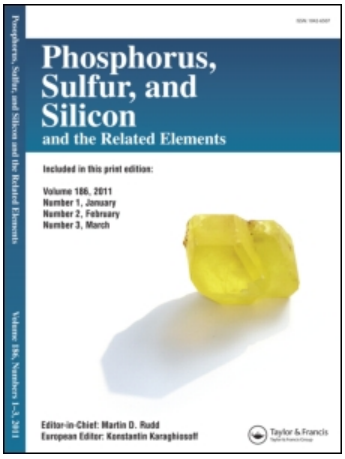

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FROM ALLENIC PHOSPHORUS DERIVATIVES TO HETEROCYCLIC COMPOUNDS. SYNTHESIS OF A 1,2,3-DIAZAPHOSPHOLE COMPOUND WITH A STRONGLY POLAR NH GROUP LINKED TO A DICOORDINATE PHOSPHORUS ATOM

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FROM ALLENIC PHOSPHORUS DERIVATIVES TO HETEROCYCLIC COMPOUNDS. SYNTHESIS OF A 1,2,3-DIAZAPHOSPHOLE COMPOUND WITH A STRONGLY POLAR NH GROUP LINKED TO A DICOORDINATE PHOSPHORUS ATOM

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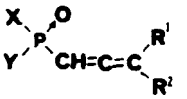
The synthesis of several derivatives containing an allenic group directly linked to a phosphoryl phosphorus atom is described. The addition of alcohol, water, hydrazines to this compounds is studied. The reaction of hydrazones (obtained from allenyldiphenylphosphine oxide) with trichlorophosphine gives rise to derivatives of 1,2,3-diazaphosphole. The hydrazone deriving from unsubstituted hydrazine leads to a compound with an NH group spectroscopically much more acidic than that of pyrrole; this NH group is presumably directly linked to the dicoordinated phosphorus atom.

Allenylphosphine oxides (I) can be used as synthetic intermediates because of their versatile reactivity.



(I)

(i) If X or Y or both are halogen atoms, they can be displaced by nucleophilic reagents such as alcohols, phenols, amines. This is a good method for preparation of new allenylphosphinyl derivatives.

(ii) Protic reagents such as alcohols, amines add to the allenic unsaturated system. Hydrazine gives rise to hydrazone and, in some cases, a cyclization may take place.

(iii) If x is a halogen atom, bidentate reagents can displace halogenide and add to the allenic system, thus leading to heterocyclic compounds.

(iv) Other heterocycles may be formed by ring closure on one of the allenic double bonds, the XYP → O group remaining unaltered.

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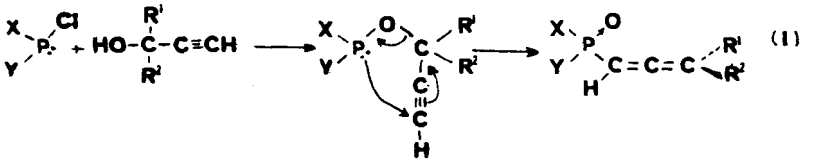
†Ferdinand Mathis suddenly departed this life February 4, 1984.

We endeavoured to study some of these reactions and to elucidate their mechanisms. The present paper deals with chemical aspects of this work. The main bulk of the spectroscopical part will be reported in another paper.

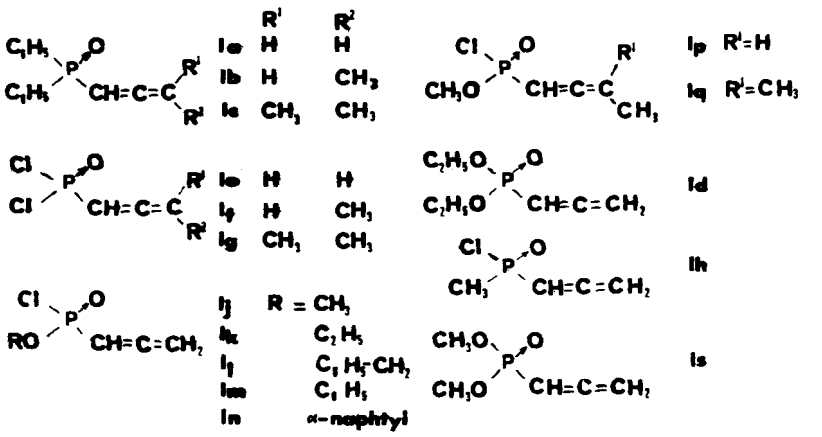
(i) *Substitution of halogen atoms linked to phosphorus.* Acid chlorides derived from tricoordinated phosphorus react with α-acetylenic alcohols to give esters which rearrange to allenylphosphine oxides (I).[1-3] The mechanism of this rearrangement (Scheme 1) has been unambiguously established.[4,5] Many such compounds have been already described (see, for instance).[3,6-10]



(I)

SCHEME 1

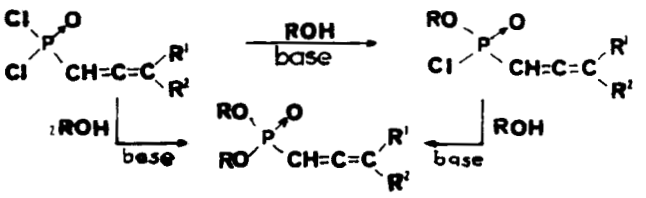
Compounds Ia, b, c, h, d, e, f, g, j, k, l, m, n, p, q (Table I) were prepared in this way.



