

Phosphorus Derivatives of Amide Oximes. Part 1. Synthesis of *N*²-[Bis(dimethylamino)phosphinoyl]amidines, 4,6-Disubstituted 2,5-dihydro-1,3,5,2-triazaphosphorine 2-Oxides, and 3-Dialkylamino-1-dimethylamino-1*H*-2,1-benzazaphosphole 2-Oxides

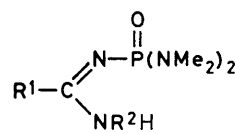
By Lucien Lopez and Jean Barrans, Hétérocycles du Phosphore et de l'Azote, chimie PC IV, 118 route de Narbonne, 31 077 Toulouse Cédex, France

The reactions of tris(dimethylamino)phosphine with amide oximes gave three types of compound, depending on the amide oxime substituents and the temperature: *N*²-[bis(dimethylamino)phosphinoyl]amidines (1), 4,6-disubstituted 2,5-dihydro-1,3,5,2-triazaphosphorine 2-oxides (2), and 3-dialkylamino-1-dimethylamino-1*H*-2,1-benzazaphosphole 2-oxides (3). With unsubstituted amide oximes only compounds (1) were formed at room temperature; at 80 °C a 1 : 1 mixture of (1) and (2) was obtained. Compounds (3) were obtained only with *N*-alkylbenzamide oximes. The formation of compounds (1)–(3) can be explained in terms of an unstable $\text{>C=N-O-P}^{\text{III}}$ intermediate. ³¹P CIDNP effects were observed during the formation of compounds (3), in support of a radical mechanism. ¹H N.m.r. and i.r. data are discussed.

AMIDE OXIMES ($\text{NH}_2\cdot\text{CR}=\text{NOH}$) have long been known to give five- or six-membered heterocyclic compounds by reaction of the oxygen and amino nitrogen atoms with an electrophilic carbon atom.¹ More recently, reactions of boron and sulphur compounds with amide oximes to give heterocyclic compounds have been described,² and we have shown that use of phosphorus compounds can lead to other heterocycles.³ Hitherto, few reactions of phosphorus compounds with amide oximes have been described: *O*-phosphorylated amide oximes have been prepared,⁴ and their solvolysis under alkaline conditions has been studied;⁵ and the reaction of dichloro(phenyl)phosphine with *N*-phenylbenzamide oxime has been shown to give the corresponding amidine hydrochloride.²

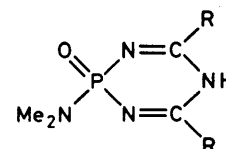
We now report our findings on the reaction of tris(dimethylamino)phosphine with unsubstituted amide oximes ($\text{NH}_2\cdot\text{CR}=\text{NOH}$) and *N*-substituted amide oximes [$\text{R}^1(\text{NR}^2\text{R}^3)\text{C}=\text{NOH}$]: three different types of tetracoordinated phosphorus compound [(1)–(3)] may be formed, depending on the experimental conditions and

the amide oxime substituents. Preliminary reports have been published on the formation of compounds (1)



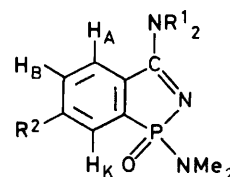
(1)

- a; R¹ = Me R² = H
 b; R¹ = PhCH₂ R² = H
 c; R¹ = Ph R² = H
 d; R¹ = Me R² = Ph
 e; R¹ = Ph R² = Me



(2)

- a; R = Prⁱ
 b; R = PhCH₂
 c; R = Ph



(3)

- a; R = Me R = H
 b; R = Et R = H
 c; R = Me R = Me
 d; R = Me R = Cl

¹ F. Eloy and R. Leaners, *Chem. Rev.*, 1962, **62**, 155.

² A. Dornow and K. Fischer, *Chem. Ber.*, 1966, **99**, 68.

³ L. Lopez and J. Barrans, *Compt. rend.*, (a) 1970, **271C**, 472; (b) 1971, **272C**, 1591; (c) 1971, **273C**, 1540; (d) L. Lopez, M. T. Boisdon, and J. Barrans, *ibid.*, 1972, **275C**; (e) L. Lopez, Thèse de doctorat d'Etat, no. 640, Toulouse, 1974.

