Organophosphorus Chemistry. Part XIV.[1] Reaction of Phosphorodiamidous Chlorides with Sulphonamides: a New Route to Diazadiphosphetidines

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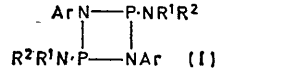
Arenesulphonamides react with tetramethylphosphorodiamidous chloride, *NN'*-dimethyl-*NN'*-diphenylphosphorodiamidous chloride, and dimethylphosphoramidous dichloride, to give 1,3-bisarylsulphonyl-1,3,2,4-diazadiphosphetidines in high yields. The dimethyldiphenylphosphorodiamidous chloride also reacts with aniline in the presence of pyridine to give a diphenyldiazadiphosphetidine, but reacts with benzamide to give an *N*-benzoyltriaminophosphine. Some spectroscopic and chemical properties of the bisarylsulphonyldiazadiphosphetidines are described.

1,3,2,4-DIAZADIPHOSPHETIDINES were first isolated by Michaelis [2] by treating arylamines or their hydrochlorides with phosphorus trichloride: 2,4-diaminodiazadiphosphetidines (I) were obtained if an excess of amine was present, whereas the corresponding 2,4-dichlorides (II) were the main products when an excess of phosphorus trichloride was used.



(I) (II)

We recently reported [1] that the dichloride (II; Ar = Ph) may also be obtained by treating phosphorus trichloride with *N*-phenylhexamethyldisilazane [equation (i)], or from phenyliminobisdichlorophosphine, obtained from aniline hydrochloride and phosphorus trichloride at ⩽75°, by thermal elimination of phosphorus trichloride [equation (ii)], or by treatment with a disilazane [equation (iii)]. Alternatively, the diamide (I; Ar = Ph, $R^1 = R^2$ = Me) may be prepared by treating phenyliminobisdichlorophosphine with dimethylaminotrimethylsilane [equation (iv)]. Since substituted phenyliminobisdichlorophosphines are readily obtained from the corresponding arylamines,[1] these reactions provide a useful route to numerous diazadiphosphetidines.

$$2PhN(SiMe_3)_2 + 2PCl_3 \longrightarrow (PhNPCl)_2 + 4Me_3SiCl \quad (i)$$

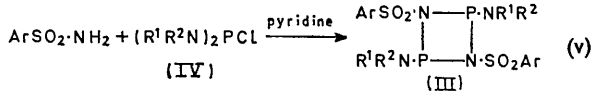
$$2PhN(PCl_2)_2 \longrightarrow 2PCl_3 + (PhNPCl)_2 \quad (ii)$$

$$PhN(PCl_2)_2 + PhN(SiMe_3)_2 \longrightarrow (PhNPCl)_2 + 2Me_3SiCl \quad (iii)$$

$$2PhN(PCl_2)_2 + 8Me_2N\cdot SiMe_3 \longrightarrow (PhNP\cdot NMe_2)_2 + 2(Me_2N)_3P + 8Me_3SiCl \quad (iv)$$

We now report a general route [equation (v)] to a new class of compounds belonging to this broad group of phosphorus–nitrogen heterocycles, namely, 1,3-bisarylsulphonyl-1,3,2,4-diazadiphosphetidines (III).

During a study of the reactions of dichlorodiazadiphosphetidines with compounds containing NH_2 groups,[3] the related acyclic N–P–N compounds, phosphorodiamidous chlorides, were also examined. When tetramethylphosphorodiamidous chloride [4] (IV; $R^1 = R^2$ = Me) was treated with benzenesulphonamide in anhydrous pyridine, a vigorously exothermic reaction ensued; unchanged pyridine and quaternary salts were removed leaving a copious white precipitate. I.r. spectroscopic analysis of this stable solid, m.p. 179—181°, did not show the expected N–H stretching mode, and ^{1}H n.m.r. analysis indicated that cleavage of one P–N bond had unexpectedly occurred, since the ratio of aliphatic to aromatic protons was 6 : 5. Elemental analysis verified this deduction; it is compatible with formula (IIIa). The presence of a four-membered ring was supported by a determination of the molecular weight by vapour pressure osmometry.



