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1,2,4,3-TRIAZAPHOSPHOLE

A NEW DICOORDINATED PHOSPHORUS COMPOUND—I. SYNTHESIS AND CHEMICAL PROPERTIES OF ITS DERIVATIVES

Y. CHARBONNEL et J. BARRANS*
Laboratoire des Hétérocycles du Phosphore et de l'Azote, Université Paul Sabatier, 31077-Toulouse Cédex, France

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Abstract—The synthesis of various derivatives of 1,2,4,3-triazaphospholes by two methods is described and two kinds of isomers are separated by a chemical method. Their chemical properties have been studied by means of ^{31}P NMR from the point of view of basicity, complexation, reactivity of the double bonds and electrophilicity of the dicoordinated P atom. Their chemical behaviour suggests that they contain a delocalized system of Π electrons.

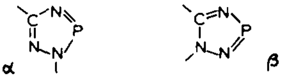
At the present time, only a few neutral dicoordinated phosphorus compounds are known:

Linear species such as ϕ–P = O[1,2] and ϕ–P = S[3] have been detected but not isolated. The linear phosphazene $(Me_3Si)_2N$–P = N–$SiMe_3$ (1) can be handled at low temperatures.[4]

If the dicoordinated P atom is included in a ring in which lie delocalized Π electrons, more stable compounds can be obtained such as phosphabenzenes[5,6] 1,4-azaphosphabenzenes,[7] 1,2,3-diazaphospholes[8] and benzodiazaphospholes.[9]†

Some substituted 2-phosphanaphtalenes[10,11] and 9-phosphaanthracenes[12] have been studied.

In preliminary communications, [13,14] we have described the synthesis and properties of a new dicoordinated phosphorus heterocycle: 1,2,4,3-triazaphosphole from which two kinds of isomers have been identified:



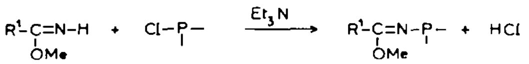
We now describe our recent results concerning the preparation and chemical properties of derivatives of these heterocycles.

PREPARATION

We have adjusted two methods of preparation: a complicated one (A) gives a mixture of the α- and β-isomers, an other (B) easier, gives only the α-isomers.

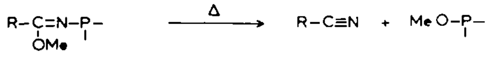
Method A (*in three steps*)

(1) *Preparation of a phosphinoimidate.* A chlorophosphine was condensed with a methyl imidate.



$$\underset{\text{OMe}}{R^1\text{–}\underset{|}{C}\text{=N–H}} + \text{Cl–}\underset{|}{P}\text{–} \xrightarrow{Et_3N} \underset{\text{OMe}}{R^1\text{–}\underset{|}{C}}\text{=N–}\underset{|}{P}\text{–} + HCl$$

This reaction and its products have been described previously[15] and we have shown that the phosphinoimidates can undergo thermal decomposition.[16]

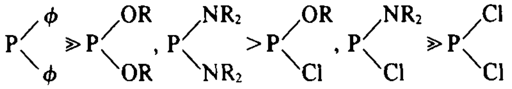


$$\underset{\text{OMe}}{R\text{–}\underset{|}{C}}\text{=N–}\underset{|}{P}\text{–} \xrightarrow{\Delta} R\text{–C}\equiv\text{N} + \text{MeO–}\underset{|}{P}\text{–}$$

On changing R^1 they can be arranged in terms of decreasing stability according to the following sequence:

$$\phi > \phi CH_2 > iPr > nBu > Me > CH_2Cl > CCl_3.$$

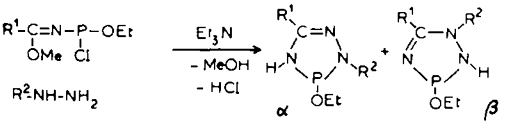
On varying the P substituents their stabilities decrease in the series:



It was noticed that dichlorophosphinoimidates are unstable even at 0°.

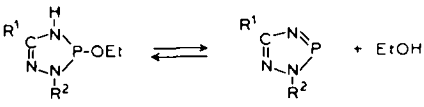
Further reactions have been performed with phosphinoimidates of general formula: $R^1\text{–}\underset{\text{OMe}}{\underset{|}{C}}\text{=N–}\underset{\text{Cl}}{\underset{|}{P}}\text{–OEt}$ (R^1 = –ϕ, –$CH_2\phi$, –iPr, –nBu) which are stable enough at 0° and are reactive at the P atom acting as an electrophile.

