

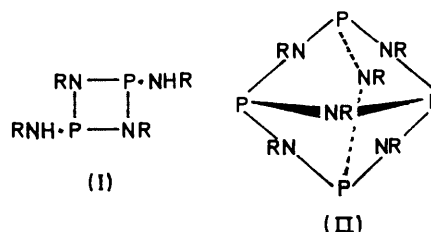
Organophosphorus Chemistry. Part XIII.¹ The Reaction of Phosphorus Trichloride with Primary Aromatic Amines

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The reaction of an excess of phosphorus trichloride with primary aromatic amines yields aryliminobisdichlorophosphines at ambient temperatures and the corresponding 1,3-diaryl-2,4-dichloro-1,3,2,4-diazadiphosphetidines at 100–120°. Dichloro-(4-nitroanilino)phosphine, isolated from the reaction of 4-nitroaniline and phosphorus trichloride, is converted by an excess of phosphorus trichloride in the presence of pyridine into 4-nitrophenyliminobisdichlorophosphine. Phosphorus trichloride reacts with hexamethyl-*N*-phenyldisilazane to give 2,4-dichloro-1,3-diphenyl-1,3,2,4-diazadiphosphetidine. Phenyliminobisdichlorophosphine reacts with hexamethyl-*N*-phenyldisilazane to give 2,4-dichloro-1,3-diphenyl-1,3,2,4-diazadiphosphetidine and with dimethylaminotrimethylsilane to give 2,4-bisdimethylamino-1,3-diphenyl-1,3,2,4-diazadiphosphetidine. ¹H N.m.r. and mass spectroscopic data for some of these compounds are discussed.

THE reaction of a primary amine, or its hydrochloride, with phosphorus trichloride yields a variety of products, the nature of which depends upon the structure of the amine and the reactant ratio. Triaminophosphines, (RNH)₃P, are the products expected to be formed when the amine is in large excess; in fact they are rarely isolated,²⁻⁴ and early reports of the isolation of trianilinophosphine⁵⁻⁷ have been questioned.⁸ Instead, treatment of an excess of an amine with phosphorus trichloride leads either to a diaminodiazadiphosphetidine (I; R = alkyl or aryl),⁹⁻¹⁴ colloquially termed an imide-amide dimer, or to the cage-like compound (II), the only well established example of which is that obtained by Holmes¹⁵ from methylamine (R = Me).

When phosphorus trichloride is in excess the outcome of such reactions is less clear-cut. An early report⁹



that diaryldichlorodiazadiphosphetidines (III; R = aryl) are formed has been disputed. Primary alkylamines and an excess of phosphorus trichloride produce

¹ Part XII, P. Cooper, R. Fields, and R. N. Haszeldine, *J. Chem. Soc. (C)*, 1971, 3031.

² A. Michaelis, *Annalen*, 1903, **326**, 129.

³ R. B. Flint and P. L. Salzberg, U.S.P. 2,151,380/1937 (*Chem. Abs.*, 1939, **33**, 5097).

⁴ K. A. Petrov, A. I. Gavrilova, and V. P. Korotkova, *Zhur. obshchei Khim.*, 1962, **32**, 915.

⁵ A. Tait, *Z. anorg. Chem.*, 1865, 648.

⁶ C. L. Jackson and E. A. Menke, *Amer. Chem. J.*, 1885, **6**, 89.

⁷ P. Lemoult, *Compt. rend.*, 1904, **138**, 1223.

⁸ H.-J. Vetter and H. Nöth, *Chem. Ber.*, 1963, **96**, 1308.

⁹ A. Michaelis and G. Schroeter, *Chem. Ber.*, 1894, **27**, 490.

¹⁰ H. W. Grimmel, A. Guenther, and J. F. Morgan, *J. Amer. Chem. Soc.*, 1946, **68**, 539.

¹¹ S. Goldschmidt and H.-L. Krauss, *Annalen*, 1955, **595**, 193.

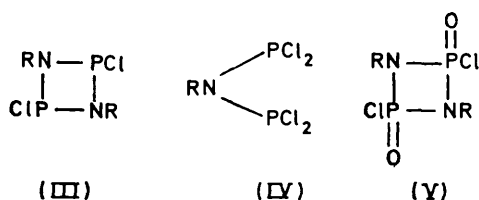
¹² G. S. Harris, *Proc. Chem. Soc.*, 1957, 118.

¹³ R. R. Holmes and J. A. Forstner, *Inorg. Chem.*, 1963, **2**, 380.

¹⁴ Fr.P. 1,389,073/1965 (*Chem. Abs.*, 1965, **62**, 16,068).