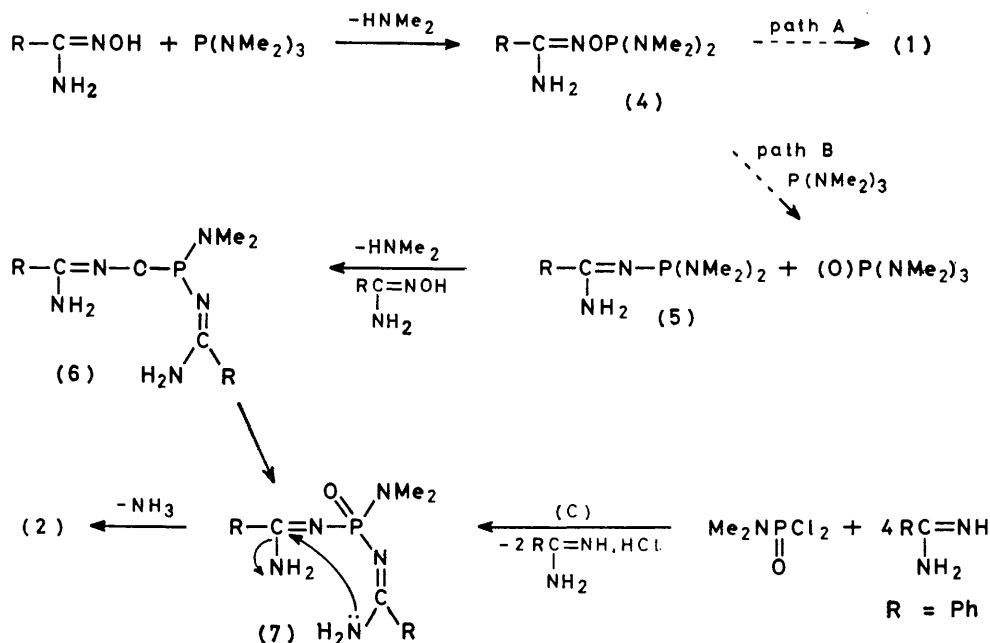
⁴ R. E. Plapinger and O. O. Owens, *J. Org. Chem.*, 1956, **21**, 1186.

⁵ R. F. Hudson and R. Woodcock, *Chem. Comm.*, 1971, 1050.

and (3).^{3a,b} By reactions of phosphoryl chloride with amidines and guanidines,⁶ or by reactions of *N*-chloroamidines with phosphites,⁷ compounds like (1) have been prepared previously. Compounds of type (2) have been prepared from phosphorylated biguanidines.⁸ Compounds (3) are members of a new family of phosphorus heterocycles.

RESULTS AND DISCUSSION

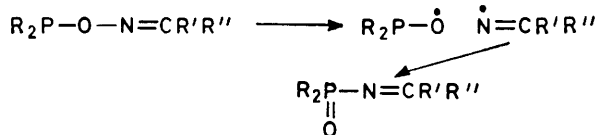
By treating tris(dimethylamino)phosphine with unsubstituted amide oximes, compounds (1) and (2) were



SCHEME 1

obtained (Scheme 1). The proportions of these compounds, deduced from ³¹P n.m.r. data, depend mainly on the reaction temperature: at room temperature we only observed the formation of (1), and at 80 °C a 1 : 1 mixture of (1) and (2) was obtained.

A ³¹P n.m.r. study of the reactions of chlorophosphites with oximes and hydroxamic esters has shown that the system (RO)₂P-O-N=CXY is unstable. The P^{III} signal is only observable below 0 °C (-139 p.p.m.); above this temperature the intermediate is transformed into the phosphine oxide (RO)₂P(=O)-N=CXY (-3 p.p.m.).⁹



SCHEME 2

Recently Hudson *et al.* have shown for this type of rearrangement that part of the reaction at least proceeds by a radical mechanism¹⁰ (Scheme 2).

⁶ F. Cramer and A. Vollmar, *Chem. Ber.*, 1958, **91**, 911.

⁷ G. I. Derkach and A. V. Kirsanov, *Zhur. obshchei Khim.*, 1962, **32**, 2254.

Running the reaction in Scheme 1 at 0 °C, or using chlorobis(dimethylamino)phosphine, did not enable us to observe the intermediate of type (4). However in the analogous reaction between amide oximes and 2-chloro- or 2-dimethylamino-1,3,2-dioxaphospholan at room temperature we have observed the ³¹P n.m.r. signal of a P^{III} intermediate [$\nu_{\max}(\text{CCl}_4)$ 3518 and 3411 cm⁻¹ (NH₂)], which could give either a tetraco-ordinate or a pentaco-ordinate phosphorus compound^{3c,e} (Scheme 3). The stabilisation of the P^{III} intermediate might be due to increased strain at phosphorus in the dioxaphospholan