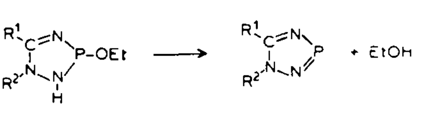
(2) *Action of a monosubstituted hydrazine.* As soon as the phosphino imidate was prepared, a monosubstituted hydrazine was added and reacted according to Scheme 4.



Since two isomeric triazaphospholines were prepared, one could expect that the P atom and the imidic C atom would have similar electrophilicities.

(3) *Elimination of alcohol.* α- and β-Triazaphospholines eliminated alcohol affording the corresponding triazaphospholes.





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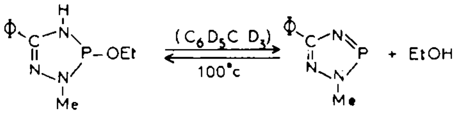
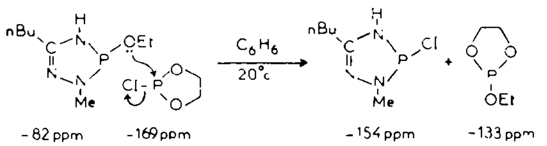
†The structure of such compounds have not been investigated fully.

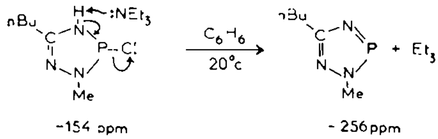
All β-isomers lost alcohol spontaneously at room temperature. The elimination only occured at higher temperatures with the α-isomers. For example the following equilibrium at 100° has been shown by proton NMR:



When both R^1 and R^2 substituents are aliphatic the elimination of alcohol was very slow and depending on the pressure applied, a violent decomposition could be observed with the formation of phosphonates or the distillation of the unchanged triazaphospholine. In this case the elimination of alcohol could be achieved by exchanging first the ethoxy group for a more labile one such as a Cl atom. Such an exchange readily took place through addition of 1-chloro-1,3,2-dioxaphospholane as was proved by the change in ^{31}P chemical shifts.



The chlorotriazaphospholine was stable at room temperature but it easily lost hydrochloric acid on addition of a tertiary base.



This elimination resembles that which gives rise to the formation of 1,2,3-diazaphospholes.[8]

This method afforded in almost all cases mixtures of α- and β-isomers, the total yields obtained from integration of ^1H or ^{31}P NMR signals are listed in Table 1.

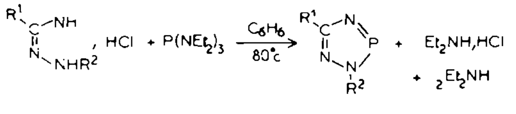
Table 1. Ratios of α and β isomers

R^1-C	-Φ	-CH_2Φ	-Φ	-CH_2Φ	-nBu
R^2-N	-Me	-Me	-Φ	-Φ	-Me
α/β	80/20	60/40	100/0	75/25	70/30

The α- and β-isomers could not be separated by the usual physical methods such as distillation, but a difference between their chemical properties provided a means of obtaining pure β-isomers (Experimental). The α-isomers were obtained by method B.

Method B

This depended on a reaction between a monosubstituted amidrazone hydrochloride and tris(diethylamino)phosphine.



Thus in a single step, pure α-isomers were obtained in high yields.

Stability. Mass spectrometry measurements proved that all the triazaphospholes isolated only exist as monomers. In these compounds the P=N bond has therefore a particular nature since all attempts to prepare open compounds with the P=N bond failed with the exception of the phosphazene (1).

Thermal stability of triazaphospholes is high: for example 5-phenyl-2-methyl-1,2,4,3-triazaphosphole distills at 250° (760 mm) without any decomposition.

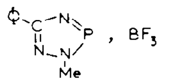
REACTIVITY

The reactivity of these compounds has generaly been studied by means of ^{31}P NMR.