(IV) (III) (v)

a; $R^1 = R^2$ = Me, Ar = Ph
b; $R^1 = R^2$ = Me, Ar = 4-MeC_6H_4
c; $R^1 = R^2$ = Me, Ar = 4-$MeO\cdot C_6H_4$
d; $R^1 = R^2$ = Me, Ar = 1-naphthyl
e; R^1 = Me, R^2 = Ar = Ph
f; R^1 = Me, R^2 = Ph, Ar = 4-MeC_6H_4

The reaction [equation (v)] proved to be of general application, and analogous bisarylsulphonyldiaminodiazadiphosphetidines (IIIb—d) were prepared in 75—80% yield by treating tetramethylphosphorodiamidous chloride with toluene-4-sulphonamide, 4-methoxybenzenesulphonamide, and naphthalene-1-sulphonamide, respectively. Their molecular weights, determined by osmometry for solutions in chloroform, are only compatible with their formulation as four-membered ring structures, and are well removed from the values to be expected from unsaturated monomers ($ArSO_2N{:}PNR^1R^2$) or higher oligomers.

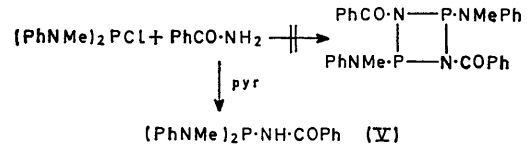
Although the phosphorodiamidic chloride $(PhMeN)_2P(O)Cl$ is known,[5] the corresponding phosphorodiamidous chloride (IV; R^1 = Me, R^2 = Ph) had not been reported previously. However, it was readily synthesised by treating phosphorus trichloride with *N*-methylaniline (2 mol. equiv.) in the presence of pyridine. The viscous oil is very water- and air-sensitive. Its structure was confirmed by analysis and ^{1}H and ^{31}P n.m.r. spectroscopy, the latter revealing the occurrence of

[1] Part XIII, A. R. Davies, A. T. Dronsfield, R. N. Haszeldine, and D. R. Taylor, *J.C.S. Perkin I*, 1973, 379.
[2] A. Michaelis and G. Schroeter, *Ber.*, 1894, **27**, 490.
[3] F. L. Bowden, A. R. Davies, A. T. Dronsfield, B. J. Edmondson, R. N. Haszeldine, D. R. Taylor, and L. Williams, unpublished results.
[4] H. Noth and H.-J. Vetter, *Chem. Ber.*, 1963, **96**, 1109.
[5] H. A. C. Montgomery and J. A. Turnbull, *J. Chem. Soc.*, 1958, 1963.

coupling between the methyl protons and the phosphorus (*ca.* 7 Hz).

The dimethyldiphenylphosphorodiamidous chloride (IV; R^1 = Me, R^2 = Ph) also reacts with sulphonamides according to equation (v), and gives the bisarylsulphonyldiazadiphosphetidines (IIIe—f) when treated with benzenesulphonamide and toluene-4-sulphonamide, respectively, in the presence of pyridine. The ^{1}H n.m.r. spectra of these compounds do not show P–H coupling; the *N*-methyl proton resonance is broad but unresolved, possibly owing to quadrupole relaxation by the intervening nitrogen atom, or to some steric hindrance to rotation about the P–N bond.[6] No attempt was made to test the latter possibility, for example by n.m.r. spectroscopy over a range of temperatures.

A single experiment aimed at the extension of this type of reaction to the synthesis of 1,3-dibenzoyldiazadiphosphetidines proved unsuccessful. Although the dimethyldiphenylphosphorodiamidous chloride (IV; R^1 = Me, R^2 = Ph) and benzamide react exothermically in the presence of pyridine, the product is the acyclic triaminophosphine (V), an unstable solid, m.p. 141°. The presence of a residual NH group is clearly indicated in its i.r. spectrum.



