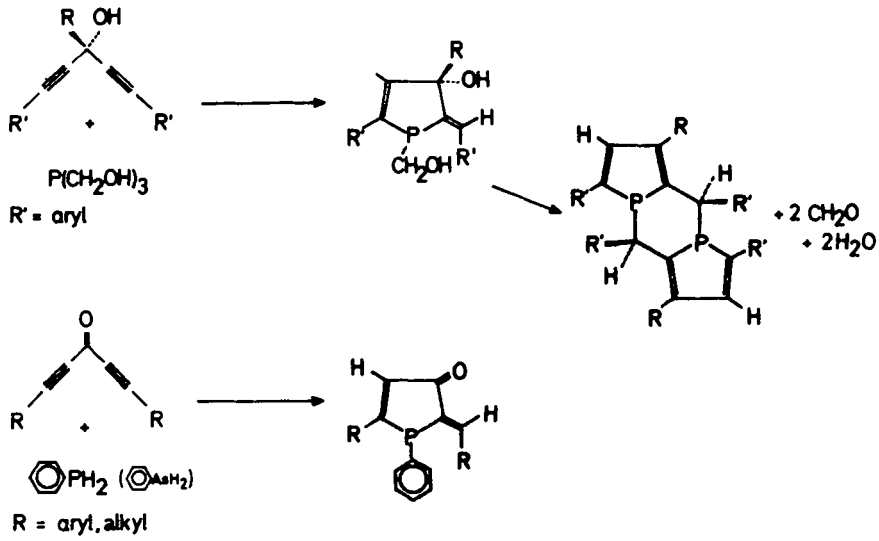

FIGURE 43

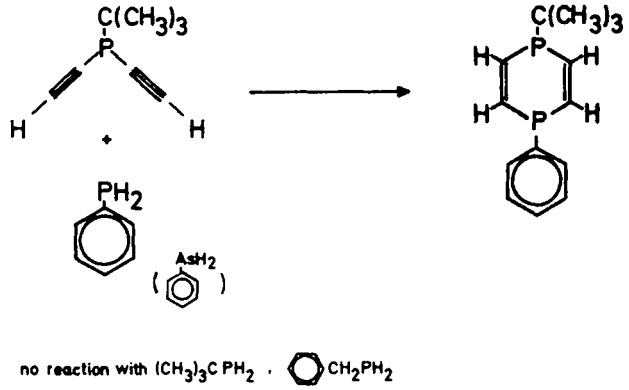

FIGURE 44

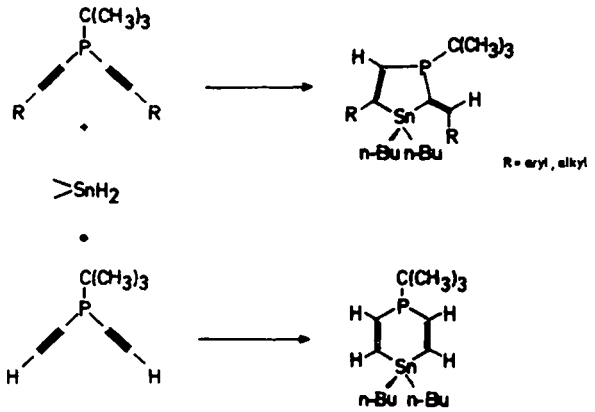

FIGURE 45

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So far so good, but alkylphosphines with good radical leaving groups, benzyl, *t*-butyl, do not undergo cycloadditions at all. Fortunately Sn-hydrides such as di-n-butyl-Sn-dihydride add quite smoothly to these acetylene-phosphines with exactly the same results: aryl- as well as alkyl-substitutents cause 5-ring formation, only the unsubstituted *bis*-ethinylphosphine provides the 6-ring, 1-*t*-butyl-4, 4-di-n-butyl-1, 1-dihydro-1-phospha-4-stannabenzene (Fig. 45).