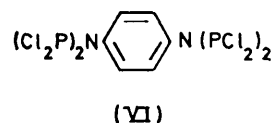
¹⁵ R. R. Holmes and J. A. Forstner, *J. Amer. Chem. Soc.*, 1960, **82**, 5509; R. R. Holmes, *ibid.*, 1961, **83**, 1334.

only alkyliminobisdichlorophosphines (IV; R = alkyl),^{16,17} and since aryliminobisdichlorophosphines can also be obtained from the reaction of phosphorus trichloride with primary arylamines,¹¹ the existence of diaryldichlorodiazadiphosphetidines (III; R = aryl) seemed to be in doubt. Furthermore, attempts to obtain dialkyldichlorodiazadiphosphetidines (III; R = alkyl) by thermal elimination of phosphorus trichloride from the corresponding iminobisdichlorophosphines (IV), or by treatment of the acyclic compound (IV; R = Me) with heptamethyldisilazane, proved unsuccessful,¹⁸ in spite of the reported synthesis of one such compound (III; R = Me) from the reaction of phosphorus trichloride with the same disilazane.¹⁹ More recently, the synthesis of the diazadiphosphetidine (III; R = Bu^t) has been achieved by two routes, though not apparently by direct interaction of phosphorus trichloride with *t*-butylamine hydrochloride.²⁰



Since we were interested in the related ring compounds based on phosphorus(v), termed diazadiphosphetidine dioxides (V),²¹ as potential monomers for the synthesis

aryliminobisdichlorophosphines (IV; R = Ar).—The preferred procedure is to dissolve the amine or its hydrochloride in a liberal excess of refluxing phosphorus trichloride, with reflux maintained until hydrogen chloride is no longer evolved (4–6 days). Water vapour and oxygen must be carefully excluded at all stages. The product is isolated by evaporating the solution to small bulk *in vacuo* at $\leq 30^\circ$, after which the chilled solution will deposit crystalline (IV). Further purification may be achieved by cautious vacuum sublimation or by recrystallisation from phosphorus trichloride (a far from ideal solvent, but one which effectively prevents elimination of PCl_3 from the labile bisdichlorophosphines). Pure aryliminobisdichlorophosphines (IV) were thus obtained from aniline (74%), *p*-anisidine (91%), and 3-nitroaniline (63%). The tetrakis(dichlorophosphine) (VI) was obtained similarly from 1,4-diaminobenzene.

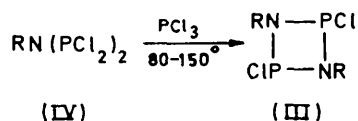


The mass spectra of these aryliminobisdichlorophosphines (IV) proved to be particularly useful (see Table 1), since they show clear parent ions (*M*) with the usual distribution of chlorine isotopes, and fragments corresponding to $M - \text{Cl}$, $M - \text{PCl}_2$, $M - \text{PCl}_3$, and $M - \text{PCl}_4$. In two instances the formation of $(\text{RNPCl})^+$ ions

TABLE 1

Ar in (IV):	Mass spectral data for aryliminobisdichlorophosphines (IV)							
	Ph		4-MeO·C ₆ H ₄		3-NO ₂ ·C ₆ H ₄		4-(Cl ₂ P) ₂ N·C ₆ H ₄	
Ion	<i>m/e</i>	Rel. int. (%)	<i>m/e</i>	Rel. int. (%)	<i>m/e</i>	Rel. int. (%)	<i>m/e</i>	Rel. int. (%)
<i>M</i>	293, 295, 297, 299	48	323, 325, 327, 329	161	338, 340, 342, 344	59	508–516	40
<i>M</i> - Cl	258, 260, 262	22	288, 290, 292	36	302, 304, 306	22	473–481	22
<i>M</i> - PCl ₂	192, 194, 196	17	222, 224, 226	174			407–413	52
<i>M</i> - PCl ₃	157, 159	43	187, 189	66	202, 204	56		
<i>M</i> - PCl ₄	122	100	152	70	167	100		
PCl ₂	101, 103, 105	101		42		163		110

of inorganic polymers, the corresponding phosphorus-(III) systems were re-examined. We find that primary aromatic amines or their hydrochlorides react with an excess of phosphorus trichloride to yield either acyclic P-N-P compounds (IV; R = Ar) or four-membered



P-N heterocycles (III; R = Ar), according to the conditions used, and that conversion of the aryliminobisdichlorophosphines into dichlorodiazadiphosphetidines (III; R = aryl) can easily be achieved under mild conditions.

¹⁶ J. F. Nixon, *Chem. Comm.*, 1967, 669.

¹⁷ J. F. Nixon, *J. Chem. Soc. (A)*, 1968, 2689.

¹⁸ R. Jefferson, J. F. Nixon, and T. M. Painter, *Chem. Comm.*, 1969, 622.

was demonstrated by the detection of metastable ions corresponding to the transition $(\text{RNPCl})^+ \longrightarrow (\text{RNP})^+ + \text{Cl}$ (at *m/e* 123.5 for R = 4-MeO·C₆H₄, and 138 for R = 3-NO₂·C₆H₄). The incorporation of two mol. equiv. of PCl_3 of crystallisation into the dichlorodiazadiphosphetidines (III), a possibility noted previously,¹¹ would lead to the same elemental composition as the bisdichlorophosphines. We exclude this, because no ions of sufficiently high *m/e* values are observed, although parent ions were detected in the mass spectra of the diazadiphosphetidines (see Table 2). ¹H N.m.r. spectroscopy is not very useful in the structural analysis of these compounds, and attempts to convert them into the

¹⁹ E. W. Abel and G. R. Willey, *Proc. Chem. Soc.*, 1962, 308; E. W. Abel, D. A. Armitage, and G. R. Willey, *J. Chem. Soc.*, 1965, 57.

²⁰ O. J. Scherer and P. Klusmann, *Angew. Chem. Internat. Edn.*, 1969, 8, 752.

²¹ M. Green, R. N. Haszeldine, and G. S. A. Hopkins, *J. Chem. Soc. (A)*, 1966, 1766.

spectroscopically more interesting bisdifluorophosphines with antimony trifluoride¹⁶ and with caesium fluoride led only to extensive decomposition, evidenced by the formation of phosphorus trichloride.