Further investigation of the reaction of (IV) with compounds containing other types of NH_2 group could prove to be rewarding. For example a preliminary study of the reaction between the phosphorodiamidous chloride (IV; R^1 = Me, R^2 = Ph) and aniline gave the diphenyldiazadiphosphetidine (I; Ar = R^1 = Ph, R^2 =

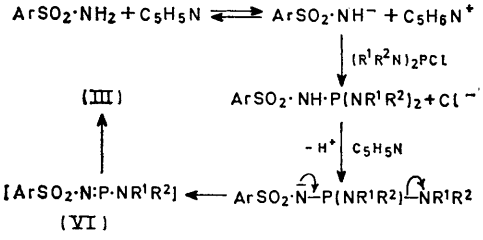
$$(PhNMe)_2PCl + PhNH_2 \xrightarrow{pyr} (PhNP{\cdot}NMePh)_2$$

Me), an unstable solid, m.p. 108—112°, which was difficult to purify. The i.r. spectrum of this material did not show an N–H stretching mode.

The mechanism for the formation of the bisarylsulphonyldiazadiphosphetidines (III) has not been firmly established. The presence of pyridine was found to be desirable for high yields to be obtained, but not essential. For example, tetramethylphosphorodiamidous chloride (IV; R^1 = R^2 = Me) and toluene-4-sulphonamide undergo an exothermic reaction in dioxan to give the diazadiphosphetidine (IIIb). A brief induction period was noted; possibly the secondary amine liberated slowly in this early period promotes the reaction as effectively as pyridine. The formation of dimethylamine hydrochloride was confirmed and *N*-methylaniline was detected in the reactions of the dimethyldiphenylphosphorodiamidous chloride (IV; R^1 = Me, R^2 = Ph) with sulphonamides.

The most probable mechanism is considered to be that shown in the Scheme, which involves the formation of an unsaturated iminophosphine (VI) which dimerises to give the ring compound (III). In the related compounds stemming from the reaction of phosphorus pentachloride with sulphonamides,[7] the existence of an equilibrium between unsaturated monomer and four-membered ring has been clearly established by molecular weight determinations in solution. That such a monomeric species should be destabilised by reduction to phosphorus(III) is fully to be expected; nevertheless, evidence for the existence of such P^{III} species as reactive intermediates is accumulating in the literature.[8]

Phosphine imides of the type $ArSO_2{\cdot}N{:}PCl_3$ generally display an intense i.r. absorption at *ca.* 1150 cm^{-1}, assigned to the P:N stretching mode of the monomeric species.[9] In view of the presence of such a band at or near 1150 cm^{-1} in the spectra of the sulphonyldiazadiphosphetidines (III), the possibility of their dissociation into monomeric P:N species had to be considered. The absorption band persists in the spectra of their solutions in chloroform, however, for which molecular weight determinations clearly establish that they are



SCHEME

present as saturated dimers. A more natural assignment of this band is to the sulphonyl group's symmetric stretching mode, which in sulphonamides [10] and sulphamides [11] characteristically appears in this region of the spectrum.

Bisarylsulphonyldiazadiphosphetidines may also be prepared from phosphoramidous dichlorides [equation (vi)]. The reaction between dimethylphosphoramidous

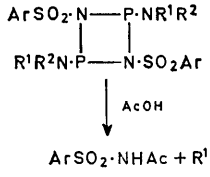
$$R^1R^2N{\cdot}PCl_2 + ArSO_2{\cdot}NH_2 \xrightarrow[-2\,HCl]{\text{pyridine}} (III) \qquad (vi)$$

dichloride and toluene-4-sulphonamide, for example, proceeds just as described for the phosphorodiamidous chlorides, and gives the diazadiphosphetidine (IIIb) in high yield. In this case the condensation reaction results