With this compound in hand, it should no longer be a problem to synthesize the 1,4-diphospha- and also the 1-phospha-4-arsabenzenes. Exchange reactions with dichlorophenylphosphine and dichlorophenylarsine proceed quite smoothly, the 1,4-dihydro-1,4-diphospha- and -1-phospha-4-arsa-benzenes are identical with those prepared by direct cycloaddition. However the important exchange reactions with *t*-butyldichlorophosphine and PBr_3 as well as the corresponding arsenous halides are still puzzling. The ^{1}H-nmr control indicates exchange reactions even at 0°C, but the originally sharp new nmr lines fade very fast and no reaction products have yet been isolated (Fig. 46).

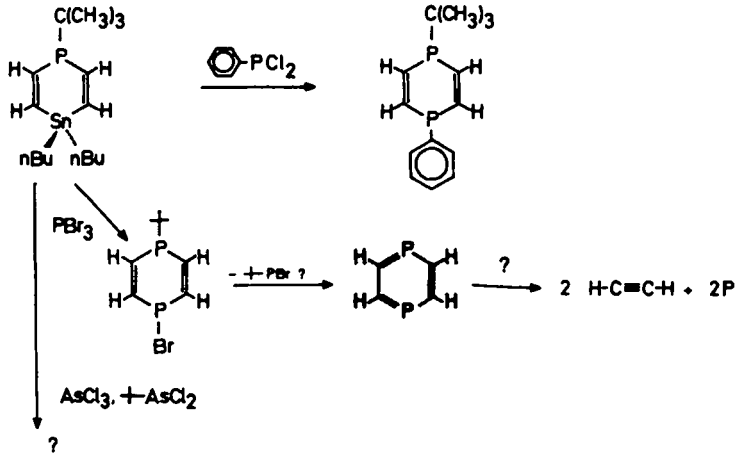
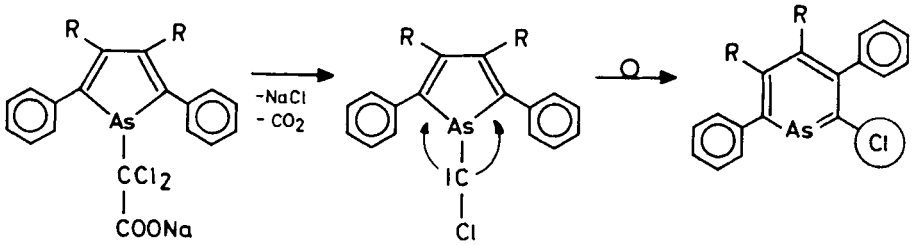


FIGURE 46



2-Cl-Arsabenzenes :

R = H m.p. 99-100°C , yield 26 % ; UV : λ_{max} 272 nm (log ε 4.59),
M.S. 326 (^{35}Cl) , rel Int 77 % 309 (3.93) , 361 sh (3.11)

R = ⬡ m.p. 187-189°C , yield 38 % ; UV : λ_{max} 256 nm (log ε 4.53),
M.S. 478 (^{35}Cl) , rel. Int. 28 % 272 sh (4.43) ; 308 sh (4.08),
354 sh (3.20)

FIGURE 47

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We still do not know what happens. Thermolysis to the diphospha- and phospha-arsabenzene is already possible at room temperature; further decomposition *via* the formation of acetylene or cyclobutadiene is speculative chemistry, but are 1,4-diphosphabenzenes stable or not? – this is still an open question.

In the final part of this article, we will discuss the problem of function groups at the phosphabenzene ring. Do phosphaphenols, -amines, phosphabenzaldehydes, -benzoic acids etc. exist of not, and what does their chemistry look like?

First of all we succeeded in synthesizing arsabenzenes with functional groups, e.g. chlorine, at the ring system. Thermolysis of the arsolyl-substituted sodium dichloroacetates and intramolecular insertion of the resulting carbene into the As-C_2 or As-C_5 bond forms the 2-chloroarsabenzenes.[32] This is a general new arsabenzene synthesis by ring-enlargement of the arsole 5-ring system (Fig. 47).