Both chlorine atoms in allenyl dichlorophosphine oxides Ie, If, Ig can be substituted in one or two steps (Scheme 2) by the action of an alcohol or a phenol, preferably in the presence of a base. We could thus prepare the chloroesters Ij, j, k, l, m, n, p, q, and the diesters Id and Is.

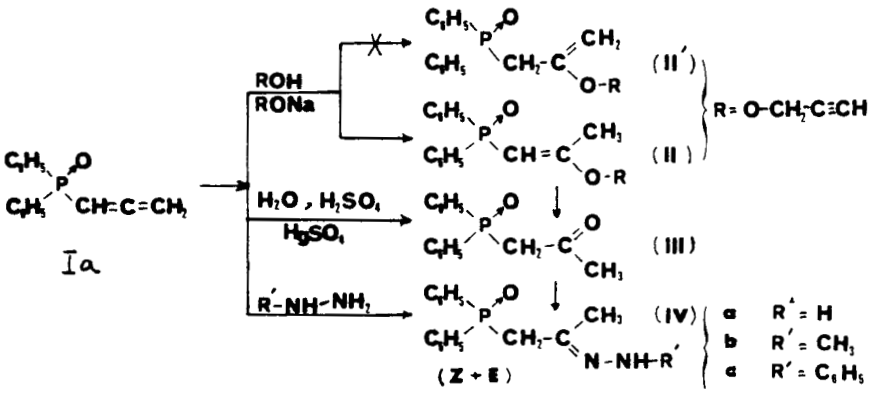
(ii) *Addition on the allenic system.* We reacted protic reagents on compound Ia, in which no interference can arise from the substituents linked to phosphorus.

(1) The only alcohol we reacted on Ia is propynol. The reaction occurs in the presence of alcoholate anion. Two isomeric vinylic ethers could be expected. The proton magnetic resonance spectrum of the product proves that only II, and not II′, is formed. The infrared spectrum of II displays the absorption bands corresponding to the P → O, C=C, C≡C and (C≡)C—H bonds.



SCHEME 2

(2) Water adds to the allenic unsaturated system in the presence of sulfuric acid plus mercuric ions. A β-ketophosphine oxide III is formed. This may afford a good procedure for preparing such compounds.



Acid hydrolysis of II leads to the ketone III.

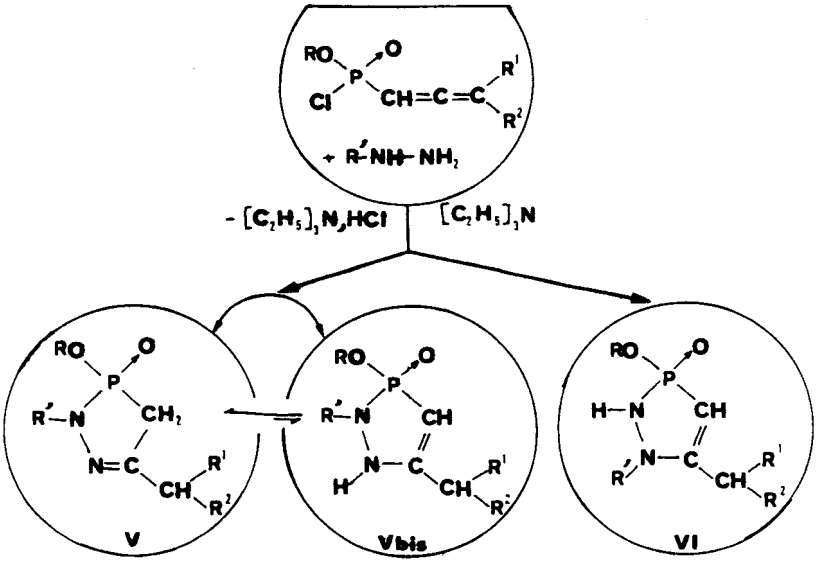
(3) Hydrazines react spontaneously on Ia to give hydrazones IV.

The structure of compounds IV is proved by the infrared spectrum: stretching bands: C=N near 1605 cm^{-1}; P → O near 1170–1190 cm^{-1}; two NH bands are observed for IVb (3255–3236 cm^{-1}) and for IVc (3236, 3200) in dilute CCl_4 solution, owing to syn-anti isomerism. The spectrum of the NH_2 group in IVa is complex and will be described in a next paper.

The hydrazones IV probably exist in a unique conformation in the solid state (one P → O stretching band in the infrared spectrum). In the dissolved state, two sets of ^1H magnetic resonance signals arise from Z and E isomers. One of them is at first less intense; the corresponding isomer is probably missing in the crystal, but begins to form during the time required for the preparation of the solution and the recording of the spectrum. In a matter of minutes, an approximately 50/50 equilibrium is attained which does not seem to be significantly sensitive to temperature changes. This point will be examined in more detail in the spectroscopic study.