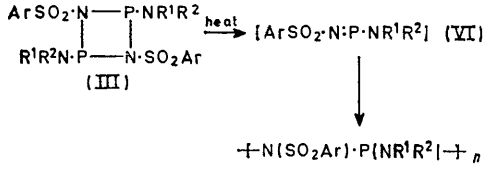
[6] R. G. Cavell, T. L. Charlton, and W. Sim, *J. Amer. Chem. Soc.*, 1971, **93**, 1130, and references cited therein.
[7] E. Fluck, *Topics Phosphorus Chem.*, 1966, **4**, 291.
[8] G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1964, 572; H. Goldwhite, R. N. Haszeldine, and D. G. Rowsell, *ibid.*, 1965, 6875; M. Green, R. N. Haszeldine, B. R. Iles, and D. G. Rowsell, *ibid.*, p. 6879; B. Fontal, H. Goldwhite, and D. G. Rowsell, *J. Org. Chem.*, 1966, **31**, 2424; C. E. Griffin, E. H. Uhing, and A. D. F. Toy, *J. Amer. Chem. Soc.*, 1965, **87**, 4757; H. Goldwhite and D. G. Rowsell, *ibid.*, 1966, **88**, 3572; A. J. Kirby and S. G. Warren, ' The Organic Chemistry of Phosphorus,' Elsevier, Amsterdam, 1967, p. 244; G. Markl and F. Lieb, *Tetrahedron Letters*, 1967, 3489.
[9] W. Weigrabe and H. Bock, *Chem. Ber.*, 1968, **101**, 1414.
[10] E. A. Robinson, *Canad. J. Chem.*, 1961, **39**, 247.
[11] A. Vandi, T. Moeller, and L. F. Audrieth, *J. Org. Chem.*, 1961, **26**, 1136.

in the elimination of 2 mol. equiv. of hydrogen chloride, and is facilitated by the presence of pyridine.

The chemical properties of the bisarylsulphonyldiazadiphosphetidines are those to be expected from the known behaviour of related P–N ring compounds.[7,12] They are readily decomposed to sulphonamides and amine salts by dilute mineral acids: the phosphorus–nitrogen bond is generally susceptible to cleavage by acid.[7] When treated with glacial acetic acid, acetylation of both the ring nitrogen and the exocyclic nitrogen atom is achieved, yielding a mixture of an *N*-acetylsulphonamide and an *NN*-disubstituted acetamide.

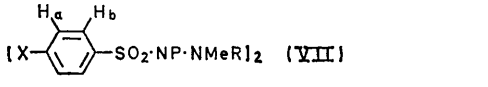


When strongly heated *in vacuo*, three of the diazadiphosphetidines (IIIb, d, and f) were smoothly transformed into glassy oligomers of unchanged composition but higher molecular weight. These low-molecular weight polymers were readily soluble in chlorinated solvents, and were of moderate to good thermal stability in air: decomposition in air on a thermal balance commenced at 250—300°. These polymers are believed to arise by reversible dissociation of the cyclic dimers



(III) into the unstable unsaturated monomers (VI), but direct polymerisation of the ring compounds (III) by cleavage of only one P–N bond cannot be excluded.

^{1}H N.m.r. chemical shift data [τ ($CDCl_3$)] for *p*-substituted disulphonyldiazadiphosphetidines (VII)



X	R	H_a	H_b	Ph	NMe [a]	ArMe	OMe
Me	Ph	2·38(d)	2·83(d)	2·75(s)	7·3(s)	7·67(s)	
Me	Me	2·34(d)	2·75(d)		7·5(s)	7·67(s)	
MeO	Me	2·28(d)	3·07(d)		7·5(s)		6·18(s)

[a] A broad resonance in all cases, but not resolved.

EXPERIMENTAL

The general techniques employed were described earlier.[1] Molecular weights (solution) were determined by vapour pressure osmometry (Mechrolab model 30/A bridge instrument).

Toluene-4-sulphonamide and benzenesulphonamide obtained commercially were used without purification. Other sulphonamides were prepared by sulphonation of the corresponding arenes with chlorosulphonic acid, followed by treatment of the sulphonyl chlorides with aqueous ammonia.[13] They were freed from sulphones by extracting the sulphonamide into cold 6M-sodium hydroxide solution, reprecipitated with dilute mineral acid, and recrystallised from ethanol. Tetramethylphosphorodiamidous chloride was prepared from phosphorus trichloride and 4 mol. equiv. of dimethylamine in dry ether, and purified by fractional distillation; b.p. 30—32° at 0·1 mmHg (lit.,[4] 29° at 0·1 mmHg).