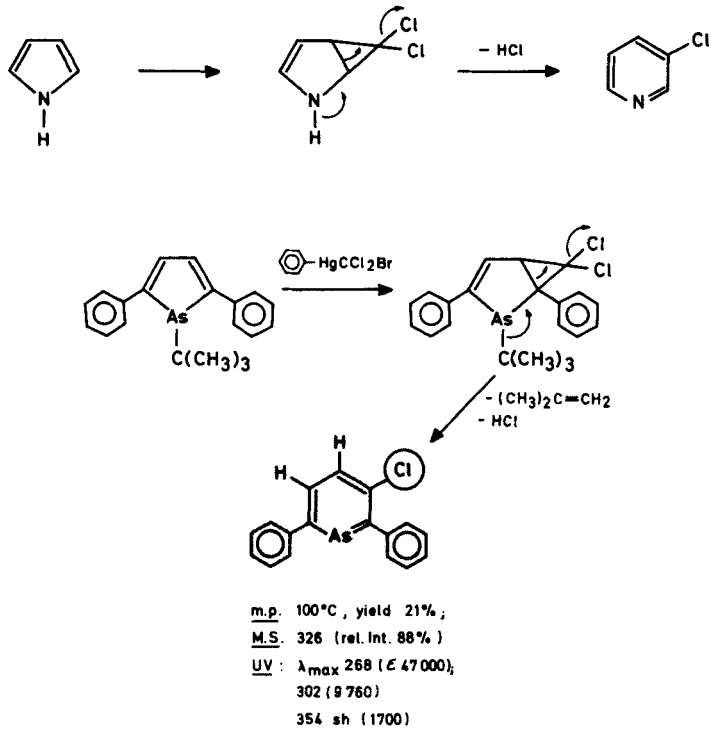

FIGURE 48

The classical pyrrole-β-chloropyridine ring enlargement can be translated into the As-language also: thermolysis of the CCl_2-adduct to 1-tert-butylarsole produces probably by a concerted mechanism 2,6-diphenyl-3-chloroarsole[33] (Fig. 48).

None of these approaches is useful for the phosphabenzenes, the yields are smaller than 1%. With 2-phenylphosphanaphthalene, we studied another approach – thermolytical – and this is a good example of how to gamble with suitable protecting and leaving groups at the P-atom.[34] Reaction of phosphanaphthalene with *t*-butyl lithium gives the deep purple reactive anion, which reacts smoothly with methyl chloroformate or with benzoyl chloride to give the 4-carbomethoxy-1, 4-dihydrophosphanaphthalene, and the 4-benzoyl derivative respectively. Whereas the latter on thermolysis loses the benzoyl group to give the starting material back, the phosphanaphthoic acid, methyl or ethyl ester, the first phosphorine derivatives with a functional group, can be isolated as yellow oils in good yields (Fig. 49).

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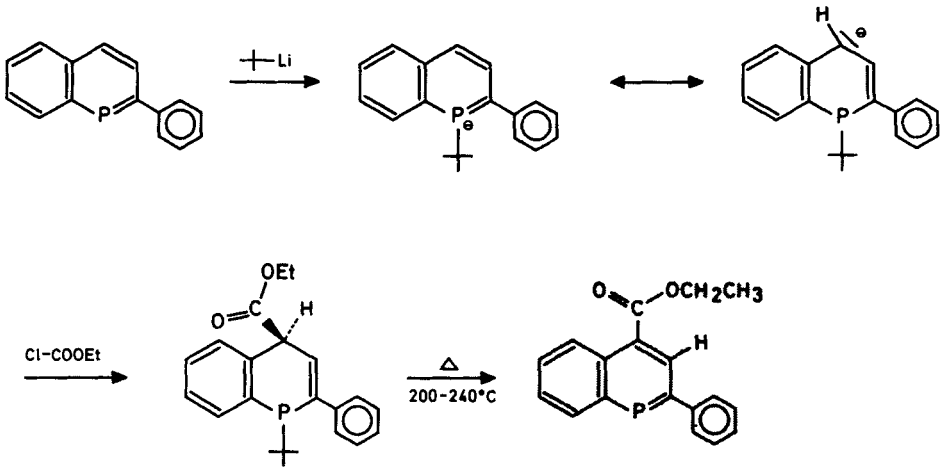