(iii) *Cyclisation reactions.* The occurrence of two reactive sites in compounds such as Ij should allow cyclisation reactions which difunctional compounds such as

TABLE II



Compounds isolated	Va	Vb	Vc	Vd	Ve	Vf	Vg; VIg	Vh; VIh	Vj; VIj
R	CH_3	C_2H_5	$C_6H_5CH_2$	C_6H_5	$C_{10}H_7$*	CH_3	CH_3	C_2H_5	C_6H_5
R^1	H	H	H	H	H	CH_3	H	H	H
R^2	H	H	H	H	H	H	H	H	H
R′	CH_3	CH_3	CH_3	CH_3	CH_3	CH_3	C_6H_5	C_6H_5	C_6H_5

*$C_{10}H_7$ = α − naphtyl.

hydrazine or substituted hydrazines. The latter leads to cyclic derivatives for which the isomeric formulas, V, V bis and VI can *a priori* be considered (Table II).

We reacted methylhydrazine or phenylhydrazine with the chloroesters Ij, k l, m, n or p in toluene solution in the presence of one equivalent of triethylamine to avoid losing half of the hydrazine as its chlorhydrate. The reactions could be followed conveniently by ^{31}P magnetic resonance. Methylhydrazine and phenylhydrazine behave somewhat differently and will be considered separately.

If methylhydrazine is added progressively to the chloroester (RO)Cl-P(O)CH=C=CH_2 in $CDCl_3$ solution in the presence of triethylamine, a new ^{31}P magnetic resonance signal appears between +19 and +22 ppm (22 for Ij).

On further addition, three others signals appear between respectively +27 and +31; +38 and +44.5; +43 and +48.5 ppm (for Ij, 31; 44.5; 48.5). As the reaction proceeds, the signal of the starting material (between +20 and 26 ppm ; 25.5 for Ij) and the signals near +20 and +29 ppm decrease: these signals eventually disappear. The peaks near 41 and 45 ppm increase and remain alone. On a preparative scale, the reactions were performed in toluene; after separation from triethylamine hydrochloride and vacuum distillation, a liquid compound was obtained in a satisfactorily

pure state, the ^{31}P M.R. signal of which corresponded to the peak near 46 ppm (47.7 for the compound formed from Ij). In all cases this compound had the structure V (without any detectable amount of tautomer V bis) and not VI.

We will discuss the case of the reaction between methylhydrazine and the oxide of allenyl methoxy chlorophosphine Ij. The structure V for the product results from the following features:

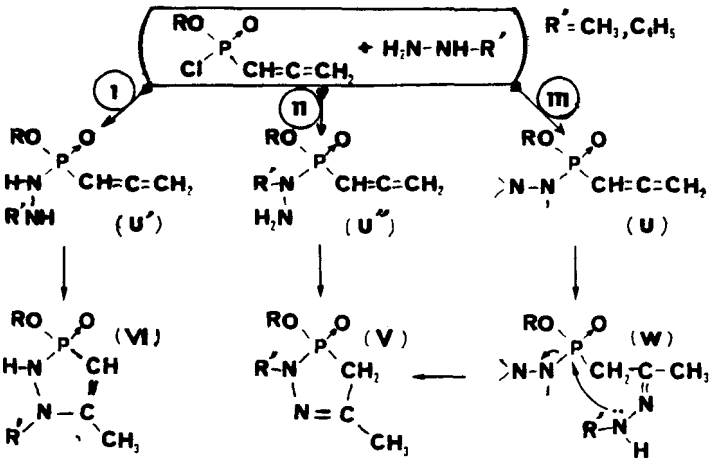
signal for *two* methylene protons ($CDCl_3$) +2.60 ppm; J (P—CH_2) 12.7Hz

signal for three methylamino protons +3.10 ppm; J (P—N—CH_3) 7.3Hz

C=N stretching band at 1600 cm^{-1}.

Structures Vbis and VI would both produce an NH absorption band which is missing in the I.R. spectrum, and a peak for one (and not two) P—CH=C proton, with ^1H near 5 ppm. Moreover, the coupling observed between the phosphorus nucleus and the *N*-methyl protons is too large for VI.

These results can easily be rationalized as follow (Scheme 3).



SCHEME 3

(i) The nucleophilic displacement of the chloride ion is much faster than addition on the allenic double bond; in fact, no signal corresponding to the structure $(H_3CO)ClP(O)CH_2$—C(=N—NH—CH_3)—CH_3 could be observed.

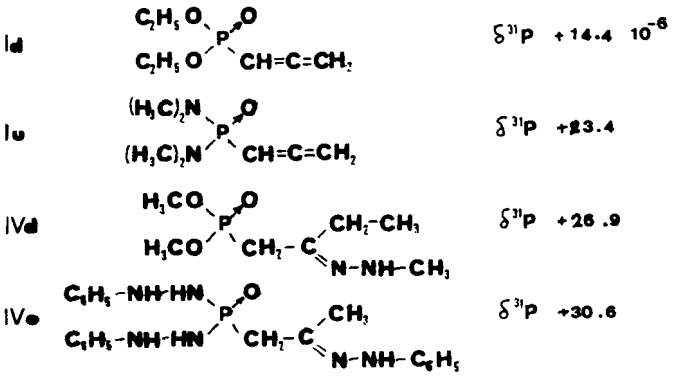
(ii) Methylamino nitrogen atom is a little more nucleophilic than NH_2 nitrogen and should react preferentially on phosphorus (intermediate U''). Higher nucleophilicity of $(H_3C)N$ in methylhydrazine has already been observed in phosphorylation.[11]

(iii) The NH_2 group in U'' adds to the allenic system, thus forming V.