Basicity. Acetic acid and trichloroacetic acid do not protonate triazaphospholes but after addition of trifluoroacetic acid, the ^{31}P NMR signals of α- and β-isomers disappear, a new signal appears at −224 ppm which in turn vanishes while the solution turns black. This behaviour is to be compared with that of some pyrroles, the protonated forms of which are unstable and decompose with formation of polymers.[17]

Basicity at the P atom is unusually low for it is not sensitive to classical quaternarising agents of aminophosphines such as methyl iodide and carbon tetrachloride.[18] The low availability of the phosphorus electron pair is also demonstrated by the absence of reactions with phenyl azide, phenyl benzoyl diazomethane, sulfur and diacetyl, even at 80°. Basicity is also low at the N atoms for they are not quaternarised by alkylating agents such as methyl iodide.

We have observed that an addition of boron trifluoride to 5-phenyl-2-methyl-1,2,4,3-triazaphosphole ($CHCl_3$ as solvent) readily produced a white crystalline adduct which we studied by NMR (solutions in CH_2Cl_2).



In ^{11}B NMR a single peak was observed at 0 ppm, this corresponds to a shielding of 15.5 ppm in comparison with BF_3 and proved that the hybridization state of boron had been changed.[19]

In ^{31}P NMR the signal was a little broader and slightly shifted upfields (+5 ppm) in comparison with the triazaphosphole. Usually complexation of phosphines with BF_3 afforded greater shifts in the opposite sense.[20-22]

In PMR the doublet corresponding to N–Me was shifted downfield (0.5 ppm) and the coupling constant remained unchanged ($^3J_{H-P} = 6.6$ Hz).

In ^{19}F NMR a single broad signal was noticed at +58 ppm without coupling with ^{11}B nor ^{31}P. This had previously been observed when complexation occured on another part of the molecule than the P atom[20] but when a P–BF_3 link was made, usually both $^2J_{P-F}$ and $^1J_{P-B}$ appeared.[21,23,24]

According to these results we concluded that complexation does not occur at phosphorus because the ^{31}P NMR signal was only slightly displaced and no P–B coupling was observed. So one may expect that attack of boron occurs at one of the dicoordinated N atoms but the possibility of a Π complex cannot be excluded.[20,25] We are preparing other boron adducts in order to resolve this problem.

Reactivity of the double bonds. The Diels–Alder addition is known to take place with unsaturated heterocyclic compounds^{26,27} such as derivatives of furan,^{28} thiophene^{29} and oxazole,^{30} but it does not occur between triazaphospholes and dienophiles such as maleic anhydride, tetracyanoethylene and dimethyl acetylene dicarboxylate. Likewise triazaphospholes are poor dienophiles for they do not give cycloadditions with phenyl azide nor with phenyl benzoyldiazomethane.

Reactions of complexation. Weak acids such as cuprous salts, mercuric salts and cadmium salts yield solid compounds which we are investigating.

Iodine, which is a polarisable electron acceptor, reacts with 5-phenyl-2-methyl-1,2,4,3-triazaphosphole in CCl_4 affording a dark brown solution. No change was observed in the ^{31}P NMR spectrum but in PMR the N-Me signal was shifted downfield (0.5 ppm) as in the case of the BF_3 adduct. This suggested an electron transfer from the triazaphosphole to iodine.

Electron acceptors usually employed in charge transfer reactions^{31,32} afford on mixing with triazaphospholes deep colours (from yellow to red) and often evolution of heat. Such reactions have been observed with picrid acid, tetracyanoethylene, benzoyl chloride, oxalyl chloride, and phtalic anhydride but in all cases ^{31}P NMR signals are not changed.

With picric acid a crystalline yellow compound was obtained which had to be handled in an inert atmosphere. It gave an ESR signal with a complex hyperfine structure and we are studying other complexes by means of ESR.

Reactivity at the phosphorus atom. In 1,4-phosphazabenzenes^{7} and 1,2,3-diazaphospholes^{33} the P atom is highly electrophilic because of the inductive attractive effect of nitrogen. For example, in 1–4 and 1–2 additions take place with alcohols and amines.

In such reactions the first step may be a nucleophilic attack on the P atom involving polarized species as suggested by Märkl for phosphazabenzenes from the results of calculations.

