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## Studies of Organophosphorochloridates. Part I. Synthesis of N-Substituted Phosphoramidic Chlorides and Acids

By R. J. W. Cremlyn,\* B. B. Dewhurst, and D. H. Wakeford, Department of Chemical Sciences, Hatfield Polytechnic, Hatfield, Hertfordshire

Novel N-substituted phosphoramidic chlorides and acids have been prepared and their i.r. spectra are discussed. Pyrophosphoryl chloride has been used for the phosphorylation of amines. Treatment of NN'-diphenylphos-phorodiamidic chloride with silver oxide gives NN'N"N"'-tetraphenylpyrophosphoramide, and not NN'-diphenylphosphenimidic amide as previously suggested. Some reactions of NN'-diarylphosphorodiamidic chlorides have been investigated.

N-SUBSTITUTED phosphoramidic dichlorides (I) and phosphorodiamidic chlorides (II) have generally been synthesised by treatment of an amine or an amine hydrochloride with phosphorus oxychloride.<sup>1a</sup> We have found the former method the most convenient, although the purity and yield of the products were sensitive to the reaction conditions. In spite of the

R<sup>1</sup>NH(R<sup>2</sup>NH)P(:O)Cl RNH·P(:O)Cl, (I) (II) $(RNH)_2P(:O)\cdot O\cdot P(:O)(NHR)_2$ R<sup>1</sup>NH·(R<sup>2</sup>N:)P:O (III) (IV)R<sup>1</sup>NH(R<sup>2</sup>NH)P(:O)·OH (V)

decreased reactivity of the chlorine atoms towards nucleophilic substitution in the amidic dichloride (I) as compared with phosphorus oxychloride, it was found that selective formation of (I) required very mild conditions to avoid further replacement of the chlorine atoms. The reactivity of (I) will be largely governed by the electronic effects of the hydrocarbon radical (R), and hence by the basicity of the original amine.

When the amidic dichloride (I) is treated with a further quantity of amine to give the diamidic chloride (II), there is also the possibility of the formation of the phosphenimidic amide (III) via subsequent elimination of hydrogen chloride. In our hands generally only (II) was obtained; though when the amidic dichloride (I; R = Ph) was treated with a strongly basic amine (e.g. cyclohexylamine) there was some evidence for the formation of the imidic amide (III) (see Experimental section).

Caven claimed <sup>2</sup> that NN'-diphenylphosphorodiamidic chloride (II;  $R^1 = R^2 = Ph$ ) by reaction with dry silver oxide in an inert solvent gave monomeric NN'-diphenylphosphenimidic amide (III;  $R^1 = R^2 = Ph$ ). Other workers <sup>1b</sup> have observed this compound as a dimer. We consider that the compound originally assigned as the monomeric phosphenimidic amide (III;  $\mathbf{R}^1 = \mathbf{R}^2 = \mathbf{Ph}$ ) is NN'N''N'''-tetraphenylpyrophosphoramide (IV; R = Ph), because on repetition of Caven's experiment the only isolable organic product was the

<sup>1</sup> G. M. Kosolapoff, 'Organophosphorus compounds,' John Wiley, New York, 1950, (a) p. 279 et seq., (b) p. 319, (c) p. 304,  $(d) p_{2} 291$ 

 <sup>2</sup> R. M. Caven, J. Chem. Soc., 1903, 82, 1045.
 <sup>3</sup> L. J. Bellamy, 'The Infra-Red Spectra of Complex Molecules,' Methuen, 2nd edn., 1958, (a) p. 312, (b) p. 205.

pyrophosphoramide (IV), which has a very similar elemental analysis to the phosphenimidic amide (III;  $R^1 = R^2 = Ph$ ). Our product showed an additional strong i.r. band at 980-960 cm.<sup>-1</sup>, in comparison with the spectrum of diphenylphosphorodiamidic chloride which was indicative of the P-O-P group; 3a this was supported by the <sup>31</sup>P n.m.r. spectrum. The structure was confirmed as (IV) by comparison with authentic NN'N''N'''-tetraphenylpyrophosphoramide [from the condensation of NN'-diphenylphosphorodiamidic acid (V;  $R^1 = R^2 = Ph$ ) with NN'-diphenylphosphorodiamidic chloride]; the pyrophosphoramide was also obtained by treatment of NN'-diphenylphosphorodiamidic acid with dicyclohexylcarbodi-imide. The formation of the pyrophosphoramide is analogous to the preparation of ethers by treatment of alkyl halides with dry silver oxide. Pyrophosphoryl chloride (VI) has been used for the phosphorylation of alcohols by phosphorus-oxygen bond fission to give the phosphorodichloridate (VII).<sup>4,5</sup> On the other hand, in presence of a tertiary base phosphorus-chlorine bond fission occurs to give the alkyl pyrophosphoryl chloride (IX):<sup>6</sup>