TABLE 2

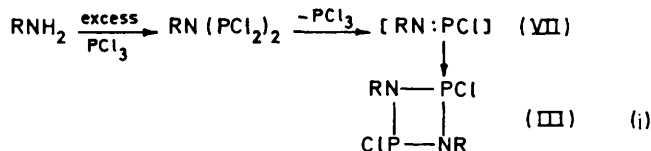
Mass spectral data for dichlorodiazadiphosphetidines (III)

Ar in (III)	Ph	Rel. int. (%)	4-MeC ₆ H ₄	Rel. int. (%)
Ion	<i>m/e</i>		<i>m/e</i>	
<i>M</i>	314, 316, 318	32	342, 344, 346	50
<i>M</i> - Cl	279, 281	6	307, 309	9
<i>M</i> - Cl ₂	166	3		
ArNPCI ⁺	157, 159	51	171, 173	127
ArNP	122	42	135	100
ArNH ₂ ⁺	93 ^a	100	107	10
ArNH ⁺	92	25	106	13
Ar	77	11	91	30

^a The high intensity of this ion suggests that partial hydrolysis of the diazadiphosphetidine occurred at the spectrometer inlet.

Diaryldichlorodiazadiphosphetidines (III; R = aryl).—The simplest procedure is to heat the amine hydrochloride with a three-fold excess of phosphorus trichloride in *sym*-tetrachloroethane until a clear solution is obtained (*ca.* 24 h). The solution is then evaporated at 120° *in vacuo*, and the residue recrystallised from phosphorus trichloride. Water and oxygen must again be carefully excluded. Diaryldichloridiazadiphosphetidines (III) were obtained in this way from aniline (48%),⁹ 4-chloroaniline (49%), *p*-toluidine (46%), and *p*-anisidine (91%). Their mass spectra (Table 2) display parent ions (*M*), with loss of one and two chlorine atoms. As in the case of the aryliminobisdichlorophosphines, there is evidence for the breakdown (RNPCI)⁺ → (RNP)⁺ + Cl.

Since aryliminobisdichlorophosphines (IV) are isolated in high yield only if the temperature during work-up is kept at or below 30°, whereas a temperature of 100–150° leads to diazadiphosphetidines (III), thermal elimination of phosphorus trichloride from initially formed bisdichlorophosphines is probably occurring at higher temperatures, possibly producing an unstable phosphorus imide (VII) which dimerises rapidly [equation (i)]. This inference was verified by the conversion



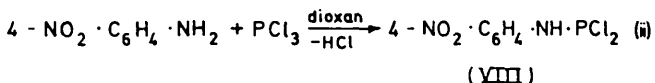
of phenyliminobisdichlorophosphine (IV; R = Ph) into the corresponding diazadiphosphetidine (III; R = Ph) at 80° *in vacuo*, and in refluxing xylene. This behaviour is in sharp contrast to that of the methyl analogue (IV; R = Me), which has been shown to be in equilibrium

²² N. N. Greenwood, B. H. Robinson, and B. P. Straughan, *J. Chem. Soc. (A)*, 1968, 230.

²³ R. G. Cavell, T. L. Charlton, and W. Sim, *J. Amer. Chem. Soc.*, 1971, **93**, 1130.

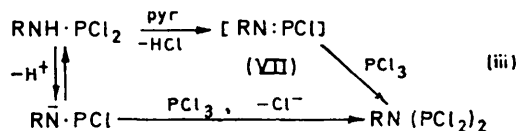
with phosphorus trichloride and the cage compound (II) at room temperature, and does not yield (III; R = Me) when heated *in vacuo*.¹⁸ This difference may be due to a change in the reactivity of the supposed intermediate (VII), which when R = Ph may be sufficiently stable to survive until dimerisation, but when R = Me rapidly inserts into any available P-Cl bond.

Dichloro-(4-nitroanilino)phosphine.—The reaction between phosphorus trichloride and an arylamine of lower basicity than those already referred to, namely 4-nitroaniline, proceeded differently. Although the initial reaction was so vigorous that an inert solvent was required to avoid decomposition and the formation of dark tars, the substitution process stopped when only one of the amine hydrogen atoms had been replaced [equation (ii)]. The product, dichloro-(4-nitroanilino)phosphine (VIII), a treacherously unstable solid, m.p. 101–104° (decomp.), exploded violently on one occasion during the final stages of its preparation.



The presence of the residual NH group in (VIII) was confirmed by elemental analysis, mass spectroscopy, and i.r. analysis. No proton resonance due to NH was observed in the n.m.r. spectrum, possibly owing to broadening by the nitrogen atom; a similar feature has been observed in the n.m.r. spectra of MeNH·P(CF₃)₂,^{22,23} and F₂P·NHMe.²³

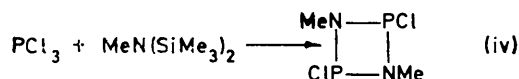
Compounds containing the NH·PCl grouping are rare but not unknown.^{2,6,20,24} Corresponding aminodifluorophosphines, RNH·PF₂, are well authenticated,^{23,25} and the strength of the P-F bond renders them less liable to eliminate hydrogen halide even when treated with base. Dichloro-(*t*-butylamino)phosphine, on the other hand, reacts rapidly with tertiary amines with loss of hydrogen chloride, giving the dichlorodiazadiphosphetidine (III; R = Bu^t).²⁰ Attempts to achieve such an elimination with (VIII) were not successful; although addition of pyridine to (VIII) in dioxan solution led to rapid precipitation of pyridine hydrochloride, no diazadiphosphetidine was isolated. However, when phosphorus trichloride was present during such an experiment, the corresponding bisdichlorophosphine (IV; R = 4-NO₂·C₆H₄) was obtained in 30% yield. This product may arise by addition of phosphorus trichloride to the imide (VII; R = 4-NO₂·C₆H₄), or by nucleophilic attack initiated by the conjugate anion of (VIII) [equation (iii)].