m.p. 87–92°C (mixture of cis/transisomers)

UV (EtOH): λ_{max} 244 nm (ε 16 000)

IR: $\nu_{C=O}$ 1735 cm^{-1} (5.76 μ)

MS: M^+ 352
base peak
$[M-C_4H_9-CO_2C_2H_4]^+$ 223

UV (EtOH): λ_{max} 368 nm

IR: $\nu_{C=O}$ 1720 cm^{-1} (5.82 μ)

MS: M^+ 294
$[M-COOC_2H_4]^+$ 222

FIGURE 49

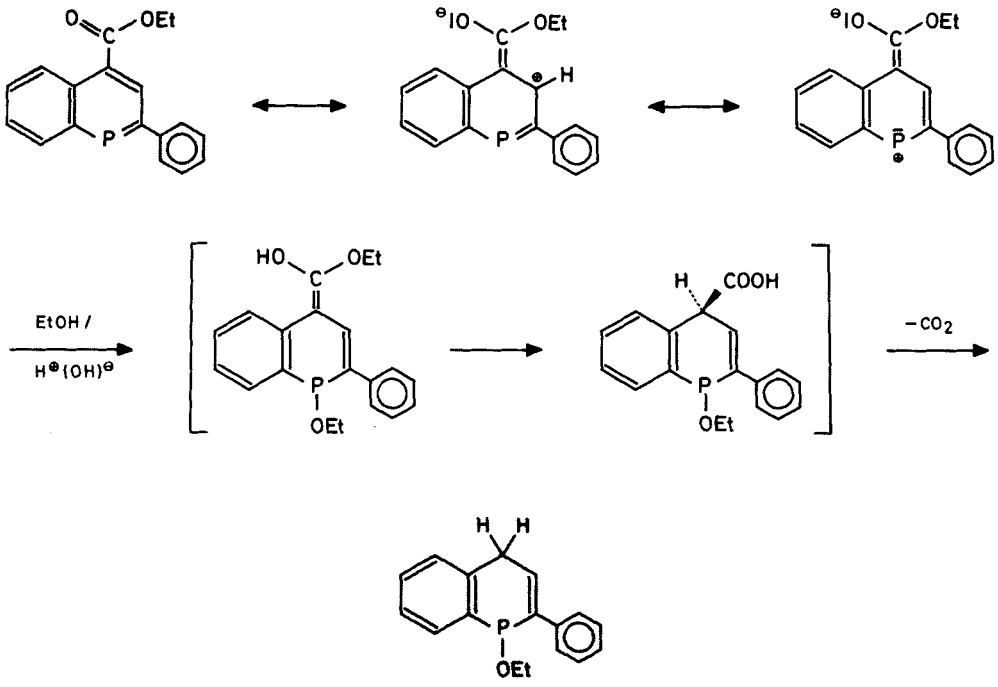

FIGURE 50

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The chemistry of this ester is again unexpected in a negative sense. Saponification with aqueous ethanolic NaOH is quantitatively accompanied by decarboxylation and addition of the nucleophilic solvent at the P-atom (Fig. 50).

Obviously, the electrophilic character of the P-atom is increased by the mesomeric effect of the ester group and the nucleophilic solvent may add in a 1,6-position. The reason for the smooth decarboxylation can be understood from the 1,4-dihydrophosphorine itself (Fig. 51).