ring.¹¹ This stabilisation has been also observed in 2-(diphenylmethyleneamino-oxy)-1,3,2-dioxaphospholan.¹⁰ From ³¹P n.m.r. spectra, we can deduce that the oxime function reacts first, and that the products (1) and (2) are formed from the same P^{III} intermediate (4). Probably their formation can be explained by a radical mechanism analogous to that in Scheme 2, but the e.s.r. signals observed during the reaction (Scheme 1) were too complicated to be interpreted. With regard to path (B) of Scheme 1, we have characterised trisdimethylaminophosphine oxide by g.l.c., but did not observed compounds (5) and (6); nevertheless reactions of *NN*-disubstituted amide oximes {Ph(N[CH₂]₅)C=NOH or Prⁿ(NET₂)C=NOH} with trisdimethylaminophosphine we have obtained trisdimethylaminophosphine oxide and a phosphinoamidine analogous to (5), [δ ³¹P -104 and -101 p.p.m.

⁸ H. Beyer, T. Pyl, and H. Lemke, *J. prakt. Chem.*, 1962, **16**, 137.

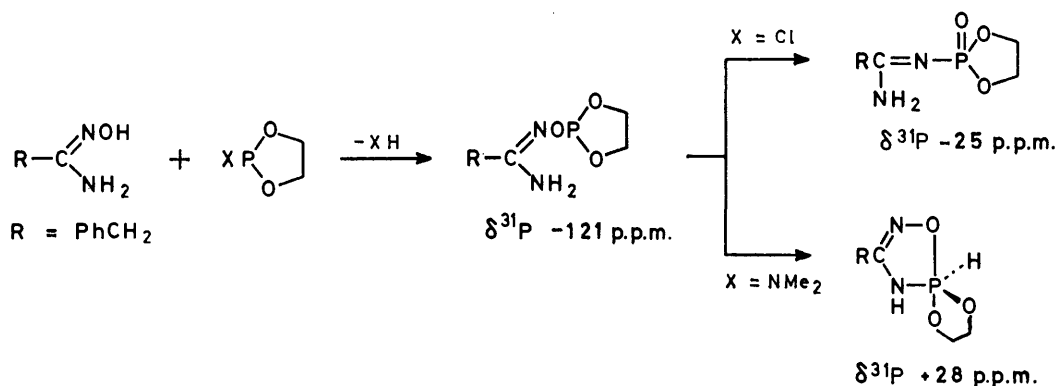
⁹ Yu. L. Kruglyak, M. A. Landau, G. A. Leibovskaya, I. V. Martinov, L. I. Saltykova, and M. A. Sokalskii, *Zhur. obshchei Khim.*, 1969, **39**, 215.

¹⁰ C. Brown, R. F. Hudson, A. Maron, and K. A. F. Record, *J.C.S. Chem. Comm.*, 1976, 663.

¹¹ C. Brown and R. F. Hudson, *Accounts Chem. Res.*, 1972, **5**, 204.

respectively; *cf.* -104 p.p.m. for $\text{Ph}(\text{NMe}_2)_2\text{C}=\text{N}-\text{P}(\text{NMe}_2)_2$.¹² By another route (C) we have prepared compound (2c) from benzamidine and dichlorodimethylaminophosphine oxide (4 : 1): at room temperature we observed a ^{31}P n.m.r. signal at -16 p.p.m., probably due to the intermediate (7); by refluxing in toluene, ammonia was eliminated to give (2c) ($\delta^{31}\text{P} -1$ p.p.m.). This reaction is analogous to that between amidines and phosphene.¹³ These results are in agreement with the proposed mechanisms of formation of (1) and (2).

Heating tris(dimethylamino)phosphine with *N*-substituted amide oximes gave compounds (1) and (3), in proportions depending on the amide oxime substituents (Table 1). We only obtained compounds (3) when R¹ was a phenyl group (even *p*-substituted), and when the amide oxime was *N*-substituted by alkyl groups.



SCHEME 3

In the reaction of 2-chloro-1,3,2-dioxaphospholan with *NN*-diethylbenzamide oxime we observed at room temperature, by ^{31}P n.m.r., a P^{III} species (-121 p.p.m.)

TABLE 1

Chemical shifts and percentages of compounds (1) and (3) from the amidoximes $\text{R}^1(\text{NR}^2\text{R}^3)\text{C}=\text{NOH}$

R ¹	R ²	R ³	(1)		(3)	
			$\delta^{31}\text{P}$ (p.p.m.)	%	$\delta^{31}\text{P}$ (p.p.m.)	%
Pr	Et	Et	-15.7^*	100		
Me	Ph	H	-18.5	100		
Ph	Ph	H	-17.4^*	100		
Ph	Me	H	-15.4	70	-42.3^*	30
Ph	Bu ^t	H	-16.3^*	70	-42.8^*	30
Ph or <i>p</i> -RC ₆ H ₄	Me	Me			$(-38,$	100
					$-39.7)$	
Ph	Et	Et			-39.5	100

* Not isolated.

which was transformed into a P^{IV} species (-21 p.p.m.). This shows that the oxime function reacts first as in unsubstituted amide oximes. The reaction leading to (3) in which a C-P bond is formed from an aminophos-

¹² Y. Charbonnel, J. Barrans, and R. Burgada, *Bull. Soc. chim. France*, 1970, 1363.