NN′-Dimethyl-NN′-diphenylphosphorodiamidous Chloride.—*N*-Methylaniline (21·9 g, 0·205 mol) in light petroleum (b.p. 30—40°) (200 ml) was added to a well stirred solution of phosphorus trichloride (14·0 g, 0·102 mol) in anhydrous pyridine (25 ml). The mixture was kept at reflux for 1 h, cooled, and filtered under dry nitrogen; the filtrate was evaporated to dryness and the residual oil distilled at reduced pressure under nitrogen to give the *phosphorodiamidous chloride* (11·6 g, 41·6 mmol, 41%) as a viscous oil, b.p. 155—157° at 0·1 mmHg (Found: C, 60·0; H, 5·7; Cl, 12·4; N, 10·1; P, 11·0. $C_{14}H_{16}ClN_2P$ requires C, 60·3; H, 5·7; Cl, 12·7; N, 10·1; P, 11·1%), $\nu_{max.}$ 3060w, 3030w, 2930w, 2890w, 2180w, 2660w, 2450w, 1595s, 1485s, 1445m, 1260s, 1180s, 1080s, 1065s, 1055m, 1025m, 995w, 910m, 850s, 755s, and 690s cm^{-1}, δ_H (w.r.t. external benzene) 3·7 (CH_3, d, J_{HP} 7 Hz) and −0·55 p.p.m. (Ph, m), δ_P (w.r.t. external 85% H_3PO_4) −138 p.p.m. (septet, J_{PH} *ca.* 7 Hz).

2,4-Bis-N-methylanilino-1,3-bisphenylsulphonyl-1,3,2,4-diazadiphosphetidine (IIIe).—Benzenesulphonamide (5·30 g, 33·8 mmol) was shaken vigorously with a solution of *NN′*-dimethyl-*NN′*-diphenylphosphorodiamidous chloride (9·40 g, 33·7 mmol) in anhydrous pyridine (24 ml) under dry nitrogen, and after an initial exothermic reaction the mixture was kept at 70° for 30 min. Unchanged pyridine was distilled off *in vacuo*, and the yellow residue shaken with wet acetone (*ca.* 15% water; 5 × 10 ml), filtered off, and washed with ether. The precipitate was recrystallised by dissolving it in hot acetone and adding water dropwise, giving white needles of the *diazadiphosphetidine* (3·10 g, 5·3 mmol, 32% yield) [Found: C, 53·4; H, 4·8; N, 9·7; S, 11·1%; *M* (4·88 g l^{-1} in *sym*-tetrachloroethane), 561. $C_{26}H_{26}N_4O_4P_2S_2$ requires C, 53·4; H, 4·5; N, 9·6; S, 11·0%; *M*, 584], m.p. 210—212°, $\nu_{max.}$ 3100w, 3060w, 3030w, 2990w, 2980w, 2960w, 2820w, 1590m, 1580m, 1485s, 1465m, 1445s, 1420w, 1340m, 1330m, 1305w, 1290w, 1260m, 1180m, 1160s, 1090m, 1080m, 1065m, 1025m, 1000m, 930s, 875m, 855s, 755s, 730s, 695m, and 690m cm^{-1}, τ ($CDCl_3$; internal Me_4Si) 2·05—2·65 (10H, complex m, Ph) and 7·31br (3H, s, Me).

2,4-Bis-N-methylanilino-1,3-bis-p-tolylsulphonyl-1,3,2,4-diazadiphosphetidine (IIIf).—Toluene-4-sulphonamide (5·5 g, 32·2 mmol), *NN′*-dimethyl-*NN′*-diphenylphosphorodiamidous chloride (9·0 g, 32·4 mmol), and pyridine (24 ml), treated as above, gave the *diazadiphosphetidine* (4·9 g, 8·0 mmol, 50%) [Found: C, 54·9; H, 5·2; N, 9·3; S, 10·6; P, 9·9%; *M* (3·65 g l^{-1} in $CHCl_3$), 625. $C_{28}H_{30}N_4O_4P_2S_2$ requires C, 54·9; H, 4·9; N, 9·1; S, 10·4; P, 10·2%; *M*, 612] (for ^{1}H n.m.r. data see Table).

