The picrate melted with decomposition at 245°. The reported m.p. for the picrate of 1,4-bis(β-hydroxyethyl)-piperazine is 245–246°. The dihydrochloride also was prepared, m.p. 204°, the reported value is 200–202°.

Preparation of Diethylene Glycol Acetates.—The diacetate of diethylene glycol and the acetate of the monoethyl ether of diethylene glycol were prepared conventionally by the action of 500 ml. of pure acetic anhydride and 10 ml. of dry pyridine on 0.75 mole of the corresponding glycol. Infrared spectra of the products showed no hydroxyl groups present. The diacetate of diethylene glycol was obtained in 50% yield, boiling at 110° at 7-mm. pressure, n^{20}_{D} 1.4300. The reported value is b.p. 148° at 26-mm. pressure.[11] The acetate of the monoethyl ether of diethylene glycol was obtained in a 40% yield, boiling at 85° at 7-mm. pressure, n^{20}_{D} 1.4210. These also were subjected to the general reaction procedure with the results listed in Tables I and II.

Attempted Reaction of Phosphorus Pentafluoride with Morpholine.—The general reaction procedure was followed as already described. Little or no reaction took place. The recovery of morpholine from the reaction mixture was 86%.

Attempts to Demonstrate a Reversible Reaction.—A charge of 44 g. (0.5 mole) of pure dioxane, 37 g. (0.5 mole) of dry ethyl ether, and 14.5 g. (0.05 mole) of p-chlorophenyldiazonium hexafluorophosphate was placed into a 250-ml. autoclave. The temperature was maintained at 100–110°. The pressure was at 170 p.s.i. for 24 hr. The autoclave was cooled in ice and opened. The mixture was fractionally distilled on an 18-in. Widmer column and 25 g. of ethyl ether and 40.2 g. of dioxane (91.4%) were recovered. The reaction was repeated at 200° with a pressure of 340 p.s.i. for 48 hr. Again, 90% of the dioxane was recovered.

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[10] F. L. Pyman, *J. Chem. Soc.*, **93**, 1802 (1908).

[11] L. H. Cretcher and W. J. Pittenger, *J. Am. Chem. Soc.*, **47**, 163 (1925).

A New Route to N-Arylphosphoramidic Acids[1a]

FRANCIS L. SCOTT,[1b] RAYMOND RIORDAN, AND PAUL D. MORTON

Research and Development Department, Pennsalt Chemicals Corporation, Philadelphia 18, Pennsylvania

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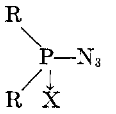
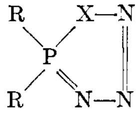
Some representative phosphoryl azides which we have synthesized possess infrared absorptions consistent with acyclic structures. The aminolysis of one such azide, and some related compounds, has been explored. In refluxing aniline, diethyl phosphoryl azide[1c] (IVa) underwent not only P—N bond cleavage but also alkyl–oxygen scission, the product being N-phenylphosphoramidic acid (Va). Compound Va was also formed when either diethyl phosphorochloridate (IVb), or O,O-diethyl N-phenylphosphoramidate (IVc), was used as the aminolysis substrate. These reactions constitute a new route to N-arylphosphoramidic acids. The mechanism of the process is discussed.

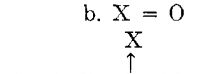
We have established elsewhere[2a] that the so-called thiocarbamyl azides are really thiatriazoles and that a similar cyclization is not apparent with the oxy analogs, the carbamyl azides. It was of interest to extend these observations to phosphorus systems and to determine whether substituted phosphoryl azides are open-chain compounds (Ia, Ib) or heterocyclic (IIa, IIb). As in our previous work[2a] our structural assignments were based on infrared data. The first of the azides we prepared, namely IIIa, showed a strong azide stretching absorption at *ca.* 2140 cm.$^{-1}$, corresponding[2b,3] to the acyclic formulation.



Ia. X = S
b. X = O



IIa. X = S
b. X = O

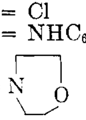


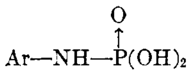
$[(C_2H_5)_2N]_2-\overset{\overset{X}{\uparrow}}{P}-N_3$

IIIa. X = O
b. X = S

$(C_2H_5O)_2\overset{\overset{O}{\uparrow}}{P}-X$

IVa. X = N_3
b. X = Cl
c. X = NHC_6H_5
d. X =





$Ar-NH-\overset{\overset{O}{\uparrow}}{P}(OH)_2$

Va. Ar = C_6H_5
b. Ar = p-ClC_6H_4

Preparation of a pure sample of a representative thioazide proved difficult—the azide co-distilled with the substituted phosphoryl chloride from which it was prepared—but the chloride–azide mixture showed characteristic azide infrared absorption. The third representative member (IVa) was prepared in high purity, and its infrared data confirmed the open-chain structure.