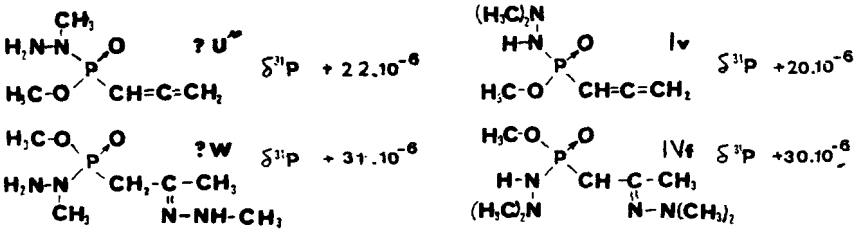
(iv) It has been proved that phosphorylation of methylhydrazine can take place, not only on $(H_3C)N$ but also on NH_2, though on a lesser extent.[12] This would explain the occurrence of the signal at 44.5 ppm in the ^{31}P M.R. spectrum of the reaction mixture, a signal which is still present at the end of the reaction. Attack of phosphorus by the NH_2 nitrogen would give intermediate U'; addition of the NH group in U' to the allenic system would give VI; the assignment of the +44.5 ppm

signal to VI is quite reasonable. From the intensities of the ^{31}P M.R. signals, the ration of V to VI is approximately 4 to 1. It is unfortunate but not surprising that the lesser product be lost during fractionation, thus preventing further identification.

The ^{31}P signals at +22 and +31 ppm can be assigned to intermediates, and the assignements can be rendered more precise by comparison with the ^{31}P chemical shifts of some compounds of known structure Id, Iu, IVd, IVe:

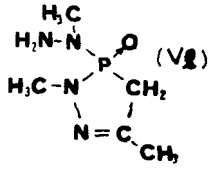


The signal at +22 ppm (between those of Id and Iu) suggests structure U″ or U′ and the signal at +31 ppm (near IVd and IVe) structure W (In both cases, the signals observed may well correspond both to the P—NH—NCH_3 and to the P—$N(CH_3)$—NH isomers.) To check this hypothesis, we reacted Ij with *N*,*N*-dimethylhydrazine. A new signal appeared at 20 ppm, presumably due to Iv, a good analogue for U″, and, shortly afterwards, a second signal at 30 ppm, reasonably assigned to IVf, analogous to W.



Still remains the question of the disappearance of intermediate W. One process only seems to account for it: nucleophilic displacement of the hydrazine residue linked to phosphorus by the distal nitrogen atom of the hydrazone group. The whole mechanism (with exclusion of improbable routes[13]) is summarized in Scheme 3.

Action of Ie on two equivalents of methylhydrazine in the presence of two equivalents of triethylamine leads to several compounds, one of which only could be isolated. Its structure is VI.



$\delta^{31}P$: +48.10^{-6}

J_{P-CH_2} : 12 Hz

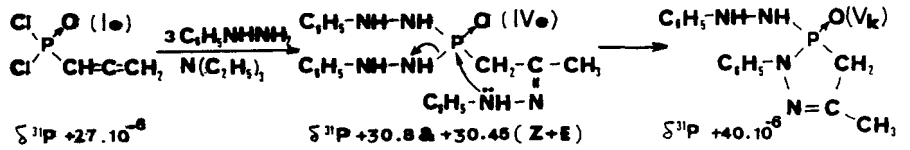
(in $CDCl_3$)

NH_2 (stretch.)	3275-80	cm^{-1}
	3190	"
NH_2 (scisor.)	1620-25	"
C=N (stretch.)	1608	"

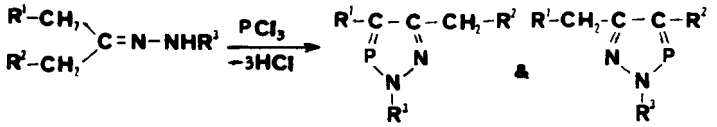
(I.R data: solid state)

The action of phenylhydrazine on compounds Ij, k, m lead to the isolation either of V without VI, or of VI without V, in a manner which seemed at first to be erratic. In fact, the N.M.R. spectra of the reaction mixtures proved that both V and VI were formed in all cases, but only one at a time could be isolated. If the mixture is vacuum distillated, V is isolated and VI is lost. If the mixture is extracted with hot anhydrous cyclohexane, VI crystallises on cooling, but V is lost.

The formation of VI is readily explained by route I in Scheme 3: the phenylamino nitrogen in phenylhydrazine is a very much weaker nucleophile than the NH_2 nitrogen, and attack on phosphorus must be due exclusively to the latter. If this is true, the formation of V cannot be explained by route II in Scheme 3. The only remaining possibility is route III, i.e., internal nucleophilic displacement of an hydrazino group by the C_6H_5NH part of the hydrazono group in intermediate W. This assumption is substantiated by the fact that the hydrazonohydrazide IVe goes over to Vk on heating.