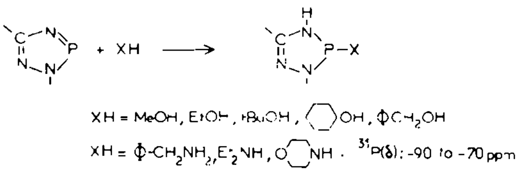
The phosphazene (**1**) also contains a highly electrophilic dicoordinated P atom,^{4} but nucleophiles such as EtOH and CCl_4 gave only 1–1 additions at phosphorus.

β-Triazaphospholes

We have observed that *β*-triazaphospholes do not react with the same reagents (alcohols, amines and CCl_4). This behaviour is surprising for a ring which contains three N atoms and one P atom and therefore poses a fundamental problem of electronic structure at the P atom.

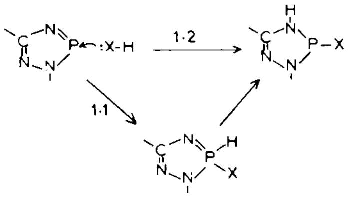
α-Triazaphospholes

(a) *Mono functional reagents.* *α*-Triazaphospholes react at once with alcohols and primary and secondary aliphatic amines.



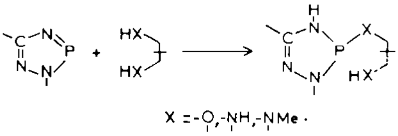
If XH is a poor nucleophile, the reaction does not occur. For example *β*-naphtol, carboxylic acids and aromatic amines do not produce any displacement of the ^{31}P NMR signals of triazaphospholes.

This kind of addition reaction is the opposite of the elimination reaction which afforded triazaphospholes and as mentioned above equilibrium can be observed. These reactions have been used to prepare pure triazaphospholines in high yields and they would be difficult to be obtained by other ways.^{34,35} The mechanism of addition has not been fully elucidated, it may consist in a simple 1-2 addition or in a 1-1 addition followed by a rearrangement.

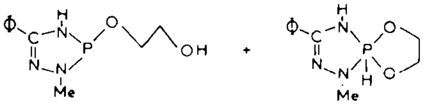


No evidence for such a P–H compound has been found by PMR at high or low temperatures but this does not completely exclude that such an intermediate could be involved.

(b) *Difunctional reagents.* Difunctional compounds such as *α*-diols, *α*-amino alcohols and *α*-diamines react in the same way.

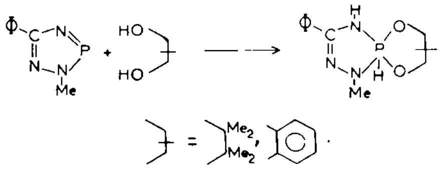


The compounds thus obtained are sometimes in equilibrium with a pentacoordinated P specie as previously observed.$^{36-38}$ For example, addition of ethanediol to 5-phenyl-2-methyl-1,2,4,3-triazaphosphole (1 : 1 ratio in CH_3CN) gives a mixture.



It is truly an equilibrium because addition of another equivalent of triazaphosphole yields the diphosphite which has been isolated:

With some diols the equilibrium was displaced to yield the spirophosphorane.



The spirophosphoranes thus isolated are similar to those previously obtained from benzamidrazone by the usual methods.^{39,40}

EXPERIMENTAL

M.ps and b.ps are uncorrected. PMR spectra were recorded on a Varian HA 100 spectrometer at 100 MHz (TMS as internal standard). Other NMR spectra were recorded on a Perkin–Elmer R 10 spectrometer: ^{31}P at 24.3 MHz (85% H_3PO_4 as external standard) ^{19}F at 56.6 MHz (CF_3COOH as external standard) and ^{11}B at 19.2 MHz (Et_2OBF_3 as external standard).

Microanalysis were performed by the "service central de microanalyse du C.N.R.S." Thiais France.

Preparation of triazaphospholes

Method A. The following process was used to obtain the compounds described in Table 2.