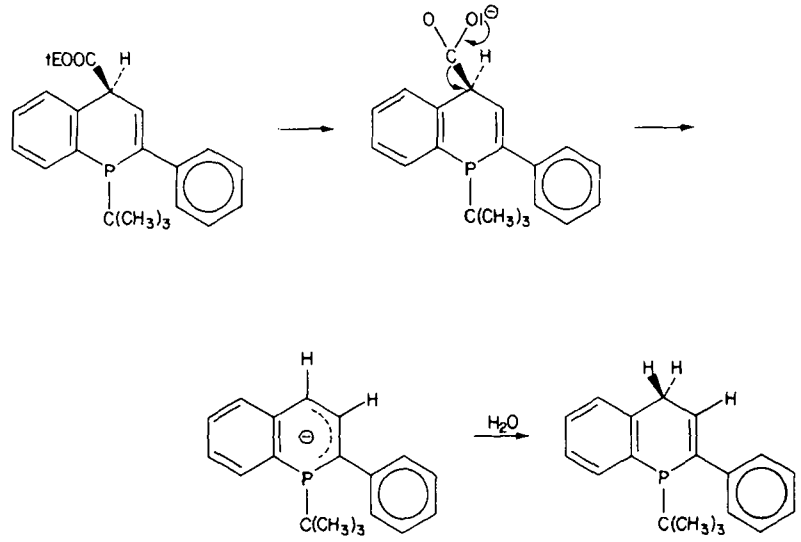

FIGURE 51

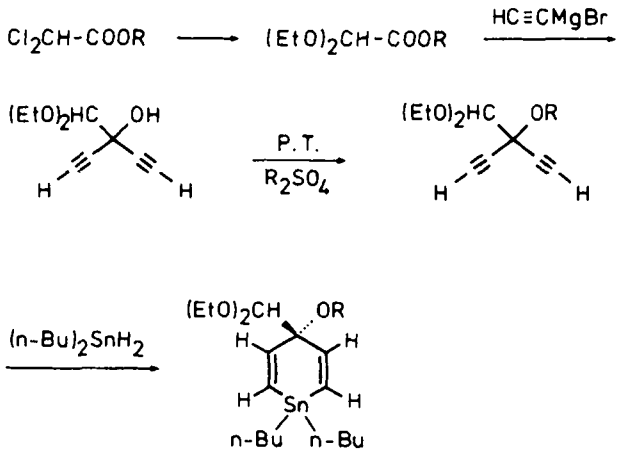

FIGURE 52

The formation of the energetically favored phosphanaphthalene anion must be the driving force for the CO_2 elimination.

There is a final possibility: are there phosphorine syntheses mentioned at the beginning of this article which could be programmed for the synthesis of phospha-, arsabenzenes with attached functional groups?

Pyrylium salts with carbalkoxy- or alkoxy groups do not form phosphorines at all. Let us consider the synthesis of 4-R-phospha- and arsabenzenes from 1,4-dihydrostannabenzenes: if it is possible to synthesize 1,4-

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dihydrostannabenzenes with functional groups in the 4-position, beside OR as leaving groups, we should have a good chance.

Starting out with glyoxylic acid acetal, we reach the dihydrostannabenzene without difficulties (Figs. 52 and 53).