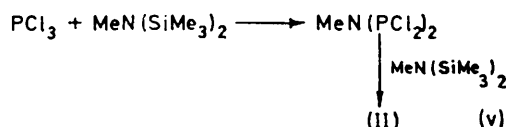
The claim by Abel and his co-workers¹⁹ to have prepared dimethyldiazadiphosphetidine (III; R = Me) by

²⁴ I. G. M. Campbell and J. K. Way, *J. Chem. Soc.*, 1960, 5034.
²⁵ C. G. Barlow, R. Jefferson, and J. F. Nixon, *J. Chem. Soc. (A)*, 1968, 2692.

treating phosphorus trichloride with heptamethyl-disilazane [equation (iv)] has been challenged,¹⁸ on the



grounds that the initial product from a 1 : 1 molar ratio of reactants is the methyliminobisdichlorophosphine (IV; R = Me), which an excess of disilazane converts into the cage compound (II) [equation (v)]. Our



observations resemble those of Abel's group, in that we find that (a) phosphorus trichloride reacts with slightly less than 1 mol. equiv. of the *N*-phenyldisilazane PhN-(SiMe₃)₂ to give the dichlorodiphenyldiazadiphosphetidine

phenyldiazadiphosphetidine (III; R = Ph) in 53% yield, and (c) the bisdichlorophosphine, treated with a fourfold excess of Me₂N·SiMe₃, gives a mixture of tris(dimethylamino)phosphine, formed by amination of eliminated PCl₃, and the diaminodiazadiphosphetidine (IX) in 60% yield (see Scheme). This product was also obtained in a separate experiment by amination of the dichlorodiazadiphosphetidine with the aminosilane.²⁶

There appears to be little tendency for cage compounds analogous to (II) to form when arylamines or their derivatives are treated with phosphorus trichloride. Only when phenyliminobisdichlorophosphine (IV) was treated with methylamine was a cage compound produced and this proved to be (II; R = Me). Since aniline was also detected amongst the products, its formation in this case almost certainly follows a transamination step, in which the less basic aniline is displaced from phosphorus by methylamine.

¹H *N.m.r.* Spectra.—The chemical shift data for *para*-substituted aromatic rings in bisdichlorophosphines,

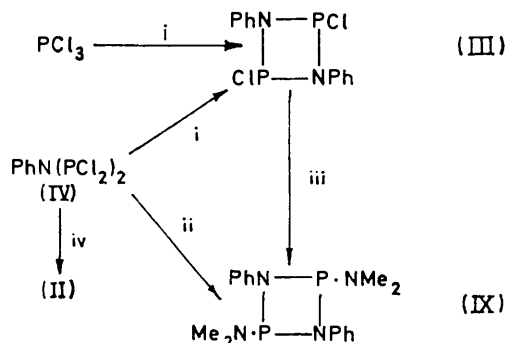
TABLE 3

¹H *N.m.r.* data for *para*-substituted Ar-N-P compounds (X)

Compound	X	Y	<i>n</i>	δ°			<i>J</i> _{AB} /Hz	Solvent
				H _A	H _B	CH ₃		
(III)	NPCl	Cl	2	-0.95d	-0.60d		9	PCl ₃
(III)	NPCl	Me	2	-0.75d	-0.58d	4.17s	4	PCl ₃
(III)	NPCl	MeO	2	-0.55d	-0.27d	2.80s	6	CCl ₄
(IV)	NO ₂	N(PCl ₂) ₂	1	-1.91d	-0.98d		8	PCl ₃
(IV)	N(PCl ₂) ₂	MeO	1	-0.71d	-0.46d	2.63s	9	CCl ₄
(VI)	N(PCl ₂) ₂	X	1	-1.01s				PCl ₃
(VIII)	NO ₂	NHPCl ₂	1	-1.75d	-0.80d		9	PCl ₃

* Relative to external benzene, in p.p.m. (a negative sign indicates a downfield shift).

ine (III; R = Ph), identical with authentic material prepared as already described, (b) phenyliminobisdichlorophosphine (IV; R = Ph) reacts smoothly with



SCHEME Reagents: i, PhN(SiMe₃)₂; ii, Me₂N·SiMe₃; iii, Me₂N·SiMe₃ (ref. 26); iv, MeNH₂

PhN(SiMe₃)₂ at ambient temperature to give chlorotri-methylsilane almost quantitatively and dichlorodi-

diazadiphosphetidines, and related compounds, are listed in Table 3. The assignments are made on the assumption that the presence of N(PCl₂)₂, NH·PCl₂, and NPCl substituents will not unduly modify the usual behaviour of the remaining substituents. If correct, they indicate that these N-P groupings are all electron-withdrawing; indeed, the N(PCl₂)₂ group exerts a deshielding effect between that of CCl₃ and NO₂, and this effect is exerted on the *meta*-proton almost as strongly as on the *ortho*-position.