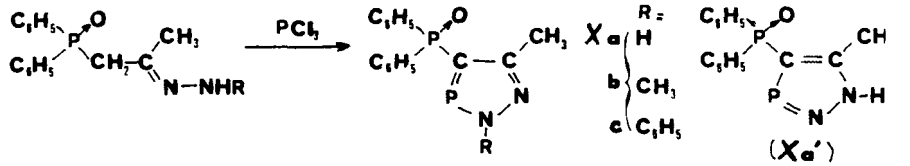


(iv) *Cyclisation between hydrazono-2 propyl diphenylphosphine oxide and phosphorus trichloride. Formation of a diazaphosphole ring with a very acidic NH group.* Schmidpeter[14–17] described a reaction (Scheme 4) leading to cyclic derivatives of dicoordinated phosphorus. The 1,2,3-diazaphosphole ring displays interesting properties: it behaves as nucleophilic, but the site of the nucleophilic attack varies widely with the nature of the electrophile (see J. H. Weinmaier[17]). Condensation between PCl_3 and unsymmetrical hydrazones containing no other heteroatoms than the functional nitrogens leads to two isomers.



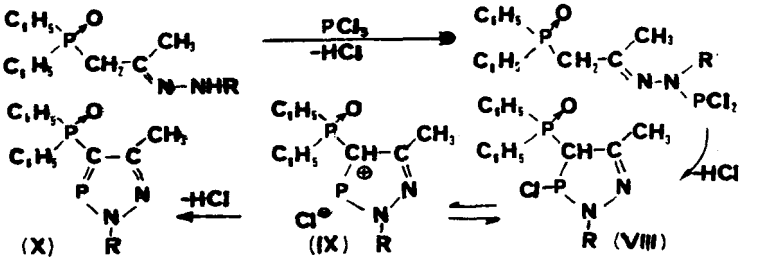
SCHEME 4

We endeavoured to extend Schmidpeter's reaction to the oxides of 2-hydrazonopropyl diphenyl phosphines IVa, IVb, IVc. We obtained the compounds Xa, Xb, Xc; in each case, one isomer only was obtained: this obviously arises from the great difference between the reactivity of the "acidic" methylene group and that of the methyl group.



The interest of these compounds is based (i) on the introduction of a dicoordinated phosphorus into a molecule containing already a tetracoordinated phosphorus atom (analogous compounds were prepared by Schmidpeter following the reverse order); (ii) if the compound derived from unsubstituted hydrazine has the structure Xa and not the tautomeric one Xa', it contains an NH group directly linked to a dicoordinated phosphorus atom; this could give in both cases information on the electronic structure of the cycle, in the same way as the properties of the NH group in pyrrole are clues to the electronic structure of the C_4N ring.

The successive steps in reaction described in Scheme 4 are known.[17] In our case, they can be described by Scheme 5



SCHEME 5

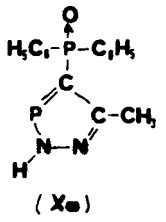
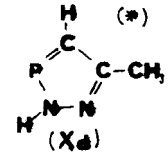
The ^{31}P NMR spectrum of the mixture free from unreacted PCl_3 shows three or fours signals: one near 20 ppm, one between 245 and 252 ppm, one between 220 and 231.5 ppm for all the reactions and one at 109 or 117 ppm only when the rest R is an hydrogen or a phenyl group. The first signal is due to the tetracoordinate phosphorus atom and the second one to the dicoordinated phosphorus atom in X. According to literature the third one is corresponding to a cationic dicoordinated phosphorus atom[17,18] and the fourth to a tricoordinated phosphorus derivative. So cyclic intermediate in the reaction can be a phosphenium chloride (IX) in equilibrium with a cyclic chlorophosphine (X) except in the case of R is a methyl group where only IX was observed.

The spectral properties of compounds X will be described elsewhere. Let us mention the large coupling constant (P—C—F—, 71 to 74 Hz, much larger than that displayed by the corresponding cations (30 to 33 Hz) IX. This coupling was not detected in the covalent intermediates VIII. The structures Xb and Xc unambiguously result from those of the hydrazones used as starting materials. Xb is confirmed by the P—N—CH_3 spin coupling (J = 7.5 Hz): in the case of Xa, the tautomeric form Xa' must be considered but, as we shall see, structure Xa can be preferred.

Methanol adds readily to compounds X to give a cyclic tricoordinated phosphorus ($^{31}P \cong 141$ ppm) which can be transformed in the corresponding tetracoordinated phosphorus atom ($^{31}P \cong 74$ ppm) by sulfur addition. Action of ethanediol or of 2.2-dimethyl butane 2.2 diol gives rise to expected spirophosphoranes (^{31}P between -27 and -40 ppm; $^1J_{PH}$ between 798 and 826 Hz).

The NH group in Xa is, spectroscopically speaking,[19] very acidic. The NH stretching frequency is very sensitive to basic solvents: 3421 cm^{-1} for the dilute solution in CCl_4, 3200 cm^{-1} in dioxane. This is a much larger shift than for pyrrole

TABLE III

Compound	T °C	δ_{NH} ppm	Half bandwidth Hz	Solvent concentration
 (Xa)	−35	13.83	25	$CDCl_3$ 10%
	−30	13.77	21	$CDCl_3$ 10%
	+60	12.70	8.5	$CDCl_3$ 10%
	+35	13.70	16	$CDCl_3$ 15%
 (Xa)	−30	14.6(d)	$J_{P-N-H} = 30$	$CDCl_3$ 10%
	−10		$\Delta U_{\frac{1}{2}} = 100$	$CDCl_3$ 10%
	+60	11.37	24	$CDCl_3$ 10%

*From reference 20.