$$\begin{array}{c} R^{1}O \cdot P(:O)Cl_{2} & \longleftarrow \\ (VII) & Cl_{2}P(:O) \cdot O \cdot P(:O)Cl_{2} \\ (VII) & (VI) \\ & \xrightarrow{R^{1}OH} \\ & & (R^{1}O)ClP(:O) \cdot O \cdot P(:O)Cl_{2} \\ (IX) \end{array}$$

Klement and Benek<sup>7</sup> obtained pyrophosphorotetramide by the action of ammonia on pyrophosphoryl chloride (VI), although Goehring and Niedenzu<sup>8</sup> found that only a trace of water was necessary to cause phosphorus-oxygen bond fission in this reaction. We have investigated the reaction of pyrophosphoryl chloride with amines: slow addition of an amine to a slight excess of the reagent (VI) in an inert solvent gave the corresponding N-substituted phosphoramidic dichloride (I). This procedure has proved useful for the phosphorylation of weakly nucleophilic amines since it occurs under milder conditions than with phosphorus oxychloride; also there is less possibility of the formation of di- and tri-substituted by-products.

4 R. J. W. Cremlyn and N. A. Olsson, J. Chem. Soc. (C), 1969,

- 2305. <sup>5</sup> W. Koransky, H. Grunze, and G. Münch, Z. Naturforsch., 1962, **17b**, 191.
  - W. Gruber and F. Lynen, Annalen, 1962, 659, 139.
  - <sup>7</sup> R. Klement and L. Benek, Z. anorg. Chem., 1956, 287, 12.
     <sup>8</sup> M. Goehring and K. Niedenzu, Chem. Ber., 1957, 90, 151.

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The reaction of aniline with the reagent (VI) in ether in the presence of a tertiary base gave a low yield of NN'N''N'''-tetraphenylpyrophosphoramide (IV; R = Ph), showing that pyrophosphoryl chloride can phosphorylate amines with phosphorus-chlorine bond fission under these conditions. This is, however, not a good method for the preparation of pyrophosphoramides since there is simultaneous phosphorus-oxygen bond cleavage. Thus with excess of aniline in benzene, the reagent (VI) gave NN'N"-triphenylphosphoric triamide. The phosphorylation of phenylhydrazine with phosphorus oxychloride gave trianilinophosphoric triamide or, under very mild conditions, a red unstable *N*-anilinophosphoramidic dichloride. oil. possibly Similar products were obtainable with pyrophosphoryl chloride. NN'-Disubstituted phosphorodiamidic chlorides (II) are rapidly hydrolysed by sodium hydroxide to the corresponding acids (V); <sup>1c</sup> several acids (V)obtained in this way have rather low m.p.s, possibly due to some decomposition during recrystallisation. The phosphorodiamidic acid structure (V) is, however, supported by analysis, equivalent-weight determination, and i.r. and n.m.r. spectral evidence.