¹³ A. Pinner, *Ber.*, 1890, **23**, 2919.

¹⁴ M. Bourneuf, *Bull. Soc. chim. France*, 1923, **33**, 1808; L. D. Freedman, G. O. Doak and J. R. Edmistein *J. Org. Chem.*, 1961, **26**, 1213; R. N. Jenkins, L. D. Freedman, and J. Bordner, *Chem. Comm.*, 1971, 1213.

phine is unexpected; to our knowledge such bonds have been formed only from chlorophosphines.¹⁴

In the reaction of chlorobis(dimethylamino)phosphine with *NN*-dimethylbenzamide oxime at 0°C , we observed by ^{31}P n.m.r. the formation of a mixture of compounds (3a) (30%) and (1) (70%). The proportions of these compounds did not change even if the solution was heated for several hours; this proved that (1) was not an intermediate leading to (3). When the same reaction was run at 0°C in toluene, ^{31}P CIDNP effects were observed: in particular two emissions appeared at -37.92 and -37.01 p.p.m. when the spectrum was recorded after 115 s; in the normal spectrum the emission lines had disappeared and the line corresponding to (3a) appeared at -38.07 p.p.m. This emission due to polarised (3a) suggested that part of the reaction, at least, proceeds

by a radical mechanism. Nevertheless two aspects of the formation of (3) are still unclear: what is the influence of the NR^2R^3 group, and how is the second molecule of dimethylamine eliminated? The suggested mechanism in Scheme 4 is therefore only tentative.

The concerted cyclisation leading to the benzoxaphosphorine (path A) seems to us improbable, since the corresponding reaction with phosphorus trichloride, more electrophilic than trisdimethylaminophosphine, did not give a cyclic compound analogous to (3).^{3c} The fact that different *para*-substituents in the benzene ring [H, Me, Cl, or OMe (not isolated)] did not change the yield of (3) seems to favour the mechanism of path B. This reaction presents some similarity to the thermal rearrangement of *NO*-diacyl-*N*-phenylhydroxylamines in aminophenol.¹⁵

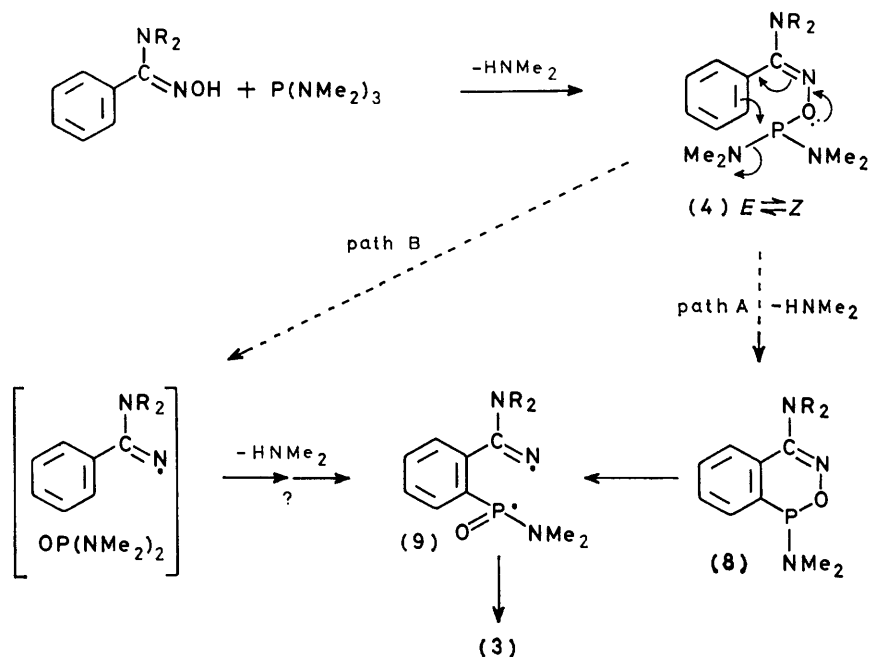
^1H N.m.r. data of compounds (1)–(3) are listed in Table 2. Compounds (1) can exist as *N*²-(phosphinoyl)amidines (A) or *N*¹-(phosphinoyl)amidine (B) according to the tautomeric equilibrium (usual in *N*-substituted amidines¹⁶) shown in Scheme 5. Both structures have been variously attributed to phosphorus derivatives of

¹⁵ L. Horner and H. Steppan, *Annalen*, 1957, **606**, 24.