EXPERIMENTAL

Moisture-sensitive trivalent phosphorus compounds were handled under dry nitrogen in a Bassaire DBI glove box. Solvents were dried thoroughly. Amine hydrochlorides were prepared from the corresponding amines and dry hydrogen chloride in anhydrous ether. Phosphorus trichloride was redistilled immediately prior to use. Hexa-

²⁶ A. R. Davies, R. N. Haszeldine, and D. R. Taylor, unpublished results.

methyl-*N*-phenyldisilazane²⁷ and dimethylaminotrimethylsilane²⁸ were prepared by published procedures and stored under anhydrous conditions.

Compounds were characterised by i.r. spectroscopy (Perkin-Elmer 137 and 257 spectrophotometers fitted with sodium chloride and grating optics, respectively), n.m.r. spectroscopy (Perkin-Elmer R10 instrument, operating at 60.00 MHz) (data in Table 3), mass spectrometry (A.E.I. MS9 instrument) (data in Tables 1 and 2), and elemental analysis (we acknowledge the assistance of Dr. Kakabadse and his staff, in this Department). All *M* values were determined by mass spectrometry, unless otherwise stated.

Phenyliminobisdichlorophosphine.—(a) *From aniline.* Redistilled aniline (60.0 g, 0.645 mol) was added dropwise to cooled vigorously stirred phosphorus trichloride (350 g, 2.55 mol) under dry nitrogen. Aniline hydrochloride was precipitated, but was not removed. The mixture was heated under reflux until clear (48 h), cooled to -20° , and filtered under nitrogen. The filtrate was concentrated to small bulk at 30° , cooled to -20° , and filtered to yield a second crop of crystals. The combined precipitates were recrystallised from PCl_3 under nitrogen, to give needles of phenyliminobisdichlorophosphine (141 g, 0.479 mol, 74% yield based on aniline), m.p. $47-48^\circ$ (lit.,¹¹ 46°).

(b) *From aniline hydrochloride.*¹¹ Finely-ground aniline hydrochloride (430 g, 3.32 mol) was dissolved in refluxing phosphorus trichloride (1.18 kg, 8.6 mol) during 72 h. The solution was filtered through a sinter, excess of PCl_3 (650 g) was recovered at reduced pressure, and the liquor was cooled to yield phenyliminobisdichlorophosphine (151 g, 1.7 mol, 51% based on PhNH_2Cl), m.p. $45-46^\circ$ after sublimation *in vacuo* at 70° [Found: C, 24.7; H, 1.8; Cl, 48.3; N, 5.0%; *M*, 293 (^{35}Cl). Calc. for $\text{C}_6\text{H}_5\text{Cl}_2\text{N}_2\text{P}_2$: C, 24.4; H, 1.7; Cl, 48.1; N, 4.8%; *M*, 295], ν_{max} 3070w, 2915w, 1585m, 1480m, 1445w, 1195s, 1170w, 1070m, 1025m, 925m, 895m, 875s, 860s, 740w, 692s, 671w, 658w, 521s, 485s, and 463m cm^{-1} . When the filtered mother liquor from this experiment was evaporated at 100° *in vacuo* until no further phosphorus trichloride was evolved, a white solid was obtained which was recrystallised from benzene and identified as dichlorodiphenyldiazidophosphetidine (92 g, 0.58 mol, 17% yield based on PhNH_2Cl), m.p. and mixed m.p. $149-151^\circ$ (from PCl_3).

4-Methoxyphenyliminobisdichlorophosphine.—4-Methoxyaniline hydrochloride (20.0 g, 0.125 mol) was similarly treated with phosphorus trichloride (100 g) to yield pale pink prisms of 4-methoxyphenyliminobisdichlorophosphine (37.5 g, 0.115 mol, 92%) [Found: C, 25.5; H, 2.1; Cl, 43.9; N, 4.4; P, 19.0%; *M*, 323 (^{35}Cl). $\text{C}_7\text{H}_7\text{Cl}_2\text{N}_2\text{OP}_2$ requires C, 25.8; H, 2.1; Cl, 43.7; N, 4.3; P, 19.0%; *M*, 325], m.p. 53° (from PCl_3), ν_{max} 3020w, 2960m, 2935m, 2840m, 2650m, 1610s, 1600m, 1585m, 1505s, 1465m, 1460m, 1380s, 1300s, 1255s, 1205s, 1180m, 1170m, 1110m, 1040s, 1010m, 940s, 895s, 880s, 795s, 715m, 640m, 609m, 541s, 515s, and 487m cm^{-1} .

3-Nitrophenyliminobisdichlorophosphine.—3-Nitroaniline hydrochloride (35.0 g, 0.201 mol) was similarly treated with refluxing phosphorus trichloride (200 g, 1.46 mol) for 6 days to give pale yellow prisms of 3-nitrophenyliminobisdichlorophosphine (42.3 g, 0.125 mol, 62%) [Found: C, 21.5; H, 1.4; Cl, 41.8; N, 8.2; P, 17.7%; *M*, 338 (^{35}Cl). $\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2$ requires C, 21.2; H, 1.2; Cl, 41.7; N, 8.2; P, 18.2%; *M*, 340], m.p. $119-121^\circ$ (from PCl_3), ν_{max} 3105w,

3085w, 1610w, 1560s, 1470w, 1345s, 1310w, 1275w, 1215m, 1160w, 1090w, 1082w, 970m, 935m, 920s, 850s, 680s, 562m, 503m, and 464s cm^{-1} .