Heath  $^{9}$  suggested that in the hydrolysis of NN'-diisopropylphosphorodiamidic fluoride by aqueous dioxan, there is simultaneous phosphorus-fluorine and phos-Later work <sup>10</sup> has phorus-nitrogen bond fission confirmed that this also applies to phosphorodiamidic chlorides, although under these conditions the deamination is considerably slower than phosphoruschlorine fission. Thus, we have found that NN'-dicyclohexylphosphorodiamidic chloride with aqueous dioxan gave the corresponding acid (V;  $R^1 = R^2 =$  $C_6H_{11}$ ) but the reaction time is critical, since the generated acid catalyses the rate of phosphorus-nitrogen fission. However, with NN'-diphenylphosphorodiamidic chloride (II;  $R^1 = R^2 = Ph$ ), the corresponding acid could not be obtained, possibly because the derived NN'-diphenylphosphorodiamidic acid would be a stronger acid and so promotes more rapid phosphorusnitrogen bond fission. All the compounds studied have a strong i.r. absorption in the 1300-1200 cm.<sup>-1</sup> region, arising from the P=O stretching vibration.36 The majority of phosphoryl compounds show this band in the 1320-1200 cm.<sup>-1</sup> range.<sup>11a</sup> We have observed that when more than one nitrogen atom is attached to phosphorus the frequency is lowered, e.g. with NN'-dibenzylphosphorodiamidic chloride (II;  $R^1 = R^2 = PhCH_2$ ) to 1200 cm.<sup>-1</sup>. The i.r. spectra of the phosphoramidic compounds showed the normal N-H stretching band at 3300-3150 cm.<sup>-1</sup>; <sup>3b</sup> both methyl N-phenyl and methyl N-p-tolylphosphoramidic chlorides had absorption bands at 1050-1031 116 and 1180 cm.<sup>-1</sup> 11c indicative of the P-O-C and P-O-CH<sub>3</sub> groups respectively. The mass spectra (at source temperatures of 200-280°

and close to the m.p. of the sample) were determined for the following NN'-disubstituted phosphorodiamidic chlorides: dibenzyl, diphenyl, benzylphenyl, and didecyl; only the diphenyl derivative showed a molecular ion (M 466). NN'-Diphenyl- and dicyclohexyl-phosphorodiamidic acids and tetraphenylpyrophosphoramide also failed to give molecular ions, probably because the compounds possessed insufficient vapour pressure at the lower temperature, while at 200-280° the aromatic compounds generally decomposed giving spectra characteristic of the parent amines. The aromatic protons of NN'-dialkyl phosphorimidic chlorides showed signals in the range  $\tau$  2.4–3.3, whilst those of the

## EXPERIMENTAL

Mass spectra were determined with an A.E.I. MS9 spectrometer at 70 eV. I.r. spectra were measured as Nujol mulls with an Infracord 257 spectrometer. N.m.r. spectra were determined with a Varian A60A spectrometer with tetramethylsilane as internal standard. M.p. determinations were made with a Kofler hot-stage apparatus. T.l.c. plates were made up with Silica Gel G and the compounds revealed with a phosphomolybdic acid spray.

diaryl compounds appeared at ca.  $\tau 1.0$ .

N-Phenylphosphoramidic Dichloride.—Method (A): with phosphorus oxychloride. This reaction was carried out as described by Caven<sup>12</sup> to give N-phenylphosphoramidic dichloride as needles (70%), m.p. 85-90° (lit.,13 87°), v<sub>max.</sub> 3080-3130s (NH), 1230s (P=O), 750s, and 690s cm.<sup>-1</sup> (monosubstituted benzene).

Method (B): with pyrophosphoryl chloride. Aniline (15.5 g., 2 mole) in benzene (60 ml.) was added dropwise to a stirred solution of pyrophosphoryl chloride (20.9 g., 1 mole) in benzene (100 ml.) at 15°. The precipitate was filtered off after 48 hr. at room temperature (the solid contained Cl and P, was soluble in water, and gave aniline with dilute sodium hydroxide solution). The filtrate, by evaporation under reduced pressure, gave a yellow oil (18.8 g.) which crystallised on trituration with light petroleum. Recrystallisation from benzene gave the amidic dichloride (14.0 g., 80%), m.p. 83-88° [i.r. spectrum identical to that from the product of method (A)].

NN'-Diphenylphosphorodiamidic Chloride.—Method (A): from phosphorus oxychloride and aniline. As described by Cook et al.,14 this reaction gave NN'-diphenylphosphorodiamidic chloride (75%), m.p. 167-170° (lit.,14 167°) (Found: C, 54.2; H, 4.6; N, 10.5. Calc. for C<sub>12</sub>H<sub>12</sub>ClN<sub>2</sub>OP: C, 54.0; H, 4.6; N, 10.6%). (The optimum yield was obtained with a reaction time of 48 hr.),  $v_{max}$  3280m, 3180s, 1615s, 1605m, 1510s, 1430s, 1310m, 1280m, 1250m, 1230-1215s, 1180m, 1170m, 1045s, 1030m, 1015s, 995s, 940m, 800m, 750s, and 700s; 7 [(CD<sub>3</sub>)<sub>2</sub>SO] 0.9 (2NH) and 2.6-3.3 (10ArH).