2,4-Bisdimethylamino-1,3-bisphenylsulphonyl-1,3,2,4-diazadiphosphetidine.— Tetramethylphosphorodiamidous chloride (10·3 g, 66·7 mmol) was rapidly added to a solution of benzenesulphonamide (11·0 g, 70·1 mmol) in anhydrous pyridine (11 ml) with vigorous swirling, and the mixture was kept at 60° for 1 h. Pyridine was distilled out, and the residue was triturated with wet acetone (5 × 10 ml),

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

[13] A. I. Vogel, ' A Textbook of Practical Organic Chemistry,' 3rd edn., Longmans, London, 1966.

filtered off, and recrystallised from hot acetone by dropwise addition of water to give the *diazadiphosphetidine* (IIIa) (11·1 g, 24·1 mmol, 72% yield based on phosphorodiamidous chloride) [Found: C, 41·7; H, 4·7; N, 12·1; P, 13·6; S, 13·9%; *M* (2·65 g l^{-1} in $CHCl_3$), 465. $C_{16}H_{22}N_4O_4P_2S_2$ requires C, 41·7; H, 4·8; N, 12·2; P, 13·5; S, 13·9%; *M*, 460], m.p. 179—180°, $\nu_{max.}$ 3100w, 3075w, 3005w, 2995w, 2940m, 2900m, 2860w, 2800w, 1590w, 1480s, 1450s, 1445w, 1350s, 1340s, 1320m, 1310m, 1295s, 1195m, 1185w, 1165s, 1155m, 1090m, 1077w, 1070w, 990m, 920s, 870s, 765m, 730m, 700m, and 690m cm^{-1}, τ ($CDCl_3$; internal Me_4Si) 2·1—2·6 (5H, m, Ph) and 7·6br (6H, s, Me_2N).

2,4-*Bisdimethylamino*-1,3-*bis*-p-*tolylsulphonyl*-1,3,2,4-*diazadiphosphetidine*.—(a) *From tetramethylphosphorodiamidous chloride*. A similar reaction between tetramethylphosphorodiamidous chloride (12·5 g, 80·9 mmol), toluene-4-sulphonamide (14·0 g, 81·9 mmol), and anhydrous pyridine (12 ml), kept at 60° for 1 h, gave white platelets of the *diazadiphosphetidine* (IIIb) (14·5 g, 29·7 mmol, 74%) [Found: C, 44·5; H, 5·3; N, 11·7; P, 13·0; S, 13·2%; *M* (3·90 g l^{-1} n $CHCl_3$), 485. $C_{18}H_{26}N_4O_4P_2S_2$ requires C, 44·3; H, 5·3; N, 11·5; P, 13·2; S, 13·1%; *M*, 488], m.p. (from acetone) 207—209°, $\nu_{max.}$ 3075w, 3060w, 3040w, 2990w, 2900m, 2850w, 2820w, 2800w, 1600m, 1500m, 1480m, 1450m, 1400m, 1340s, 1305m, 1295s, 1210w, 1185s, 1160s, 1125w, 1115w, 1090s, 1065m, 1025m, 1020w, 985s, 980, 920s, 850s, 825s, 815m, 720s, 710s, and 680s cm^{-1}, δ_P −178 p.p.m. (w.r.t. ext. 85% H_3PO_4) (unresolved s); for ^1H n.m.r. data see Table. The diazadiphosphetidine (IIIb) was also prepared from tetramethylphosphorodiamidous chloride (5·31 g, 34·4 mmol) and toluene-4-sulphonamide (5·70 g, 33·4 mmol) in dioxan (15 ml) in 24% yield.

(b) *From* NN-*dimethylphosphoramidous dichloride*. Dimethylphosphoramidous dichloride (10·5 g, 72·0 mmol) was added to a cold, stirred, solution of toluene-4-sulphonamide (12·3 g, 72·0 mmol) in dry pyridine (17 ml). After a brief induction period a vigorous reaction ensued; when this subsided the mixture was kept at 60° for 1 h, and worked up as described above to give the bis-*p*-tolylsulphonyldiazadiphosphetidine (IIIb) (14·4 g, 29·5 mmol, 82%), m.p. and mixed m.p. 208°.