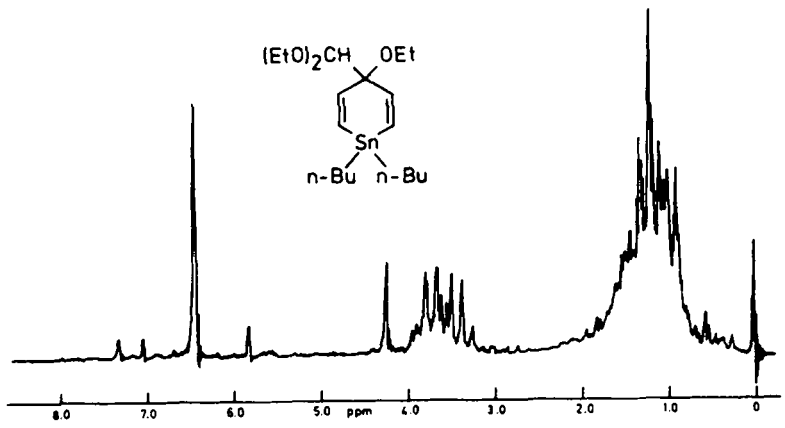

FIGURE 53

The exchange reaction with $AsCl_3$ proceeds smoothly and, again, in an unexpected manner (unexpected, since we did not think about the problem before). In the As-Cl intermediate, which can be isolated, the acetal group is an excellent, cationic leaving group; on thermolysis, the 4-alkoxy-arsabenzenes are formed exclusively but not a trace of the unexpected arsabenzaldehyde acetal[35] (Figs. 54 and 55).

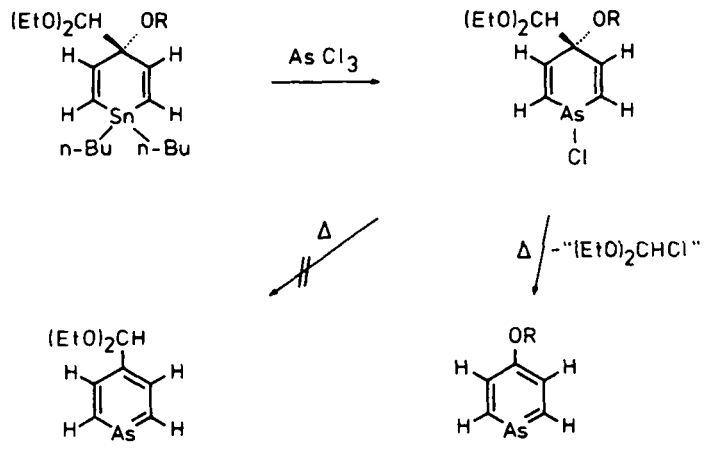

FIGURE 54

These 4-alkoxyarsabenzenes, and also the subsequently prepared 4-alkoxy-phosphabenzenes, behave in the mass spectrometer exactly like phenol ethers. The ether cleavage to arsa- and phosphaphenols however has not yet been successful.

How can we make the alkoxy group in the 4-position a better leaving group than the dialkoxymethyl group?

By reaction with Sn-hydrides, the chlorarsine intermediates can be reduced to the secondary arsines with an As-H bond, and now the leaving group situation is completely reversed. The As-H intermediates cannot be

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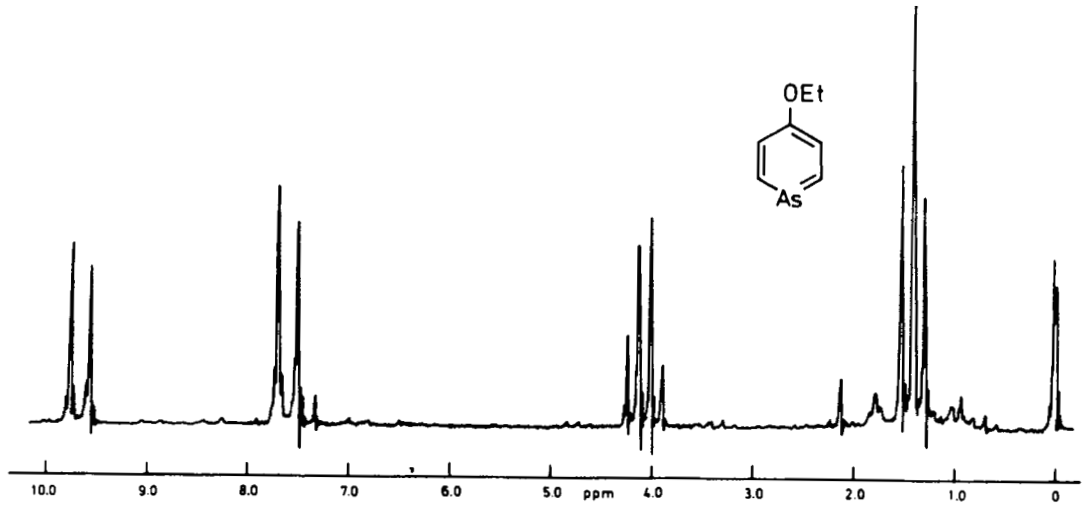