Method (B): with phosphorus oxychloride and aniline hydrochloride. As described by Zetzsche and Büttiker,<sup>13</sup> this reaction gave the diamidic chloride (65%), m.p. 166-168° [identical i.r. spectrum to that from the product of method (A)].

<sup>&</sup>lt;sup>9</sup> D. F. Heath, J. Chem. Soc., 1956, 3804.
<sup>10</sup> E. W. Crunden and R. F. Hudson, J. Chem. Soc., 1962, 3591.
<sup>11</sup> D. E. C. Corbridge, 'Topics in Phosphorus Chemistry,' eds.
M. Grayson and E. J. Griffith, Interscience, London, 1969, vol. 6, (a) p. 258, (b) p. 278, (c) p. 279.

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 F. Zetzsche and W. Büttiker, Ber., 1940, 73, 47.
 H. G. Cook, J. D. Ilett, B. C. Saunders, G. J. Stacey, H. G. Watson, I. G. E. Wilding, and S. J. Woodcock, J. Chem. Soc., 1040 2020. 1949, 2921.

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NN'-Di-p-Methoxyphenylphosphorodiamidic Chloride.--A solution of p-anisidine (24.6 g.) in ether (250 ml.) was added dropwise to a stirred solution of phosphorus oxychloride (7.7 g.) in ether (100 ml.) at  $-15^{\circ}$ . The mixture was left at room temperature for 20 hr. and the pale pink solid was washed with water and recrystallised from chlorobenzene to give NN'-di-p-methoxyphenylphosphorodiamidic chloride as needles (10 g.), m.p. 143-146° (Found: C, 51·9; H, 5·0; N, 8·4.  $C_{14}H_{16}Cln_2O_3P$  requires C, 51·5; H, 4·9; N, 8·6%),  $v_{max}$  3280s, 3195s (NH), 1240—1215s (P=O), 830s (1,4-disubstituted benzene). T.l.c. with etheracetone (4:1),  $R_{\rm F}$  0.84.

Recrystallisation of the product from benzene gave crystals, m.p. 137-140°. T.l.c. [ether-acetone (4:1)] gave two spots  $R_{\rm F}$  0.54 and 0.84. Repeated recrystallisation of (1 g.) from ethanol-carbon tetrachloride gave tri-p-methoxyphenylphosphoric triamide as needles (50 mg.), m.p. 186° (Found: C, 61.0; H, 6.0; N, 10.15.  $C_{21}H_{24}N_3O_4P$  requires C, 61.0; H, 5.9; N, 10.2%),  $v_{max}$ . 3360-3140m, 1510s, 1300m, 1280s, 1250s, 1220m, 1180s, 1165s, 1030s, 975m, 935s, and 825s. T.l.c. with etheracetone (4:1),  $R_{\rm F}$  0.54.

NN'-Di-p-Tolylphosphorodiamidic Chloride.--p-Toluidine (32 g.) was treated with phosphorus oxychloride (11.5 g.)in ether, as described by Michaelis, to give the diamidic chloride (15 g.), m.p. 202-206° (lit., 15 210°) (Found: C, 57.3; H, 5.5; N, 9.3. Calc. for C<sub>14</sub>H<sub>16</sub>ClN<sub>2</sub>OP: C, 57.1; H, 5.5; N, 9.5%);  $\tau$  [(CD<sub>3</sub>)<sub>2</sub>SO] 1.1 (2NH), 2.85— 3.2 (8ArH), and 7.7-7.95 (2Me).