Reaction of amines with thiatriazoles can result in displacement of an azide moiety and in that respect both the thiatriazoles and carbamyl azides resemble one another.[4] We have investigated whether phosphoryl azides are liable to aminolysis. Thus IVa was refluxed in an excess of aniline for forty hours. After that time clear indication of azide loss was obtained, but no P—O bond rupture (as would be evidenced by the

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[1] (a) Presented in part at the Third Delaware Valley Regional American Chemical Society Meeting, Philadelphia, February, 1960, Abstracts, p. 66; (b) to whom inquiries concerning reprints should be sent. Present address: Chemistry Department, University College, Cork, Ireland; (c) We have used the nomenclature for phosphorus compounds, suggested by the Organic Division of the American Chemical Society and described in *Chem. Eng. News*, **30**, 4516 (1952).

[2] (a) See for example F. L. Scott, *Experientia*, **13**, 275 (1957); see also P. A. S. Smith and D. H. Kenny, *J. Org. Chem.*, **26**, 5221 (1961), for other references. (b) After this work had been presented[1a] and was being written for publication, both diarylphosphonyl azides, see R. K. Baldwin and R. M. Washburn, *J. Am. Chem. Soc.*, **83**, 4466 (1961), and imidophosphoryl azides, see H. Boch and W. Wiegräbe, *Angew. Chem.*, **74**, 327 (1962), were found to be acyclic.

[3] L. J. Bellamy, "Infrared Spectra of Complex Molecules," Methuen & Co., Ltd., London, 1954, chap. 15.

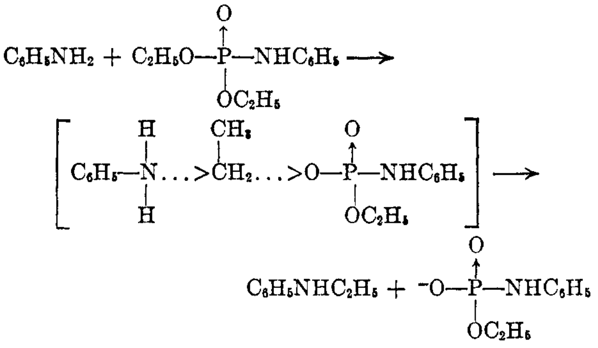
[4] Compare, *e.g.*, F. L. Scott, *Chem. Ind.* (London), 1350 (1956); F. L. Scott, F. C. Britten, and J. Reilly, *J. Org. Chem.*, **21**, 1519 (1956); F. L. Scott and M. T. Scott, *J. Am. Chem. Soc.*, **79**, 6077 (1957).

formation of the corresponding substituted phosphoric triamide or diamide) was detected. Instead alkyl–oxygen bond cleavage was observed, and N-phenylphosphoramidic acid (Va) was isolated in *ca.* 70% yield. This reaction constitutes a new route to Va.[5] Using IVa as a starting material (to synthesize Va) was inconvenient because of the extremely high toxicity of the former substance. However, we subsequently found that Va was formed when either diethyl phosphorochloridate (IVb) or O,O-diethyl N-phenylphosphoramidate (IVc) was refluxed in aniline. This synthesis of Va from IVc has been found to be more sensitive to the reaction temperature used than to the solvent employed. When IVc and an excess of aniline were heated either in benzene solution, or in an excess of aniline alone, at 75° for seventy-two hours, no Va was formed, whereas when they were heated in toluene (at 110° for 170 hours), or xylene (at 138° for 24 hours), Va was formed in 32% yield.

The cleavage of the amide (IVc) to Va suggests that with both the azide (IVa) and the chloride (IVb) the first product formed in a solution of these materials in aniline is IVc and this then aminolyses to Va. Amine-induced alkyl–oxygen scission in substituted phosphoramidates has been described previously.[6] In this previous work the amide moiety of the phosphoramidate itself acts as a nucleophile towards an O-ester function of a neighboring phosphoramidate molecule and inevitably, the amide moiety is alkylated.