FIGURE 55

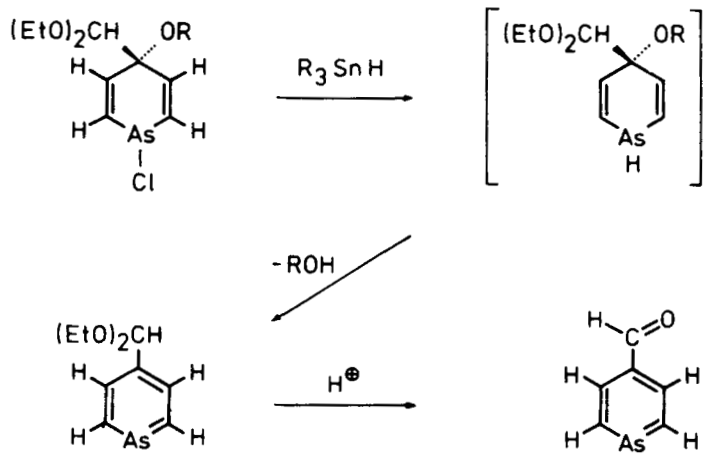

FIGURE 56

intercepted; they eliminate methanol or ethanol spontaneously and the arsabenzaldehyde-diethylacetal can be isolated by distillation under high vacuum[36] (Figs. 56 and 57).

With acidic ion-exchange resins in aqueous acetone, the acetal can be hydrolyzed within 15 minutes. Again, by high vacuum distillation, the arsabenzaldehyde can be isolated as a pale yellow oil which smells strongly like benzaldehyde; hence we have succeeded in preparing an arsabenzaldehyde in the real sense of the word (Fig. 56).

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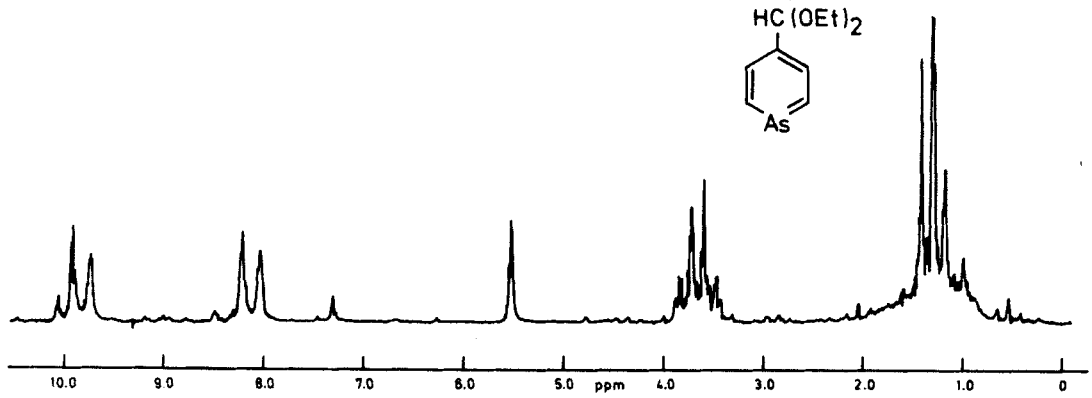