¹⁶ R. L. Shriner and F. W. Neumann, *Chem. Rev.*, 1944, **35**, 351; D. Prevorsek, *J. Phys. Chem.*, 1962, **66**, 759; G. Schwenker and K. Bösl, *Pharmazie*, 1969, **24**, 653; *Arch. Pharm.*, 1970, **303**, 980; S. O. Chua, M. J. Cook, and A. R. Katritzky, *J.C.S. Perkin II*, 1974, 546.

amidines or guanidines analogous to (1),^{6,7,17} but without arguments. In decoupled ³¹P {¹H} n.m.r. spectra of (1) in CDCl₃ we saw only one signal, even at -50 °C; this favours the presence of only one isomer (A) or (B) with *E* or *Z*-configuration. At -30 °C slow exchange

structure (A). ¹H N.m.r. spectra of compounds (1a-c), in CDCl₃, showed two signals due to non-equivalent NH groups. At -50 or -70 °C these signals became narrow, but no ²J_{NH,P} was visible. We considered that the NH non-equivalence was due to intramolecular association



SCHEME 4

TABLE 2

¹H N.m.r. spectra (100 MHz; δ values; *J* in Hz; solvent CDCl₃)

N ² -(Phosphinoyl)amidines		R ¹	R ²	(NMe ₂) ₂	NH(1)	NH(2)	NH ₂ *
(1a)	Me	2.06 (d, <i>J</i> 1)		2.62 (d, <i>J</i> 10)	7.88	6.32	7.40
(1b)	PhCH ₂	7.2 (s)		2.53 (d, <i>J</i> 10)	8.10	5.24	7.66
	PhCH ₂	3.5 (d, <i>J</i> 1)					
(1c)	Ph	7.30—8.00 (m)		2.63 (d, <i>J</i> 10)	8.32	6.54	8.20
(1d)	Me	2.34	Ph 7.15—7.70 (m)	2.63 (d, <i>J</i> 10)	10.09		
(1e)	Ph	7.1—7.55 (m)	Me 2.8 (d, <i>J</i> 3.5)	2.70 (d, <i>J</i> 10)	8.05		
1,3,5,2-Triazaphosphorine-2-oxides							
	(2a)	Me ₂ CH	1.10 (d, <i>J</i> 6.4), 1.21 (d, <i>J</i> 6.4)		2.54 (d, <i>J</i> 10.3)		12.3
		Me ₂ CH	2.7—3.08				
	(2b)	PhCH ₂	6.90—7.24 (m)		2.32 (d, <i>J</i> 11)		1.53
		PhCH ₂	δ_B 3.33, δ_A 3.62 (<i>J</i> _{AB} 15)				
			δ_B 3.35, δ_A 3.59 (<i>J</i> _{AB} 14.5)				
	(2c)	Ph	7.4—8.5 (m)		2.63 (d, <i>J</i> 10.5)		11.1
2,1-Benzazaphosphole 1-oxides							
	(3a)	Me	3.46		2.58 (d, <i>J</i> 10)		
	(3b)	MeCH ₂	1.39 (t, <i>J</i> 7.1)		2.62 (d, <i>J</i> 9.4)		
		MeCH ₂	3.86 (q, <i>J</i> 7.1)				
	(3c)	Me	3.45	Me 2.40	2.58 (d, <i>J</i> 10)		
	(3d)	Me	3.50		2.65 (d, <i>J</i> 10)		

* Solvent (CD₃)₂SO.

allowed observation of ²J_{NH,P} in compounds with a=P(:O)-NH- group.¹⁸ In ¹H n.m.r. spectra of compounds (1) ²J_{NH,P} was not observed, even at -70 °C, implying that these compounds have the N²-(phosphinoyl)amidine

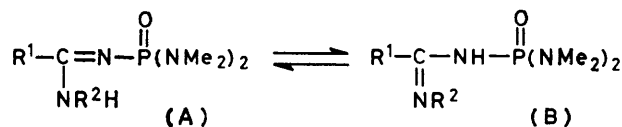
between the oxygen of the phosphoryl group and one hydrogen of the NH₂ group. We have attributed the low field NH(1) signal to the associated hydrogen nucleus.¹⁹ At low temperature δ [NH(1)] did not change,

¹⁸ A. Chabane, Thèse de spécialité, no. 1616, Toulouse, 1974.