2,4-*Bisdimethylamino*-1,3-*bis*-4-*methoxyphenylsulphonyl*-1,3,2,4-*diazadiphosphetidine*.—A mixture of tetramethylphosphorodiamidous chloride (6·0 g, 38·8 mmol), 4-methoxybenzenesulphonamide (7·5 g, 40·2 mmol) and dry pyridine (11 ml), treated as above, gave white platelets of the *diazadiphosphetidine* (IIIc) (8·69 g, 16·7 mmol, 86% yield) [Found: C, 41·7; H, 5·2; N, 10·7; P, 11·4; S, 12·2%; *M* (3·17 g l^{-1} in $CHCl_3$), 514. $C_{18}H_{26}N_4O_6P_2S_2$ requires C, 41·5; H, 5·0; N, 10·8; P, 11·9; S, 12·3%; *M*, 520], m.p. (from acetone) 205—206°, $\nu_{max.}$ 3110w, 3080w, 3020w, 2960m, 2920m, 2860w, 2830w, 2810w, 2570w, 2060w, 2040w, 1920w, 1600s, 1560m, 1500s, 1460m, 1430m, 1415m, 1345s, 1300s, 1260m, 1180w, 1155s, 1115m, 1090m, 1065w, 1025m, 1010w, 975m, 915s, 870m, 805m, 720m, 700s, and 680s cm^{-1}; for ^1H n.m.r. data see Table.

2,4-*Bisdimethylamino*-1,3-*bis*-1-*naphthylsulphonyl*-1,3,2,4-*diazadiphosphetidine*.— Tetramethylphosphorodiamidous chloride (6·91 g, 44·7 mmol), naphthalene-1-sulphonamide (9·33 g, 45·1 mmol), and dry pyridine (12 ml) were treated similarly to give white prisms of the *diazadiphosphetidine* (IIId) (9·89 g, 17·7 mmol, 79%) [Found: C, 51·6; H, 4·8; N, 10·4; P, 11·4; S, 11·4%; *M* (4·70 g l^{-1} in $CHCl_3$), 560. $C_{24}H_{26}N_4O_4P_2S_2$ requires C, 51·4; H, 4·7; N, 10·0; P, 11·1; S, 11·5%; *M*, 560], m.p. (from acetone) 219—221°, $\nu_{max.}$ 3070w, 2980w, 2940w, 2900w, 2850w, 2810w, 1595w, 1570w, 1505w, 1485m, 1445m, 1435w, 1350m, 1330s, 1295m, 1265m, 1215w, 1200w, 1190w, 1160s, 1145w, 1130s, 1080w, 1065m, 1030w, 985s, 920s, 860s, 855s, 830m, 805m, 770s, 740w, 715w, 695s, and 640m cm^{-1}.

2,4-*Bis*-N-*methylanilino*-1,3-*diphenyl*-1,3,2,4-*diazadiphosphetidine*.— *NN'*-Dimethyl-*NN'*-diphenylphosphorodiamidous chloride (8·38 g, 30·1 mmol), aniline (3·0 g, 32·3 mmol), and dry pyridine (10 ml), kept under dry nitrogen at 25° for 1 h with occasional shaking, gave, after evaporating off unchanged pyridine and extracting the residue with wet acetone (6 × 10 ml), a white solid. This was recrystallised from 30 : 1 hexane–chloroform to give white leaflets of a substance believed to be the 1,3-diphenyldiazadiphosphetidine (4·10 g, 9·21 mmol, 61% yield) [Found: C, 64·8; H, 6·0; N, 12·5%; *M* (4·48 g l^{-1} in *sym*-tetrachloroethane), 386. Calc. for $C_{26}H_{26}N_4P_2$: C, 68·4; H, 5·7; N, 12·7%; *M*, 456], m.p. 108—112°, $\nu_{max.}$ 3080w, 3060w, 3030w, 2940w, 2860w, 2880w, 2820w, 1505s, 1490s, 1450m, 1390m, 1340m, 1290s, 1185m, 1155m, 1105w, 1080m, 1060s, 1025m, 1005w, 950w, 905s, 890s, 845s, 820m, 750s, 685s, 680m, and 655m cm^{-1}.