Our work shows that a completely external nucleophile can serve as an alkylation acceptor and enable phosphoramidate O-alkyl cleavage[7] to be effected without sacrificial alkylation of the phosphoramidate amide moiety. By this means the original nitrogen–phosphorus bond structure of the amidate is preserved. We envisage an S_N2 type displacement by the external nucleophile, in the phosphoramidate dealkylation, *cf.* 6 thus:

Step 1:



$$C_6H_5NH_2 + C_2H_5O-\underset{OC_2H_5}{\underset{|}{\overset{O}{\overset{\uparrow}{P}}}}-NHC_6H_5 \longrightarrow$$

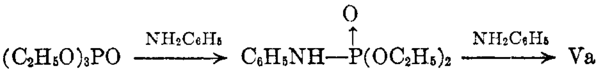
$$\left[C_6H_5-\underset{H}{\underset{|}{\overset{H}{\overset{|}{N}}}}\ldots>\overset{CH_3}{\overset{|}{C}}H_2\ldots>O-\underset{OC_2H_5}{\underset{|}{\overset{O}{\overset{\uparrow}{P}}}}-NHC_6H_5\right] \longrightarrow$$

$$C_6H_5NHC_2H_5 + {}^{-}O-\underset{OC_2H_5}{\underset{|}{\overset{O}{\overset{\uparrow}{P}}}}-NHC_6H_5$$

Step 2 then involves a similar alkyl–oxygen scission and leads to Va.

That the actual mechanism may be more complex than that just suggested was revealed when a sample of the amide IVc was heated in an excess of *p*-chloroaniline (for two hours at 180–185°). On work-up, N-(*p*-chlorophenyl)phosphoramidic acid (Vb) was isolated in 90% yield. Thus under our conditions of phosphoramidic acid synthesis, the amine environment can not only effect alkyl-oxygen scissions but also evidently phosphoramide exchange.

No formation of N,N′, N″-triphenyl phosphoric triamide was detected, as already mentioned, in any of the reactions of IVa, IVb, or IVc with aniline; hence no P—O bond scission occurred. If P—O bond cleavage was even comparable in reactivity to the alkyl–oxygen scission then the reaction of triethyl phosphate and aniline might also yield Va, *via* the following sequence:



$$(C_2H_5O)_3PO \xrightarrow{NH_2C_6H_5} C_6H_5NH-\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2 \xrightarrow{NH_2C_6H_5} Va$$

The reaction of triethyl phosphate and aniline has already been performed by Billman and coworkers,[8] but they were concerned with the alkylation of the amine and did not pursue the fate of the phosphorus-containing material beyond stating that salts of orthophosphoric acid were formed. We have confirmed Billman's observations that the major phosphorus-containing product from the reaction of aniline and triethyl phosphate is dianilinium orthophosphate. There also appeared to be formed some monoanilinium orthophosphate, but no trace of the phosphoramidic acid (Va) was detected.[9]

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[5] Previous routes to Va recorded in the literature include (a) the pyrolysis of $C_6H_5NH\overset{O}{\overset{\uparrow}{P}}(OC_4H_9)_2$, see H. Goldwhite and B. C. Saunders, *Chem. Ind.* (London), 663 (1956); H. Goldwhite and B. C. Saunders, *J. Chem. Soc.*, 2409 (1957); and (b) the hydrogenolysis of $C_6H_5NH\overset{O}{\overset{\uparrow}{P}}(OCH_2C_6H_5)_2$, see H. G. Cook, *et al.*, *ibid.*, 2921 (1949); V. M. Clark and A. R. Todd, *ibid.*, 2023 (1950); and F. R. Atherton, H. J. Openshaw, and A. R. Todd, *ibid.*, 382 (1945).

[6] The previous methods involve pyrolysis of the phosphoramidates, see W. Gerrard and G. J. Jeacocke, *Chem. Ind.* (London), 1538 (1954); J. I. G. Cadogan, *J. Chem. Soc.*, 1079 (1957); and especially H. E. Baumgarten and R. A. Setterquist, *J. Am. Chem. Soc.*, **81**, 2132 (1959); and H. E. Baumgarten and R. E. Allen, *J. Org. Chem.*, **26**, 1533 (1961).

[7] When the nucleophile is a stronger base than aniline, monodealkylation of the phosphoramidates occurs, see J. Cheymol, P. Chabrier, M. Selim, and T. N. Thanh, *Compt. rend.*, **249**, 1240 (1959); T. N. Tanh and M. Selim, *ibid.*, **250**, 2724 (1960); and J. Cheymol, P. Chabrier, M. Selim, and T. N. Tanh, *ibid.*, **251**, 550 (1960). Some related experiments of ours on the aminolysis of IVd, or IVc in an excess of morpholine, described in the Experimental, were inconclusive as to the extent of mono- *vs.* dialkyl cleavage.