(139 cm^{-1} between CCl_4 and dioxane). This suggests a sp^2 hybridization for the corresponding nitrogen atom; which can be accounted for by structure Xa. The stretching absorption band due to the associated NH group appears at 3130 cm^{-1} in $CHCl_3$ and at 3050–3100 cm^{-1} in the solid state. Those facts suggest hydrogen bonding of NH with a very good proton acceptor, either the pyridinic nitrogen atom or the phosphorylic oxygen atom. That the association in $CHCl_3$ is intermolecular is proved by the decrease of the relative intensity of the 3130 cm^{-1} band on dilution. It was interesting to investigate the P → O stretching band; it appears in the spectrum of the solid at 1175 cm^{-1}, a rather low value pointing to hydrogen bonding. The corresponding band in CCl_4 or in $CHCl_3$ is hidden by solvent absorption. However, it appears at 1198 cm^{-1} in the acetonitrile solution, where the NH group can be supposed to be associated with the solvent. This 23 cm^{-1} shift is a good argument for P → O · · · H—N bonding in the solid.

The magnetic resonance signal of the NH proton of Xa appears at low field (^1H + 13.03 ppm for the 10% solution in $CDCl_3$ at +35°C) and its shifts to still lower field on cooling, or at higher concentration (Table III); this is consistent with intermolecular association by strong hydrogen bonds. Bobkova *et al.*[20,21] observed similar facts for the compound Xd.

The NH signal of Xa is broad even at 60°C and its width increases significantly on cooling, an indication of moderately rapid proton exchange. The value of the *J*(P—N—H), or *J*(P—N—N—H), coupling constant would allow to discriminate between Xa and Xa′. However, lowering the temperature did not cause the splitting of the NH peak of Xa. On the contrary, Bobkova observed this splitting at −30 °C in $CDCl_3$ for her compound (Table III). The value of the *J* constant is in accordance with structure Xd. It is very likely that our compound has the corresponding structure Xa.

There is another reason, though not compelling by itself, to prefer Xa to Xa'. It has been proposed that there is some N(p)–(d)P π conjugation when N and P are directly linked, and that this conjugation tends to render the NH group (if present) more acidic. For instance, $\nu_{CCl_4}-\nu_{dioxane}$ is 13 cm^{-1} for $(C_2H_5)_2NH$ and 20 cm^{-1} in $(t—Bu)_2P—NH(i—Pr)$; this effect being still greater if electron attracting substituents are linked to the phosphorus atom.[22] A non empirical pseudopotential calculation[23,24] shows that this conjugation is, at least, plausible. That it be present in our compound should contribute to the high acidity of the NH group.

The high acidity of the NH proton in Xa suggests a strong conjugation of the lone pair of the corresponding nitrogen atom with the formal double bonds in structure X or even in structure Xa'. This result is in good agreement with the known structure of some 1,2,4,3-triazaphospholes.[25] But until now, no such determination has been made for 1,2,3-diazaphospholes.

EXPERIMENTAL PART

1. Allenylphosphine oxides (Ia, b, c, d, e, f, g, h, j, k, l, m, n)

1.1. Allenyldiphenylphosphine oxides Ia, b, c and allenyldichlorophosphine oxides Ie, f, g. These compounds were prepared according to the procedure described by Charrier.[3]

1.2. Allenylphosphonic acid monoester Ij, k, l, m, n and diesters Id, Is.

Two solutions are prepared, one (a) of 0.1 mole allenyldichlorophosphine in 200 ml anhydrous ether, one (b) of 0.1 mole of triethylamine and 0.1 mole of the alcohol or phenol ROH (R = CH_3, C_2H_5, $C_6H_5CH_2$, C_6H_5, α-naptyl) in 50 ml of the same solvent. Solution (b) is added dropwise to freshly prepared solution (a) at −70°C under stirring. Stirring is continued during 1 hr after the end of the addition. The mixture is then allowed to warm up to room temperature. Solid triethylamine chlorhydrate is filtered off, the solvent evaporated in vacuo and the residue fractioned by low pressure distillation (Table IV). The purified product thus obtained is used immediately to prepare the diazaphospholine oxides.

Id and Is were prepared by reacting the propadienylphosphonate chloride Ij or Ik (0.1 mole) on 0.1 mole of the alcohol ROH, or 0.1 mole of propadienyldichlorophosphine Ie on 0.2 mole of ROH. In both cases, the reaction is performed in anhydrous ethereal solution in the presence of triethylamine at 0 °C. The diesters are distilled under low pressure (Id, Eb. 122 °C/12 Torr; Is, Eb. 58 °C/0.1 Torr, yield 61%).

2. Addition reactions on the allenic double bond in allenyl-diphenyl-phosphineoxide Ia.

2.1. Alcoholysis of Ia to the vinyl ether II.

0.05 mole propynol are added to a solution of 0.05 mole Ia in 100 ml chloroform (the mixture remains unaltered after one night at room temperature). On adding ten drops of a satured solution of sodium methylate in methanol, the mixture warms up slightly. It is then heated during 5 min. Methanol is evaporated. A solid precipitates, which is washed with hexane and recrystallized from benzene, thus affording II.