NN'-Dibenzylphosphorodiamidic Chloride.—Benzylamine (42.8 g.) with phosphorus oxychloride (15.3 g.) in ether, as described for the preparation of the di-p-methoxyphenyl  $derivative, \ gave \ NN'-dibenzyl phosphorodiamidic \ chloride$ as needles from ethanol (20 g.), m.p. 109-111° (Found: C, 57.0; H, 5.5; N, 9.4; P, 10.9;  $C_{14}H_{16}CIN_2OP$  requires C, 57.1; H, 5.5; N, 9.5; P, 10.5%),  $\nu_{max}$ , 3250–3190s (NH), 1200s (P=O), 750s, and 700s (monosubstituted benzene);  $\tau$  (CDCl<sub>3</sub>) 1·4 (2NH), 2·4-2·8 (10ArH), and 6.0 (4CH<sub>2</sub>).

NN'-Didecylphosphorodiamidic Chloride .-- Similar treatment of decylamine (31.4 g.) with phosphorus oxychloride (7.6 g.), except that addition was made at 0°, gave NN'-didecylphosphorodiamidic chloride as needles from ether (11.8 g.), m.p. 73-76° (Found: C, 61.2; H, 11.1; N, 7.1; P, 7.4. C<sub>20</sub>H<sub>44</sub>ClN<sub>2</sub>OP requires C, 60.8; H, 11.2; N, 7.1; P, 7.8%),  $\nu_{max}$  3260–3200s (NH) and 1215s (P=O). Use of half the quantity of decylamine also gave the diamidic chloride (6 g.).

NN'-Dicyclohexylphosphorodiamidic Chloride.-Cyclohexylamine (39.6 g.) and phosphorus oxychloride (15.3 g.)gave NN'-dicyclohexylphosphorodiamidic chloride as needles from dioxan (22 g.), m.p. 120-122° (Found: C, 52.0; H, 9.0; N, 9.7; P, 11.1. C<sub>12</sub>H<sub>24</sub>ClN<sub>2</sub>OP requires C, 51.7; H, 8.7; N, 10.1; P, 11.1%),  $\nu_{max.}$  3270s (NH) and 1230s (P=O); τ (CDCl<sub>3</sub>) 1.8 (2NH) and 7.75-9.05 (22 aliphatic H).

Dimorpholinophosphorochloridate.—Morpholine (69.7 g.) was added dropwise to an ethereal solution of phosphorus oxychloride (30.6 g.) at  $0^\circ$ , and the mixture was stirred 20 hr. at room temperature; the solid was extracted with carbon tetrachloride and the filtrate by evaporation gave the phosphorochloridate as a powder from light petroleum

 <sup>15</sup> A. Michaelis, Annalen, 1903, **326**, 129.
 <sup>16</sup> H. A. C. Montgomery and J. H. Turnbull, J. Chem. Soc., 1958, 1963.

(50-60°) (35 g.), m.p. 76-80° (lit.,<sup>16</sup> 81°), v<sub>max</sub> 1250s (P=O), and 1120-1100s (C-O-C).

N-Benzyl-N'-phenylphosphorodiamidic Chloride.--A solution of benzylamine (21.4 g.) in ether (70 ml.) was added dropwise to a stirred suspension of N-phenylphosphoramidic dichloride (20.9 g.) in ether (150 ml.) at 0°. The precipitate, after 20 hr. at room temperature, was well washed with water and recrystallised from benzene to give N-benzyl-N'-phenylphosphorodiamidic chloride as needles (20 g., 72%), m.p. 114-116° (Found: C, 55.5; H, 5.1; N, 9.9; P, 11.2. C<sub>13</sub>H<sub>14</sub>ClN<sub>2</sub>OP requires C, 55.6; H, 5.0; N, 10.0; P, 11.0%), v<sub>max.</sub> 3230–3180s (NH), 1210s (P=O), 750s, 745s, and 695s (two monosubstituted benzene groups).

N-Decyl-N'-phenylphosphorodiamidic Chloride.-Decylamine (15.7 g.) with N-phenylphosphoramidic dichloride (10.5 g.) in ether (160 ml.) gave, after 2 hr. at room temperature, a precipitate of the amine hydrochloride (9.8 g.), and N-decyl-N'-phenylphosphorodiamidic chloride by evaporation of the ethereal filtrate. Recrystallisation from benzene-light petroleum (50-60°), or ethanol, gave the diamidic chloride (15.4 g.), m.p. 85-86° (Found: C, 58.4; H, 8.5; N, 8.6; P, 9.9. C<sub>16</sub>H<sub>28</sub>ClN<sub>2</sub>OP requires C, 58.1; H, 8.5; N, 8.5; P, 9.4%),  $v_{max}$  3250–3140s (NH), 1230s (P=O), 750s, and 695s (monosubstituted benzene).