Dichloro-(4-nitroanilino)phosphine.—4-Nitroaniline (69.0 g, 0.50 mol) in dioxan (300 ml) was added slowly to phosphorus trichloride (150 g, 1.09 mol) in dioxan (50 ml), with stirring and cooling under dry nitrogen. The mixture was kept at reflux for 10 min and filtered hot, and the filtrate was cautiously evaporated (see Discussion section) to dryness at 30° *in vacuo*. The semi-solid residue (37.5 g) was recrystallised from PCl_3 to give dichloro-(4-nitroanilino)phosphine (22.5 g, 0.094 mol, 37%) as pink needles [Found: C, 29.2; H, 2.1; Cl, 30.0%; *M*, 238 (^{35}Cl). $\text{C}_6\text{H}_5\text{Cl}_2\text{N}_2\text{O}_2\text{P}$ requires C, 30.1; H, 2.1; Cl, 29.7%; *M*, 239], m.p. $101-104^\circ$ (decomp.), ν_{max} 3240m (N-H str.), 3120w, 3080w, 3040w, 2920w, 2440w, 1920w, 1660m, 1595s, 1530s, 1505s, 1495s, 1395m, 1380w, 1335s, 1295m, 1240m, 1110m, 1010w, 915s, 850s, 765m, 750m, 690m, 660m, 532m, 492m, 460s, and 449s cm^{-1} .

4-Nitrophenyliminobisdichlorophosphine.—4-Nitroaniline (30.5 g, 0.221 mol) in dioxan (300 ml) was added under nitrogen to a well stirred dioxan solution of phosphorus trichloride (50.0 g, 0.365 mol), with cooling. 4-Nitroaniline hydrochloride was filtered off and dry pyridine (50.0 g) added to the filtrate. The mixture was left, with occasional shaking, for 12 h, then filtered, and the filtrate was evaporated to dryness *in vacuo* at $20-25^\circ$ to give 4-nitrophenyliminobisdichlorophosphine (11.6 g, 34.1 mmol, 31%) as pale yellow air-sensitive prisms [Found: C, 21.2; H, 1.2; Cl, 41.5; N, 8.5; P, 18.0%; *M*, 338 (^{35}Cl). $\text{C}_6\text{H}_4\text{Cl}_2\text{N}_2\text{O}_2\text{P}_2$ requires C, 21.2; H, 1.2; Cl, 41.8; N, 8.2; P, 18.2%; *M*, 340], m.p. $116-118^\circ$ (from PCl_3), ν_{max} 3110w, 3090w, 3050w, 2840w, 1610m, 1590m, 1570s, 1485m, 1360m, 1340s, 1310m, 1285w, 1215m, 1160w, 1150m, 1015w, 935s, 905s, 855m, 825m, and 720m cm^{-1} .

NN'-Tetrakis(dichlorophosphino)-*p*-phenylenediamine (VI).—A fine suspension of *p*-phenylenediamine (30.0 g, 0.28 mol) in phosphorus trichloride (200 g) was kept at reflux for 10 days under dry nitrogen. Dry ether (200 ml) was added, and the supernatant liquor decanted from the lower layer, which was again extracted with 1:1 PCl_3 -ether. The combined extracts were evaporated to dryness *in vacuo* at 30° to give the tetrakis(dichlorophosphino) (VI) (18.5 g, 36.3 mmol, 13%), which crystallised from PCl_3 as long needles [Found: C, 14.7; H, 0.8; Cl, 54.8%; *M*, 508 (^{35}Cl). $\text{C}_6\text{H}_4\text{Cl}_8\text{N}_2\text{P}_4$ requires C, 14.1; H, 0.8; Cl, 55.3; *M*, 512], m.p. $151-152^\circ$ (sealed tube), ν_{max} 3090w, 1920w, 1510m, 1490s, 1410w, 1345w, 1290w, 1275m, 1260m, 1210s, 1190s, 1110m, 1050w, 1020s, 975w, 940s, 910s, 895s, 790s, 559s, 532m, 518s, 490s, 481s, and 461s cm^{-1} .

2,4-Dichloro-1,3-diphenyl-1,3,2,4-diazadiphosphetidine.—(a) *From aniline hydrochloride.* Finely divided aniline hydrochloride (200 g, 1.55 mol) was dissolved in a refluxing solution of phosphorus trichloride (600 g, 4.37 mol) in *sym*-tetrachloroethane (1 l) during 24 h. The solution was filtered hot through a glass wool plug, and evaporated to dryness *in vacuo* at up to 110° ; the white residue was extracted with hot phosphorus trichloride (100 ml) (hot benzene may also be used) and chilled to -20° (5 h) to yield 2,4-dichloro-1,3-diphenyl-1,3,2,4-diazadiphosphetidine (117 g, 0.372 mol, 48% yield based on PhNH_2Cl) as long needles, m.p. $153-155^\circ$ after further recrystallisations (lit.,⁹ $136-137^\circ$) [Found: C, 45.6; H, 3.4; Cl, 22.8%;

²⁷ U. Wannagat, C. Krüger, and H. Niederprüm, *Z. anorg. Chem.*, 1962, **314**, 89.