FIGURE 57

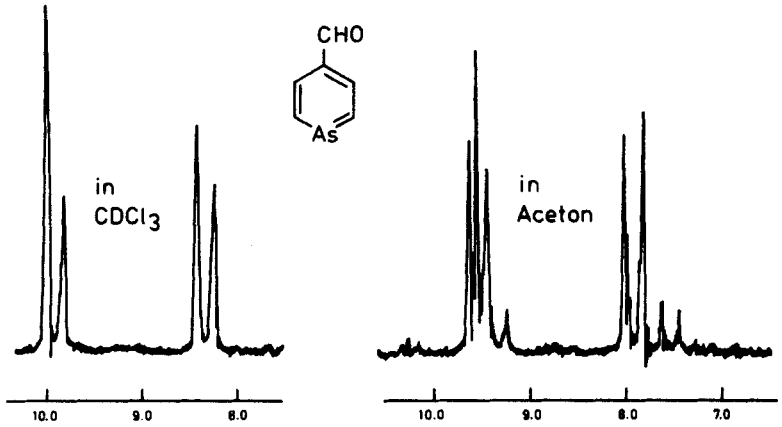

FIGURE 58

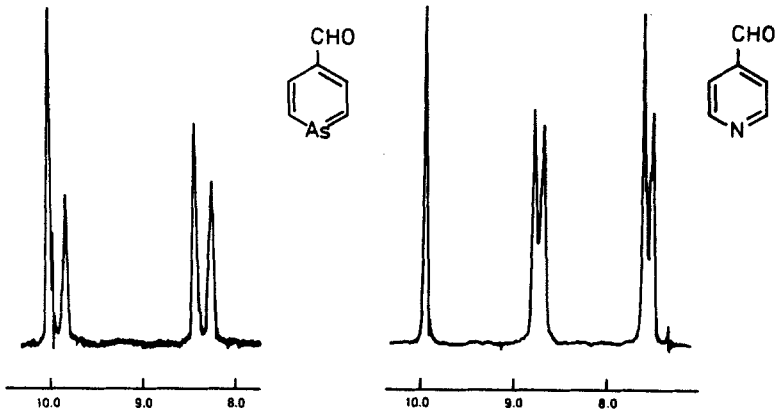

FIGURE 59

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In the ^{1}H-nmr, the ring-H appear far downfield; H_α at 0.07 τ (D), $J_{H\text{-}H}$ = 12 Hz, H_β at 1.67 τ (D), the aldehyde proton is even further downfield [−0.03 τ (D)] than the CHO-proton in benzaldehyde [0.0 τ (S)] and pyridine-4-aldehyde [0.07 τ (S)] (Figs. 58 and 59).

However, with respect to the phosphabenzaldehyde, the exchange reaction of the dihydrostannabenzene with PBr_3 did not work as well as with $AsCl_3$. Since we still do not know the mechanism of the Sn/As, and the Sn/P-exchange reactions, we certainly need mechanistic studies in order to improve these preparative results.

Finally, we have already started to study the chemistry of the arsabenzaldehyde. First results prove the possibility of aldol additions and condensations with this compound (Fig. 60). In the presence of basic ionic exchange resins, acetone adds to the aldehyde group; strong aqueous alkali catalyzes the formation of arsabenzalacetone as condensation product.

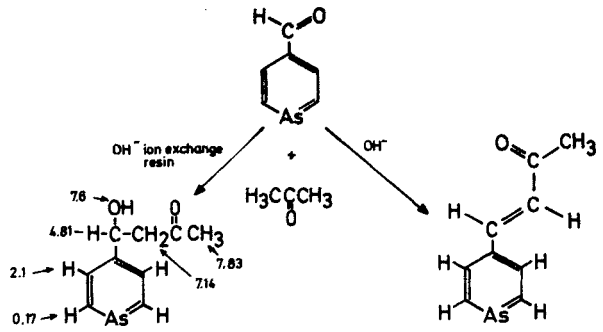

FIGURE 60

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