N-Phenylmorpholinophosphorodiamidic Chloride.---Morpholine (17.6 g.) with N-phenylphosphoramidic dichloride (20.9 g.), as described in the preparation of the N-benzyl-N'-phenyl derivative, gave N-phenylmorpholinophosphorodiamidic chloride as a powder from light petroleum (60-80°) (26 g.), m.p. 103-105° (lit.,<sup>17</sup> 100-101°) (Found: C, 46.0; H, 5.4; N, 10.7. Calc. for  $C_{10}H_{14}ClN_2O_2P$ : C, 46.1; H, 5.4; N, 10.7%).

Methyl-N-phenylphosphoramidic Chloride.-Treatment of aniline (18.6 g.) with methylphosphorodichloridate 18 in benzene, as described by Caven,<sup>12</sup> gave methyl-N-phenylphosphoramidic chloride as needles from light petroleum (60-80°) (15 g.), m.p. 83-84° (lit.,<sup>12</sup> 83°) (Found: C, 40.9; H, 4.4; Cl, 16.8; N, 6.8; P, 15.0. Calc. for C<sub>7</sub>H<sub>9</sub>ClNO<sub>2</sub>P: C, 40.9; H, 4.4; Cl, 17.2; N, 6.8; P, 15.1%), v<sub>max</sub> 3160s (NH), 1250s (P=O), 1180m (P=O=CH<sub>3</sub>), 1080---1030s (P-O-C), 755s, and 690s (monosubstituted benzene).

Methyl-N-p-tolylphosphoramidic Chloride.-This compound was prepared from p-toluidine (21.4 g.) and methylphosphorodichloridate as described by Caven.<sup>12</sup> Recrystallisation from benzene gave the amidic chloride as prisms (14 g., 65%), m.p. 113-116° (lit.,12 115-116°) (Found: C, 43.5; H, 5.1; Cl, 15.7; N, 6.2; P, 14.0. Calc. for  $C_8H_{11}CINO_2P$ : C, 43.8; H, 5.0; Cl, 16.1; N, 6.4; P,  $14\cdot1\%),\ \nu_{max}$  3140s (NH), 1240s (P=O), 1185m (P=O-CH\_3), 1080m, 1050–1040s, 990–950s, and 830s (1,4-disubstituted benzene).

Attempted Preparation of NN'-Dianilinophosphorodiamidic Chloride.---A solution of phenylhydrazine (21.6 g.) in ether (50 ml.) was added dropwise to a stirred solution of phosphorus oxychloride (7.6 g.) in ether (200 ml.) at  $-10^{\circ}$ . After 2 hr. at room temperature, the solid was washed with water, and recrystallised from methanol to give NN'N"-trianilinophosphoric triamide (8 g.), m.p. 179-181° (lit.,<sup>18</sup> 185–187°) (Found: C, 58.0; H, 5.7; N, 22.3; P, 8.6. Calc. for  $C_{18}H_{21}N_6OP$ : C, 58.7; H, 5.7; N, 22.8; P, 8.4%),  $\nu_{max.}$  3320s, 3280s (N–H), 1200s (P=O), 755s, and

17 M. Ikehara and E. Ohtsuha, Chem. and Pharm. Bull. (Japan),

1963, 11, 435. <sup>18</sup> L. F. Audrieth and A. D. F. Toy, J. Amer. Chem. Soc., 1942, **64**, 1553.

700s (monosubstituted benzene). The i.r. spectrum was identical to that of an authentic sample of the triamide.<sup>18</sup>

Reaction of Phenylhydrazine with Pyrophosphoryl Chloride. —Pyrophosphoryl chloride (1 g.) in anhydrous ether (10 ml.) was gradually added to a stirred solution of phenylhydrazine (5 ml., 12 moles) in ether (5 ml.). After 10 min., the white precipitate was washed with water, and recrystallised from dioxan to give NN'N''-trianilinophosphoric triamide (0.9 g.), m.p. 180—182°, identical (mixed m.p. and i.r.) with an authentic sample (Found: C, 58·55; H, 5·9; N, 23·1; P, 8·4. Calc. for C<sub>18</sub>H<sub>21</sub>N<sub>6</sub>OP: C, 58·7; H, 5·7; N, 22·8; P, 8·4%). A repeat of the reaction in toluene at  $-40^{\circ}$ , with addition of the amine to the pyrophosphoryl chloride gave an uncrystallisable solid, which rapidly decomposed to a red oil.