²⁸ O. Mjorne, *Svensk kem. Tidskr.*, 1950, **62**, 120 (*Chem. Abs.*, 1950, **44**, 9342).

M, 314 (³⁶Cl). Calc. for C₁₂H₁₀Cl₂N₂P₂: C, 45.7; H, 3.2; Cl, 22.5%; *M*, 315], ν_{\max} , 2840m, 2585w, 1585m, 1520m, 1495s, 1460s, 1270m, 1195w, 1095w, 1075w, 1020w, 917s, 745s, 720m, 680s, 665w, 616w, 523m, 510m, and 423s cm⁻¹.

(b) From phenyliminobisdichlorophosphine. Freshly sublimed phenyliminobisdichlorophosphine (5.83 g, 19.8 mmol) was refluxed in xylene (25 ml) for 24 h, and the solution was evaporated to dryness. The white residue was fractionally sublimed at up to 65° *in vacuo* to give a sublimate of the bisdichlorophosphine (1.03 g, 18% recovery), m.p. and mixed m.p. 45–46°, and a residue which was identified spectroscopically (i.r.) as the dichlorodiazadiphosphetidine (1.61 g, 5.1 mmol, 63% based on bisdichlorophosphine consumed), m.p. and mixed m.p. 150–152° (from PCl₃). In a further experiment, the bisdichlorophosphine (15.7 g, 53.2 mmol) was heated in a sealed, evacuated, Pyrex tube at 80° for 72 h, to give the bisdichlorophosphine (5.3 g, 34% recovery) and the dichlorodiazadiphosphetidine (4.2 g, 13.3 mmol, 75% yield).

(c) From hexamethyl-*N*-phenyldisilazane. A mixture of phosphorus trichloride (4.02 g, 29.3 mmol) and hexamethyl-*N*-phenyldisilazane (6.56 g, 27.7 mmol) was kept for 6 days at room temperature in a sealed Pyrex tube, to give chlorotrimethylsilane (5.16 g, 47.5 mmol, 86% yield based on disilazane) identified spectroscopically (i.r.), and an oily solid which was extracted with benzene. The extract was evaporated to dryness *in vacuo* and the residue identified as the dichlorodiazadiphosphetidine (1.6 g, 10.1 mmol, 69% yield based on PCl₃), m.p. and mixed m.p. 149–151° (from PCl₃).

2,4-Dichloro-1,3-bis-(4-chlorophenyl)-1,3,2,4-diazadiphosphetidine.—4-Chloroaniline hydrochloride (41.0 g, 0.25 mol) was treated as described for aniline hydrochloride [method (a)] with phosphorus trichloride (100 g) to give needles of 2,4-dichloro-1,3-bis-(4-chlorophenyl)-1,3,2,4-diazadiphosphetidine (23.2 g, 60.4 mmol, 48% yield based on ArNH₂Cl) [Found: C, 37.2; H, 2.1; Cl, 37.2; N, 7.6; P, 16.0%; *M*, 382 (³⁶Cl). C₁₂H₈Cl₄N₂P₂ requires C, 37.5; H, 2.1; Cl, 37.0; N, 7.3; P, 16.2%; *M*, 384], m.p. 165–167° (from PCl₃), ν_{\max} , 3040w, 2930w, 1870w, 1615w, 1595m, 1580m, 1510m, 1490s, 1410m, 1375s, 1365m, 1345m, 1310w, 1275s, 1260s, 1180m, 1115m, 1090m, 1010m, 960w, 920s, 810s, 725s, 690w, 660w, 488s, 465s, and 425w cm⁻¹.

2,4-Dichloro-1,3-bis-(4-methylphenyl)-1,3,2,4-diazadiphosphetidine.—*p*-Toluidine hydrochloride (36.0 g, 251 mmol) was similarly treated with phosphorus trichloride (100 g) to give 2,4-dichloro-1,3-bis-(4-methylphenyl)-1,3,2,4-diazadiphosphetidine (19.7 g, 57.8 mmol, 46% based on ArNH₂Cl) as needles, m.p. 149–150° (from PCl₃) [Found: C, 48.7; H, 4.1; Cl, 20.6; N, 8.5; P, 17.9%; *M*, 342 (³⁶Cl). C₁₄H₁₄Cl₂N₂P₂ requires C, 48.9; H, 4.1; Cl, 20.7; N, 8.2; P, 18.1%; *M*, 343], ν_{\max} , 3020w, 2980w, 2940w, 2910w, 2860w, 2590w, 1880w, 1610m, 1580m, 1515s, 1380m, 1260s, 1180w, 1120m, 1100m, 1020m, 920s, 880s, 700m, 640w, 597w, 546w, 512m, and 480s cm⁻¹.

2,4-Dichloro-1,3-bis-(4-methoxyphenyl)-1,3,2,4-diazadiphosphetidine.—*p*-Anisidine hydrochloride (40.0 g, 0.251 mol) was similarly treated with phosphorus trichloride (100 g) to give 2,4-dichloro-1,3-bis-(4-methoxyphenyl)-1,3,2,4-diazadiphosphetidine (42.6 g, 0.114 mol, 91% based on ArNH₂Cl) (Found: C, 44.8; H, 3.8; N, 6.9%). C₁₄H₁₄Cl₂N₂O₂P₂ requires C, 45.1; H, 3.75; N, 7.5%) as a pale pink glass. Its molecular weight was determined by osmometry (Mechrolab model 30/A) in CCl₄ (Found: *M*, 215–340. Calc. for C₁₄H₁₄Cl₂N₂O₂P₂: *M*, 375) at a concentration of

11.4 g l⁻¹. Its i.r. spectrum showed bands at 3370w, 3110w, 3070w, 3040w, 3000w, 2950w, 2930w, 2900w, 2840w, 2540w, 2060w, 2030m, 1870m, 1755w, 1600s, 1585m, 1500s, 1460s, 1440s, 1295s, 1250s, 1200s, 1170m, 1055m, 1040s, 985s, 920m, and 870m cm⁻¹.