TABLE IV

Compound	No.	Eb°C/Torr	
$CH_3O(Cl)P(O)CH=C=CH_2$	Ij	53/0.001	41
$C_2H_5O(Cl)P(O)CH=C=CH_2$	Ik	68/0.01	45
$C_6H_5CH_2O(Cl)P(O)CH=C=CH_2$	Il	86/0.001	35
$C_6H_5O(Cl)P(O)CH=C=CH_2$	Im	105/0.001	46
$\alpha - C_{10}H_7O(Cl)P(O)CH=C=CH_2$	In	112/0.001	40
$CH_3O(Cl)P(O)CH=C=CHCH_3$	Ip	61/0.01	38
$CH_3O(Cl)P(O)CH=C=C(CH_3)_2$	Iq	50/0.01	43

Calculated for $C_{18}H_{17}O_2P$, %: C, 72.96; H, 5.78, P, 10.45; 0, 10.81; found: C, 72.99–73.11; H, 5.87–5.81; P, 10.86–10.90; 0, 10.31–10.28.

2.2. Hydratation of Ia to the ketone III.

0.5 g concentrated sulfuric acid and 0.5 g mercuric sulfate are added to a solution of 0.2 mole Ia in 30 ml of aqueous methanol (70% by weight). The solution is heated to gentle boiling during five hours. Methanol is evaporated. The remaining aqueous solution is extracted with chloroform and the extract dried with sodium sulfate. The β-keto phosphine oxide precipitates on evaporating the solvent. It is recrystallised from benzene. Yield 87%.

Calculated for $C_{15}H_{15}O_2P$; C, 59.76; H, 5.85; P, 11.99; 0, 12.40; found: C, 69.85–69.90; H, 5.97–5.87; P, 11.83–11.78; 0, 12.54–12.47. Mass spectrum: molecular peak, m/e 258.

2.3. Hydrazonophosphineoxides IVa, b, c, from the action of hydrazines on Ia..

0.025 mole of the appropriate hydrazine (hydrazine hydrate, methylhydrazine or phenylhydrazine for IVa, IVb or IVc respectively) are added to a solution of 0.025 mole of Ia in 100 ml chloroform. The mixture is refluxed during four hours, the solvent evaporated off and the solid residue recrystallized from benzene. Yield: 55% (IVa), 60% (IVb), 58% (IVc).

IVa:mp 140 °C; calculated for $C_{15}H_{17}N_2OP$, %: C, 65.17; H, 6.29; N, 10.29; P, 11.38; 0, 5.69; found: C, 66.60–66.15; H, 5.37–6.35; N, 10.10; P, 11.34–11.49; O, 5.43. Mass spectrum: molecular peak m/e 272.

IVb: mp 152 °C; calculated for $C_{15}H_{19}N_2OP$, %: C, 67.12; H, 6.69; N, 9.78; P, 10.62; O, 5.59; found: C, 67.33–67.29; H, 6.75–6.79; N, 9.61–9.65; P. 10.68–10.71; O. 5.67–5.89. Mass spectrum: molecular peak m/e 286.

IVc: mp 165 °C; calculated for $C_{21}H_{21}N_2OP$ %: C, 72.47; H, 6.08; N, 8.05; P, 8.92; O, 4.60; found: C, 72.55–72.60; H, 6.16–6.12; N, 7.97–7.95; P, 9.03–8.97; O, 4.31–4.40. mass spectrum: molecular peak m/e 348.

3. Preparation of 3-oxo-1,2,3-diazaphospholine derivatives

3.1. Addition of methylhydrazine on chloroesters RO(Cl)P(O)CH=C=CH—R' (Ij, k, l, m, n, p), leading to 3-oxo-1,2,3-diazaphospholines Va, b, c, d, e, f.

A solution of methylhydrazine (0.05 mole) and triethylamine (0.05 mole) in 100 ml toluene is added dropwise under stirring to a cold (−30 °C) solution of 0.05 mole of the appropriate allenylmonochlorophosphonic ester (Ij, k, l, m, n, p) dissolved in 500ml toluene. The mixture is allowed to warm up to room temperature, then refluxed during one hour. Triethylamine chlorhydrate is filtered off and washed with toluene: the toluene liquors are collected, the solvent evaporated under vacuum and the liquid residue distilled at low pressure.

Va: Eb 76–8°C/0.1 Torr; yields 61%. Calculated for $C_5H_{11}N_2O_2P$, %: C, 37.04; H, 6.84; N, 17.28; P, 19.10; O, 19.74; found: C, 37.11–37.15; H, 6.90–6.92; N, 17.17–17.20; P, 19.02–18.98; O, 19.82–19.79. Mass spectrum: molecular peak m/e 162 (100%).

Vb: Eb 72°C/0.005 Torr; yield 53%. Calculated for $C_6H_{13}N_2O_2P$, %: C, 40.91; H, 7.44; N, 15.90; P, 17.58; C, 18.17; found C, 41.09–41.06; H, 7.49–7.52; N, 15.86; P, 17.52–17.50; O, 18.93–18.07.

Vc: Eb 118°C/0.8 Torr. Identified by I.R. and N.M.R. spectroscopy. Yield 40%.

Vd: Eb 120°C/0.001 Torr; yield 71%. Calculated for $C_{10}H_{13}N_2O_2P$, %: C, 53.57; H, 5.84; N, 12.49; P, 13.82; C, 14.28; found: C, 53.69–53.64; H, 5.93–5.90; N, 12.36–12.30; P, 13.68–13.71; C, 14.36–14.39. Mass spectrum: molecular peak, m/e 224 (30%); m/e 131 (100%) (M—C_6H_5OH); m/e 94 (30%) (C_6H_5OH); m/e 77 (10%) (C_6H_5).