Reaction of Aniline with Pyrophosphoryl Chloride in the Presence of a Tertiary Base.—Pyridine (3.2 g., 4 moles)in ether (10 ml.) was added to a stirred solution of pyrophosphoryl chloride (2.5 g.) in ether (30 ml.) at 0°. Subsequently, aniline (3.7 g.) in ether (10 ml.) was added dropwise to the stirred solution and the temperature was kept at 0° for 1½ hr. The orange precipitate was boiled with water for 3 hr., and the white solid was recrystallised from ethanol to give tetraphenylpyrophosphoramide as needles (0.5 g.), m.p. 206—210° (lit.,<sup>19</sup> 222°) identified (mixed m.p. and i.r.) with an authentic specimen.

A repeat of the reaction with benzene and double the amount of aniline gave NN'N''-triphenylphosphoric triamide (1.8 g.), m.p. 209—210° (from ethanol) (lit.,<sup>18</sup> 211—214°) (Found: C, 66.8; H, 6.0; N, 12.8; P, 9.2. Calc. for C<sub>18</sub>H<sub>18</sub>N<sub>3</sub>OP: C, 66.9; H, 5.6; N, 13.0; P, 9.6%),  $\nu_{max}$ . 3380—3360m (NH), 1220s (P=O), 750s, and 700s (monosubstituted benzene), which was identical (i.r.) with an authentic specimen.

NN'N''N'''-Tetraphenylpyrophosphoramide.-This compound was obtained by a modification of the method of Zeile and Kruckenberg: <sup>19</sup> NN'-Diphenylphosphorodiamidic chloride (10 g.) and NN'-diphenylphosphorodiamidic acid (10 g.) were dissolved in pyridine (50 ml.). After 2 hr. at room temperature, the mixture was poured into icewater, giving a white solid. Recrystallisation from ethanol or cyclohexanone gave tetraphenylpyrophosphoramide as needles (14 g., 78%), m.p. 212-214° (lit.,19 222°) (Found: C, 60.0; H, 5.1; N, 11.7; P, 13.3. Calc. for C<sub>24</sub>H<sub>24</sub>N<sub>4</sub>O<sub>3</sub>P<sub>2</sub>: C, 60·2; H, 5·1; N, 11·7; P, 12·9%); <sup>31</sup>P n.m.r. spectrum (tetrahydrofuran) showed a chemical shift of +9.5 p.p.m. relative to 85% phosphoric acid (cf. chemical shift of  $+8 \pm 1$  p.p.m. for an aqueous solution of ammonium pyrophosphate),  $^{20} \nu_{max}$  3180s (NH), 1610s, 1510s, 1430m, 1290s, 1250s, 1220s, 1040m, 1010m, 990s, 980—960m (P-O-P), 950m, 920s, 755s, and 695s (monosubstituted benzene).

Reaction of NN'-Diphenylphosphorodiamidic Chloride with Silver Oxide.—NN'-Diphenylphosphorodiamidic chloride (10 g.) and silver oxide (10 g.) were boiled under reflux in benzene (100 ml.) for 1 hr. The filtrate was evaporated under reduced pressure to give a brown solid. Recrystallisation from acetonitrile gave tetraphenylpyrosphoramide (5 g.), m.p. 204—206° (mixed m.p. with an authentic sample 208—211°) (cf. ref. 2).

NN'-Diphenylphosphorodiamidic Acid.—NN'-Diphenylphosphorodiamidic chloride (5 g.) was dissolved in 5N-<sup>19</sup> K. Zeile and W. Kruckenberg, Ber., 1942, **75**, 1127.