¹⁹ (a) F. Mathis, Monographie de chimie organique 'Structure et Propriétés Moléculaires, VII,' ed. Masson, Paris, 1970, p. 421; (b) P. Laszlo, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 231.

¹⁷ V. I. Shevchenko and A. A. Koval, *Zhur. obshchei Khim.*, 1967, **37**, 1111; H. Beyer, T. Pyl, and H. Lemke, *J. prakt. Chem.*, 1962, **16** (3-4), 132.

but the NH(2) signal was shifted to low field [1.02 for (1a) at -42°C ; 0.26 for (1b) at -55°C , and 1.08 p.p.m. for (1c) at -70°C]. In $(\text{CD}_3)_2\text{SO}$ the protons of the NH_2 group became equivalent, because of association with the



SCHEME 5

solvent. A $^3J_{\text{HN},\text{CH}_3}$ value of 3.5 Hz is observed for (1e), in agreement with the N^2 -(phosphinoyl) structure.

I.r. data for compounds (1) in the 3 500–3 200 cm^{-1} region are listed in Table 3. The data for (1a–c) are

TABLE 3

		I.r. data *					
		$\nu(\text{NH}_2 \text{ antisym.})/\text{cm}^{-1}$		$\nu(\text{NH}_2 \text{ sym.})/\text{cm}^{-1}$			
		Free	Associated	Free	Associated		
(1a)	(a)		3 501	3 410	3 280	3 227	3 185sh
	(b)		3 498	3 405	3 295	3 237	3 190sh
(1b)	(a)	3 500	3 480	3 412	3 275	3 220	3 180sh
	(b)	3 500	3 477	3 405	3 295	3 230	
(1c)	(a)		3 502		3 275	3 225	3 200
	(b)		3 499		3 295	3 240	3 210sh
				$\nu(\text{NH})/\text{cm}^{-1}$			
(1d)	(a)			3 442			
	(b)			3 436			
(1e)	(a)			3 458			
	(b)			3 450			

* (a) CCl_4 solution; (b) CHCl_3 solution. Strongest band in italics.

TABLE 4

^1H N.m.r. data for aromatic protons of compounds (3c and d)

	δ_{HK}	δ_{HA}	δ_{HB}	J_{AB}	$^5J_{\text{AK}}$	$^4J_{\text{BK}}$	$^3J_{\text{KX}}$	$^4J_{\text{AX}}$	$^5J_{\text{BX}}$
(3c)	7.53	7.66	7.26	7.98	0.69	1.65	10.07	2.37	1.62
(3d) *	7.50	7.21	7.04	8.43	0.53	2.07	9.28	2.39	1.09

* These data replace those given in ref. 3b.

complex in this region; we propose, tentatively that (1a and b) exist mainly in associated form, in equilibrium with a little of the free form. The two weak bands at 3 510 and 3 410 cm^{-1} could be due to the antisymmetric and symmetric NH_2 stretching vibrations of the free form. The strong band at 3 500 cm^{-1} could be attributed to the associated antisymmetric NH_2 stretching vibration, and the three bands at 3 300–3 200 cm^{-1} to associated symmetric NH_2 vibrations. The presence of conformational isomers, of similar interconversion energy, could explain the multiplicity of the associated symmetrical NH_2 band; the variation of frequencies and intensities with a solvent of different dielectric constant can indicate the presence of a conformational equilibrium situation.²⁰

For compounds (2) the chemical shifts of the groups R are slightly different; this may be due to a small distortion of the ring. The values of $\delta(\text{NH})$ are much higher for (2a and c) than for (2b), probably as a result of $\text{NH} \cdots \pi$ type association between the NH and benzyl groups.^{19a} Aromatic protons of compounds (3) show coupling with phosphorus and give complex systems when $\text{R}^2 = \text{H}$.

Aromatic protons of (3c) (R^2 decoupled) and (3d) form the ABK part of an ABKX system ($\text{X} = \text{P}$), which was resolved by use of the LAOCOON III program (Table 4).

EXPERIMENTAL

M.p.s were taken with a Buchi apparatus. ^{31}P N.m.r. spectra were recorded with a Perkin-Elmer R10 spectrometer (85% H_3PO_4 as external standard; negative chemical shifts to low field). Decoupled $^{31}\text{P}\{^1\text{H}\}$ spectra were recorded with a Bruker WH-90 spectrometer. ^{31}P CIDNP effects were observed with a JEOL PS 100 spectrometer. ^1H N.m.r. spectra were recorded with a Varian HA 100 apparatus (Me_4Si as internal standard). I.r. spectra were recorded with a Perkin-Elmer 125 spectrometer. Mass spectra of compounds (2) and (3) were recorded with a Ribier QMC-51 spectrometer. Trisdimethylaminophosphine oxide was detected by g.l.c. [Aerograph A 90P, carrier gas He, detection by thermistance, SE30 or Chromosorb (d_2)]. Microanalyses were performed by the Service Central de Microanalyse du CNRS, Thiais, France. Amide oximes were prepared according to known methods,¹ and commercial trisdimethylaminophosphine was employed.