Ve: Eb 150°C/0.001 Torr; yield 48%. Identified by I.R. and N.M.R. spectroscopy.

Vf: Eb 80°C/0.001 Torr; yield 70%. Calculated for $C_6H_{13}N_2O_2P$, %: C, 40,91; H, 7.44; N, 15.90; P, 17.58; O, 18.17; found: C, 41.02–41.04; H, 7.54–7.60; N, 15.81–15.79; P, 17.45–17.48; O, 18.22–18.25.

3.2. Reaction of methylhydrazine on allenyldichlorophosphine Ie leading to derivative Vi of 3-oxo-1,2,3-diazaphospholine.

The same procedure is used as in 3.1, starting from 2 equivalents methylhydrazine and 2 equivalents triethylamine for one equivalent of allenyldichlorophosphine Ie. The crude product is submitted to three distillations. Among all constituents of the mixture, one only is isolated; it is Vl; Eb 60°C/0.05 Torr; yield 35%.

Calculated for $C_5H_{13}N_4OP$, %: C, 34.09; H, 7.44; N, P, 17.58; O, 9.09; found: C, 34.20–34.17; H, 7.53–7.56; N, 31.57–31.84; P, 17.39–17.45; O, 9.18–9.21. mass spectrum: molecular peak m/e 176 (100%); m/e 131 (95%) (M—CH_3NNH_2); m/e 85 (75%) (CH_3—C(CH_2)=N—N—CH_3 + H^+); m/e 91 (75%) (HN—N (CH_3)PO).

3.3. Reaction between phenylhydrazine and chloroesters RO(Cl)P(C)CH=C=CHR' (Ij, k, m) leading to compounds Vg, h, j and VIg, h, j.

The same procedure is used as in 3.1 up to the evaporation of toluene, phenylhydrazine being used instead of methylhydrazine. The crude residue is either purified by distillation, thus affording Vg, Vh or Vj, or extracted with hot anhydrous cyclohexane; Vlg, Vlh, or Vlj crystallizes then in low yield; these compounds are very sensitive to air and to humidity and their melting points could not be measured.

Vg: Eb 100°C/0.001 Torr; yield 50%; mass spectrum: molecular peak m/e 224.

Vlg: mass spectrum: molecular peak m/e 224.

Vh: Eb 90°C/0.001 Torr; yield 36%.

Vlh: yield 42%; identified by I.R. and N.M.R. spectroscopy.

Vj: Eb 163°C/0.001 Torr; yield 40%; identified by I.R. and N.M.R. spectroscopy.

Vlj: yield 45%. Calculated for $C_{15}H_{15}N_2O_2P$; %: C, 62.94; H, 5.28; N, 9.79; P, 10.82; O, 11.17; found: C, 63.08–63.05; H, 5.35–5.40; N, 9.63–9.69; P, 10.70–10.68; O, 11.27–11.24.

3.4. Reaction between phenylhydrazine and allenyldichlorophosphine Ie leading to 3-oxo-1,2, 3-diazaphospholine derivative Vk and to the hydrazonodihydrazide IVe.

The procedure is similar to that described in 3.2. Recrystallization of the crude product from toluene affords Vk. The mother liquor is treated by hexane; a pasty product separates which is recrystallized from toluene; the mother liquor is again treated with hexane, and after three such crystallization, the hydrazonehydrazide IVe is isolated.

Vk: yield 30%. Calculated for $C_{15}H_{17}N_4OP$; %: C, 60.65; H, 5.71; N, 18.68; P, 10.34; O, 5.22; found: C, 60.12–60.16; H, 5.85–5.80; N, 18.52–18.56; P, 10.20–10.25; O, 5.31–5.28; mass spectrum: molecular peak m/e 300.

IVe: calculated for $C_{21}H_{25}N_6OP$, %: C, 61.75; H, 6.17; N, 20.58; P, 7.58; O, 3.92. found: C, 61.90–61.84; H, 6.26–6.30; N, 20.45–20.39; P, 7.39–7.45; O, 4.03–4.07.

4. Derivatives of 1,2,3-diazaphosphole, Xa, b, c.

0.25 mole PCl_3 are added dropwise to 0.05 mole of the hydrazone IVa, IVb or IVc at −60°C under stirring. The mixture is allowed to return to room temperature, then refluxed during 2 hours. The solid product is washed with petroleum ether to remove excess PCl_3, dried *in vacuo* and purified by sublimation at low pressure.

Xa: sublimation temperature at 11 Torr: 60°C; yield 50%. Calculated for $C_{15}H_{14}N_2OP_2$, %: C, 60.01; H, 4.70; N, 9.33; P, 20.63; O, 5.33; found: C, 59.74–59.50; H, 4.84–4.78; N, 9.03–9.06; P, 20.26; O, 5.60–5.63. Mass spectrum: molecular peak m/e 300 (80%); m/e 299 (70%) (N—H); m/e 285 (3%) (M—CH_3); m/e 201 (100%) $(C_6H_5)_2PO$).

Xb: sublimes at 53°C/11 Torr; yield 40%. Identified by N.M.R. spectroscopy of ^1H and ^{31}P.

Xc: sublimes at 75°C/11 Torr; yield 45%. mass spectrum: molecular peak, m/e 376.

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