Benzamidobis-N-*methylanilinophosphine*.— *NN'*-Dimethyl-*NN'*-diphenylphosphorodiamidous chloride (6·85 g, 24·6 mmol) was added to a solution of benzamide (3·0 g, 24·6 mmol) in dry pyridine (10 ml) and the mixture was stirred at 60° for 30 min under nitrogen. Unchanged pyridine was distilled off and the oily residue shaken with methanol (25 ml), leaving a white solid which was recrystallised from 20 : 1 methanol–acetone to give *benzamidobis*-N-*methylanilinophosphine* (2·05 g, 5·64 mmol, 46% yield based on phosphorodiamidous chloride) (Found: C, 69·2; H, 6·3; N, 11·3. $C_{21}H_{22}N_3OP$ requires C, 69·4; H, 6·1; N, 11·6%) as an unstable, light-sensitive solid, m.p. 141°, $\nu_{max.}$ 3300m, 3260w, 3070w, 3020w, 2990w, 2820w, 1675s, 1620s, 1580m, 1500w, 1495s, 1460s, 1405s, 1320m, 1255m, 1180m, 1170w, 1115m, 1075m, 1025s, 1000w, 935w, 895w, 845m, 815m, 790m, 740m, 730m, 715w, and 695m cm^{-1}.

Reaction of the Diazadiphosphetidine (IIIb) *with Acetic Acid*.—Glacial acetic acid (3·50 g, 58·4 mmol) and the diazadiphosphetidine (IIIb) (6·0 g, 12·3 mmol) were kept in refluxing toluene (20 ml) for 1 h; the clear supernatant liquid was decanted off, cooled to −15° for 24 h, and filtered. The precipitate was identified as *N*-acetyltoluene-4-sulphonamide (3·11 g, 14·6 mmol, 59%), mixed m.p. with an authentic sample prepared from toluene-4-sulphonamide and acetic anhydride, 137° (lit.,[13] 137°). The toluene filtrate was fractionally distilled to give toluene and *NN*-dimethylacetamide (1·54 g, 17·7 mmol, 72%), b.p. 84° at 33 mmHg, n_D^{20} 1·4371 (lit.,[14] 84° at 32 mmHg, n_D^{22} 1·43708).

Action of Heat on Disulphonyldiazadiphosphetidines.— —(a) *Compound* (IIIb). The diazadiphosphetidine (IIIb) (4·40 g, 9·02 mmol) was kept at 207—215° for 1 h *in vacuo* to give an unidentified sublimate (0·4 g), dimethylamine (0·1 g), and a brown residue which was Soxhlet extracted with ethanol-free chloroform for 2 h. The extract was filtered and evaporated to dryness to give a brown glassy *polymer* (3·30 g, 75%) [Found: C, 40·6; H, 5·2; N, 9·9%; *M* (11·1 g l^{-1} in chloroform), 7190. $(C_9H_{13}N_2O_2PS)_{30}$ requires C, 44·3; H, 5·2; N, 11·5%; *M*, 7320] which

[14] 'Dictionary of Organic Compounds,' vol. 2, 4th edn., Eyre and Spottiswoode Ltd., London, 1965, p. 1135.

melted over the temperature range 70—100° and could be drawn into brittle threads when soft.

(b) *Compound* (IIId). The diazadiphosphetidine (IIId) (5·0 g, 8·95 mmol) was kept at 240—245° for 2 h *in vacuo* and the residue was extracted as above to give a brown *polymer* (4·70 g, 94%) [Found: C, 50·2; H, 5·0; N, 9·4%; *M* (3·94 g l^{-1} in *sym*-tetrachloroethane), 1060. $(C_{12}H_{13}N_2O_2PS)_4$ requires C, 51·4; H, 4·7; N, 10·0%; *M*, 1120], melting over the range 110—160°.

(c) *Compound* (IIIf). The diazadiphosphetidine (IIIf) (5·0 g, 8·15 mmol) was kept at 210—220° for 1 h *in vacuo* to give an unidentified sublimate (0·5 g) and a dark brown glassy *polymer* (3·66 g, 73%) [Found: C, 52·9; H, 5·0; N, 8·4%; *M* (9·85 g l^{-1} in chloroform), 2560. $(C_{14}H_{15}N_2O_2PS)_8$ requires C, 54·9; H, 4·9; N, 9·1%; *M*, 2448], melting range 115—135°.

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