N^2 -[bis(dimethylamino)phosphinoyl]acetamidine (1a).—A mixture of acetamide oxime (7.4 g, 0.1 mol) and tris(dimethylamino)phosphine (16.3 g, 0.1 mol) was dissolved in anhydrous benzene (100 ml) at room temperature. The solution was refluxed for 2 h with stirring, and the dimethylamine formed was removed in a nitrogen stream. A viscous oil was decanted from the solution, which was evaporated under reduced pressure; the residue was extracted with ether (300 ml) and the extract was cooled at -10 to 0°C for 24 h. The solid (4 g) was filtered off and crystallised from toluene to give the product (1a), m.p. 105° , $\delta^{31}\text{P} - 22.8$ p.p.m.; ν_{max} (KBr) 1 635 (C=N), 1 575 (NH_2), and 1 200 cm^{-1} (P=O) (Found: C, 37.4; H, 8.8; N, 29.0; P, 15.95. $\text{C}_6\text{H}_{17}\text{N}_4\text{OP}$ requires C, 37.55; H, 8.95; N, 29.2; P, 16.15%).

In a similar way were obtained (with different final purifications) N^2 -[bis(dimethylamino)phosphinoyl]phenylacetamidine (1b), m.p. 100° (from benzene); $\delta^{31}\text{P} - 22$ p.p.m.; ν_{max} (KBr) 1 630 (C=N), 1 570 (NH_2), and 1 185 cm^{-1} (P=O) (Found: C, 54.05; H, 7.9; N, 20.85; P, 11.6. $\text{C}_{12}\text{H}_{21}\text{N}_4\text{OP}$ requires C, 53.8; H, 7.9; N, 20.9; P, 11.55%); N^1 -[bis(dimethylamino)phosphinoyl]benzamidine (1c), sublimed at 30 – 40° and 10^{-3} mmHg, m.p. 115° (from benzene); $\delta^{31}\text{P} - 22.8$ p.p.m.; ν_{max} (KBr) 1 650 (C=N), 1 590 (NH_2), and 1 175 cm^{-1} (P=O) (Found: C, 52.1; H, 7.75; N, 21.95; P, 12.15. $\text{C}_{11}\text{H}_{19}\text{N}_4\text{OP}$ requires C, 52.0; H, 7.55; N, 22.05; P, 12.2%); N^2 -[bis(dimethylamino)phosphinoyl]- N^1 -phenylacetamidine (1d), m.p. 147° (from benzene); $\delta^{31}\text{P} - 18.5$ p.p.m.; ν_{max} (KBr) 1 620 (C=N) and 1 195 cm^{-1} (P=O) (Found: C, 53.25; H, 7.85; N, 19.75; P, 11.6. $\text{C}_{12}\text{H}_{21}\text{N}_4\text{OP}$ requires C, 53.8; H, 7.9; N, 20.9; P, 11.55%); N^2 -[bis(dimethylamino)phosphinoyl]- N^1 -methylbenzamidine (1e), m.p. 67 – 70° [from benzene-hexane (1 : 2)]; $\delta^{31}\text{P} - 15.4$ p.p.m.; ν_{max} (KBr) 1 620 (C=N) and 1 206 cm^{-1} (P=O) (Found: C, 53.4; H, 7.55; N, 20.3; P, 11.4. $\text{C}_{12}\text{H}_{21}\text{N}_4\text{OP}$ requires C, 53.8; H, 7.9; N, 20.9; P, 11.55%); 1,3-bis(dimethylamino)-1H-2,1-benzazaphosphole 1-oxide (3a), m.p. 169° (from benzene); $\delta^{31}\text{P} - 39.5$ (R10), -38.07 p.p.m. (JEOL); $M^+ 237$ (Found: C, 55.5; H, 6.9; N, 17.5; P, 13.15. $\text{C}_{11}\text{H}_{16}\text{N}_3\text{OP}$ requires C, 55.75; H, 6.8; N, 17.75; P, 13.1%); 3-diethylamino-1-dimethylamino-1H-2,1-benzazaphosphole 1-oxide (3b), m.p. 133° (from benzene)

²⁰ J. P. Majoral, R. Pujol, and J. Navech, *Compt. rend.*, 1972, **274C**, 213.