Reactions of Phenyliminobisdichlorophosphine.—(a) With hexamethyl-*N*-phenyldisilazane. A solution of phenyliminobisdichlorophosphine (3.05 g, 10.3 mmol) and hexamethyl-*N*-phenyldisilazane (2.6 g, 11.0 mmol) in benzene (30 ml), kept in a sealed Pyrex tube for 7 days at 20–25°, gave benzene, chlorotrimethylsilane (2.07 g, 19.1 mmol, 87%), identified by i.r. spectroscopy, and an involatile solid which was recrystallised from PCl₃ to give 2,4-dichloro-1,3-diphenyldiazadiphosphetidine (1.6 g, 5.1 mmol, 99%), m.p. and mixed m.p. 149–151°, spectroscopically identical with an authentic sample.

(b) With dimethylaminotrimethylsilane. When dimethylaminotrimethylsilane (21.5 g, 0.184 mol) was added dropwise to a stirred suspension of the bisdichlorophosphine (27.0 g, 92 mmol) in petroleum (b.p. 30–40°), an exothermic reaction occurred. Refluxing was maintained for 30 min after the addition was complete, the mixture was cooled, and volatile products and the solvent were removed *in vacuo*. Fractionation of the volatile material (6 in Vigreux column) gave chlorotrimethylsilane (15.4 g, 0.142 mol, 77%), b.p. 58°, *NNN'*-tetramethylphosphorodiamidous chloride (1.41 g, 9.1 mmol), b.p. 30–32° at 0.1 mmHg, and *NN*-dimethylphosphoramidous dichloride (9.8 g, 67 mmol), b.p. 143–146°. Recrystallisation of the involatile residue from benzene gave 2,4-bis(dimethylamino)-1,3-diphenyl-1,3,2,4-diazadiphosphetidine (IX) (6.8 g, 20.5 mmol, 45% based on dichlorophosphine), m.p. 188°, identified by i.r. comparison with an authentic sample.²⁶ In a further experiment, in which the bisdichlorophosphine (3.8 g, 13 mmol) and the dimethylaminosilane (6.2 g, 53 mmol) were kept in a sealed Pyrex tube for 24 h at ambient temperature, fractionation of the volatile products gave hexamethylphosphonous triamide (1.5 g, 9.2 mmol), chlorotrimethylsilane (4.97 g, 45.8 mmol), and dimethylamine (0.23 g), and a residue which was extracted with benzene. The extract was evaporated and the residue vacuum sublimed at 150° to give the dimethylaminodiazadiphosphetidine (IX) (1.3 g, 3.9 mmol, 60%), m.p. and mixed m.p.²⁶ 206–208°.

(c) With methylamine. A mixture of methylamine (3.53 g, 114 mmol) and the bisdichlorophosphine (4.04 g, 13.6 mmol) was kept in a sealed Pyrex tube for 24 h at ambient temperature to give methylamine (0.71 g, 23 mmol, 20% recovery) [Found: *M* (Regnault's method), 31. Calc. for CH₅N: *M*, 31] and an involatile residue which was extracted with anhydrous ether. The ether-insoluble residue was shown to be methylamine hydrochloride (3.52 g, 52 mmol) by i.r. spectroscopy. The ether extract was evaporated to dryness *in vacuo*, and the residue fractionally sublimed at 20–25° and 0.1 mmHg to give aniline and, at 60° and 0.1 mmHg, phosphorus tri-*N*-methylimide (II) (1.2 g, 4.0 mmol; 59% based on bisdichlorophosphine) [Found: C, 24.1; H, 6.3; N, 28.0; P, 41.5%; *M* (Mechrolab, in benzene), 278. Calc. for C₈H₈N₂P₄: C, 24.2; H, 6.1; N, 28.2; P, 41.6%; *M*, 298], m.p. 122–123° (lit.,¹⁵ 122–123°), identified spectroscopically.¹⁵

(d) Attempted synthesis of the fluoro-analogue. The bisdichlorophosphine (21.2 g, 72 mmol) and anhydrous caesium fluoride (43.8 g, 0.29 mol) were stirred at 170° in tetrahydrothiophen dioxide (35 ml) for 4 h. Distillation gave phosphorus trifluoride (5.46 g, 62 mmol) [Found: *M* (Regnault's

method), 87. Calc. for PF_3 : M , 87], phosphorus trichloride (8.4 g, 61 mmol), aniline (2.1 g, 23 mmol), the solvent, and a black solid residue from which pure material could not be isolated. Similarly, when the bisdichlorophosphine (10.7 g, 36 mmol) was distilled with finely divided antimony trifluoride (8.65 g, 49 mmol), only phosphorus trifluoride

(4.15 g, 42 mmol) was isolated; a black, evil-smelling resinous residue was not examined further.

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