<sup>20</sup> J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution N.M.R. Spectroscopy,' Pergamon Press, 1966, p. 1146. sodium hydroxide solution (100 ml.) with cooling. Neutralisation with hydrochloric acid gave NN'-diphenylphosphorodiamidic acid (4.5 g.) as plates, m.p. 199—205° (from dioxan) (lit., 199—200,<sup>21</sup> 213,<sup>22</sup> 214—216 <sup>23</sup>) (Found: C, 57.9; H, 5.3; N, 11.0; P, 12.5. Calc. for  $C_{12}H_{13}N_2O_2P$ : C, 58.1; H, 5.3; N, 11.3; P, 12.5%),  $v_{max}$ . 3300s, 2720—2640m, 2300m, 1510s, 1410m, 1305, 1290m, 1235m, 1190m, 1170m, 1105s, 1040s, 1020s, 1010m, 1000s, 960m, 750s, and 700s;  $\tau$  (CDCl<sub>3</sub>) 2.8—3.4 (10ArH). Treatment with cyclohexylamine in warm acetone gave the *cyclohexylammonium salt*, m.p. 175—178° (Found: C, 62.0; H, 7.6; N, 12.6; P, 8.9%; Equiv. wt. 345.  $C_{18}H_{26}N_3O_2P$  requires C, 62.2; H, 7.5; N, 12.1; P, 8.9%; Equiv. wt. 345).  $v_{max}$ . 3400s, 3260m (NH), 1295s (P=O), 750s, and 690s (monosubstituted benzene).

NN'-Di-o-Tolylphosphorodiamidic Acid.— o-Toluidine (42.8 g.) was treated with phosphorus oxychloride (15.3 g.)in ether as previously described. After 3 days at room temperature, o-toluidine hydrochloride (28 g.) was filtered off, and evaporation of the filtrate gave a brown oily solid (30 g.). Partial dissolution in 5N-sodium hydroxide, filtration, and neutralisation (dilute hydrochloric acid) gave di-o-tolylphosphorodiamidic acid (12 g.), m.p. 97-99° (lit.,<sup>1d</sup> 120°) (Found: C, 60.7; H, 6.1; N, 10.3; P, 11.1%; Equiv. wt. 285. Calc. for C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>P: C, 60.9; H, 6.2; N, 10.1; P, 11.2%; Equiv. wt. 276). Similar alkaline hydrolysis of the corresponding diamidic chlorides gave the following NN'-disubstituted phosphorodiamidic acids: di-p-tolyl-, m.p. 172-174° (dioxan) (lit., 1d 193-(Found: C, 60.6; H, 6.3; N, 9.9; P, 11.0%; 194°). Equiv. wt. 287); dicyclohexyl-, m.p. 143° (Found: C, 55.6; H, 9.7; N, 10.8; P, 12.1.  $C_{12}H_{25}N_2O_2P$  requires C, 55.4; H, 9.7; N, 10.8; P, 11.9%),  $\nu_{max}$  3390s, 3280s (NH), 2750—2640w (multiple bands) (P–O–H) 1255— 1240s (P=O); Benzyl phenyl-, cream powder (53%), m.p. 120° (Found: C, 59.2; H, 5.7; N, 10.8; P, 12.0.  $C_{13}H_{15}N_2O_2P$  requires C, 59.5; H, 5.8; N, 10.7; P, 11.8%), v<sub>max.</sub> 3340m, 3200m (NH), 3020-2320m (multiple bands) (P-O-H), 1260-1240s (P=O), 750s, 700s, and 690s (two monosubstituted benzene groups). Dibenzyl-, needles (acetone), m.p. 114-116° (Found: C, 60.5; H, 6.2; N, 10.1; P, 11.4. C<sub>14</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>P requires C, 60.9; H, 6.2; N, 10.1; P, 11·2%).

Attempted Preparation of Methyl N-Phenylphosphoramidic Acid.—Methyl-N-phenylphosphoramidic chloride (3.5 g.), dissolved in water (50 ml.) containing sodium hydroxide (4 g.), was passed through an Amberlite IR 120 ion-exchange column. Evaporation of the eluant under reduced pressure gave an oily solid, which, by trituration with acetonitrile, afforded a compound, (2.4 g.), m.p. >300°. The i.r. spectrum resembled that of aniline hydrochloride suggesting P-N bond fission.

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<sup>23</sup> W. Autenrieth and P. Randolph, Ber., 1900, 33, 2099.