$\delta^{31}\text{P}$ —39.5 p.p.m.; M^+ 265 (Found: C, 59.05; H, 7.8; N, 15.45; P, 11.6. $\text{C}_{18}\text{H}_{20}\text{N}_3\text{OP}$ requires C, 58.9; H, 7.6; N, 15.85; P, 11.7%); 1,3-bis(dimethylamino)-6-methyl-1H-2,1-benzazaphosphole 1-oxide (3c), m.p. 160° [from benzene-hexane (1:1)]; $\delta^{31}\text{P}$ —40 p.p.m.; M^+ 251 (Found: C, 57.5; H, 7.15; N, 17.2; P, 12.2. $\text{C}_{12}\text{H}_{18}\text{N}_3\text{OP}$ requires C, 57.4; H, 7.25; N, 16.75; P, 12.35%); 6-chloro-1,3-bis(dimethylamino)-1H-2,1-benzazaphosphole 1-oxide (3d), m.p. 152° [from benzene-hexane (1:1)]; $\delta^{31}\text{P}$ —38 p.p.m.; M^+ 271.5 (Found: C, 48.75; H, 5.6; Cl, 13.05; N, 15.25; P, 11.35%). $\text{C}_{11}\text{H}_{15}\text{ClN}_3\text{OP}$ requires C, 48.65; H, 5.55; Cl, 13.05; N, 15.45; P, 11.45%).

2-Dimethylamino-2,5-dihydro-4,6-di-isopropyl-1,3,5,2-triazaphosphorine 2-Oxide (2a).—A mixture of isobutyramide oxime (10.2 g, 0.1 ml) and tris(dimethylamino)phosphine (16.3 g, 0.1 ml) in dry benzene (100 ml) was stirred and heated as for (1a). Ether (100 ml) was added to the concentrated solution, which was then cooled at 0 °C for 12 h. The solid was filtered off and crystallised from benzene to give the product (2a), m.p. 201—203°; $\delta^{31}\text{P}$ —4.8 p.p.m.; ν_{max} (CH_2Cl_2) 3 411 (NH), ν_{max} (KBr) 1 650, 1 628 (C=N), and 1 204 cm^{-1} (P=O); M^+ 244 (Found: C, 49.2; H, 8.55; N, 22.85; P, 12.85. $\text{C}_{10}\text{H}_{21}\text{N}_4\text{OP}$ requires C, 49.2; H, 8.7; N, 22.95; P, 12.7%).

4,6-Dibenzyl-2-dimethylamino-2,5-dihydro-1,3,5,2-triazaphosphorine 2-Oxide (2b).—In the crystallisation of (1b)

from benzene, a part of the solid was insoluble in this solvent; this fraction crystallised from ethanol to give the product (2b), m.p. 231—233°; $\delta^{31}\text{P}$ —2.8 p.p.m.; ν_{max} (CH_2Cl_2) 3 390sh and 3 357 (NH), ν_{max} (KBr) 1 640, 1 599 (C=N), and 1 202 cm^{-1} (P=O); M^+ 340 (Found: C, 64.15; H, 6.25; N, 16.35; P, 9.15. $\text{C}_{18}\text{H}_{21}\text{N}_4\text{OP}$ requires C, 63.6; H, 6.25; N, 16.5; P, 9.15%).

2-Dimethylamino-2,5-dihydro-4,6-diphenyl-1,3,5,2-triazaphosphorine 2-Oxide (2c).—A solution of dichloro(dimethylamino)phosphine oxide (4.05 g, 0.25 mol) in dioxan (50 ml) was added over 15 min with stirring to benzamidine (12 g, 0.1 mol) in dioxan (50 ml) at 0 °C. The solution was stirred at room temperature for 15 min, the hydrochloride was then filtered off, and the filtrate was refluxed for 2 h. The solution was evaporated under reduced pressure to leave a solid which was crystallised from toluene; m.p. 205°; ν_{max} (CH_2Cl_2) 3 380 (NH), ν_{max} (KBr) 1 630, 1 590 (C=N), and 1 222 cm^{-1} (P=O); M^+ 312 (Found: C, 61.3; H, 5.55; N, 17.7; P, 9.85. $\text{C}_{16}\text{H}_{17}\text{N}_4\text{OP}$ requires C, 61.5; H, 5.45; N, 17.95; P, 9.95%).

We thank Professor R. F. Hudson, Dr. C. Brown, and Dr. K. A. F. Record for their collaboration during the short stay of (L. L.) at the Chemical Laboratory of the University of Kent. ^{31}P CIDNP effects were studied by Dr. C. Brown.

[6/2106 Received, 16th November, 1976]