Table 2. Physical constants and ^{31}P NMR chemical shifts of triazaphospholes

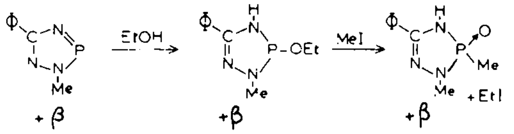
R-C	Ø	Ø	ØCH$_2$	ØCH$_2$	Ø	ØCH$_2$	nBu	iPr
R-N	Me	Me	Me	Me	Ø	Ø	Me	Me
Isomèr	α	β	α+β	β	α	α+β	α+β	α
B_p °C (mm)	105^a (0,1)	163^a (15)	110 (0,1)	168^a (15)	155^a (0,1)	148^a (0,1)	110 (15)	72 (15)
Method	B	A	A	A	A	A	A	B
$\delta^{31}P$ ^{b}	−256	−261	−250 −255	−255	−245	−245 −257	−256 −260	−255

a : cristallize from 50 to 70 °C but easily remain undermolten

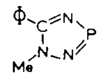
b : in ppm (H_3PO_4 85% external standard) negative at low fields

A 500 ml reaction flask fitted with a mechanical stirrer and a dropping funnel was flushed with dry N_2 and then filled with 14.7 g (0.1 mole) of dichloroethoxyphosphine in 100 ml of dry benzene. Under cooling with ice and stirring, a soln of 13.5 g (0.1 mole) of methyl benzimidate and 11 g (0.11 mole) of Et_3N in 50 ml dry benzene was added through the dropping funnel (15 min). The mixture was stirred 10 min more and then 4,6 g (0.1 mole) of methyl hydrazine and 11 g (0.11 mole) of Et_3N in 50 ml dry benzene was quickly added through the dropping funnel (5 min). After 15 min at room temp. the mixture was heated under reflux while stirring. Then $Et_3N.HCl$ was filtered off under N_2, washed with 50 ml dry benzene and the soln thus obtained was concentrated under reduced pressure. The residue was heated under reflux for 30 min at 0.1 mm in a distillation apparatus and then distillated at the same pressure. An oily mixture of α-and β-phenyl-methyl-triazaphospholes (average ratio 4:1) was thus obtained† b.p. 105–115° (0.1 mm), yield: 9 g (50%). Such mixture was used to study the chemical properties by ^{31}P NMR.

To get the pure β-isomer, the previous mixture (9 g) was dissolved in 40 ml dry benzene and an excess of EtOH (5 g) was added. After 5 min stirring an excess of MeI (14 g) was added and the soln refluxed for 30 min. This process did not change the β-isomer but transformed the α-isomer into a phosphonate.

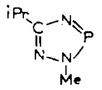


The soln obtained was concentrated under reduced pressure and the β-isomer could easily be separated from the residue by distillation: oil, b.p. 112° (0.1 mm). Second distillation afforded. b.p. 163° (12 mm) colourless solid m.p. 50°, yield: 1–2 g.



Preparation of α-triazaphospholes

Method B. The following example illustrates this method: A 250 ml reaction flask flushed with dry N_2 was filled with i-Pr-C-NH_2, HCl, (15 g; 0.1 mole), dry benzene (100 ml) and
||
N-NHMe
tris(diethylamino)phosphine (24.7 g; 0.1 mole). The mixture was refluxed for 1.5 hr with magnetic stirring and the diethylamine formed was removed by a stream of N_2. The soln obtained after filtration was concentrated under reduced pressure, distillation of the residue afforded. b.p. 72° (15 mm), yield 10 g. Colourless liquid, highly hygroscopic.



DISCUSSION

All the results confirmed the following observations:

The low basicity of the N atoms suggest that they are in the sp^2 hydridization state, two seem of the pyridine type but less basic than pyridine itself, and one of the pyrrole type.

The failure of the P atom to react with acids, quaternarizing agents and some oxidising agents shows that its electron lone pair is not as free as in aminophosphines.

In α-isomers the P atom has an electrophilicity which can be compared with that in phosphazabenzenes and in diazaphospholes, but they do not seem to react like the phosphazene (**1**).

Triazaphospholes do not show any dienic character nor a dienophilic behaviour.

Such observations are in agreement with a cyclic delocalization of Π electrons in the triazaphosphole rings. In a further paper we shall show that the data from various usual spectroscopic methods (NMR, UV, IR, mass) agree with such an interpretation. Structure determination of a couple of α- and β-isomers by X-rays diffraction and calculations, from PES data, are being performed.

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†If the two substituents are aliphatic and light, the mixture obtained here contained the triazaphosphole β, the triazaphospholine α and only some percents of triazaphosphole α; but the β-isomer can be extracted by the same following method as for the example described.

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