[8] See J. H. Billman, A. Radike, and B. W. Mundy, *J. Am. Chem. Soc.*, **64**, 2977 (1942); D. G. Thomas, J. H. Billman, and C. E. Davis, *ibid.*, **68**, 895 (1946); and compare also W. H. C. Rueggeberg and J. Chernack, *ibid.*, **70**, 1802 (1948).

[9] The predominance of alkyl–oxygen cleavage with compounds of type IV with a nucleophile such as aniline is in line with the very interesting data of R. F. Hudson and L. Keay, *J. Chem. Soc.*, 2463 (1956); R. F. Hudson and D. C. Harper, *ibid.*, 1356 (1958). Their data would suggest that any nucleophile with sufficiently *high nucleophilicity towards carbon* would succeed in cleaving IVc, and similar substances, to yield Va or its salts.

Experimental[10]

Synthesis of O,O-Diethyl Phosphoryl Azide.—Into a 3-l., three-necked flask equipped with a stirrer, dropping funnel and reflux condenser were added 500 ml. of dry acetone and 56.6 g. (0.87 mole) of sodium azide. To the vigorously stirred, refluxing suspension was slowly added over a period of 20 min., 50 g. (0.29 mole) of freshly distilled diethyl phosphorochloridate. (This latter compound as used had a b.p. of 99° at 15 mm. and had n^{25}_D 1.4157. *Anal.* Calcd. for $C_4H_{10}ClO_3P$: Cl, 20.58. Found: Cl, 20.88.)

The acetone suspension was maintained at reflux while being vigorously stirred for 20 hr. It was then cooled and the salt filtered off using a filter aid. The salt was washed with acetone, the washings were added to the original mother liquor, and the whole was distilled. After the solvent had been stripped, the yellow residual fluid was vacuum fractionated. The center cut, b.p. 101–103°/10–11 mm., n^{25}_D 1.4251, weighed 39.5 g. and corresponded to a conversion of 76%. Its infrared spectrum showed a strong absorption at 2140 cm.$^{-1}$ characteristic of the azide group's stretching absorption.[3] It was diethyl phosphoryl azide (IVa) (*CAUTION*).[11]

Anal. Calcd. for $C_4H_{10}N_3O_3P$: C, 26.92; H, 5.59; N, 23.46; P, 17.29. Found: C, 27.04; H, 5.61; N, 23.59; P, 17.31.

It was insoluble in water but completely miscible with ether, ethanol, and acetone.

Related Azide Syntheses.—Tetraethylphosphorodiamidic azide (IIIa) was also synthesized. This involved, first, the synthesis of tetraethylphosphorodiamidic chloride by the reaction of phosphorus oxychloride and diethylamine in chloroform. The substituted phosphorodiamidic chloride had a b.p. of 101–104° (1–5 mm.).

Anal. Calcd. for $C_8H_{20}ClN_2OP$: Cl, 15.67; N, 12.36; P, 13.69. Found: Cl, 15.55; N, 12.20; P, 14.75.

This material was found to deposit a white crystalline solid (probably diethylamine hydrochloride) on standing and so had always to be freshly prepared before use. The chloride was treated with sodium azide in refluxing acetone as was described in the synthesis of IVa above. After workup the product IIIa boiled at 104°/0.8 mm., and was obtained in 97% yield. It had a refractive index of n^{20}_D 1.4678. Its infrared spectrum showed the characteristic azide absorption at 2140 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{20}N_5OP$: N, 30.1; P, 13.3. Found: N, 30.9; P, 13.4 (Cl, 2.08).

The detection of the small quantity of chloride in the microanalysis showed the presence of a little unchanged starting chloride in the product.

Similarly the synthesis of the analogous thio compound (IIIb) was attempted. First thiophosphoryl chloride and diethylamine reacted in chloroform solution. Vacuum fractionation of the product mixture showed two substances, one, b.p. 65–67°/0.7 mm.

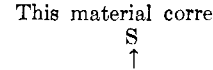
Anal. Calcd. for $C_4H_{10}Cl_2NPS$: Cl, 34.6; N, 6.8. Found: Cl, 33.5; N, 7.0. This is obviously the dichloride,

$[(C_2H_5)_2N]\underset{\underset{S}{\downarrow}}{-P-}Cl_2$.

The second fraction, b.p. 106° (0.9 mm.) had the following analysis.

Anal. Calcd. for $C_8H_{20}ClN_2PS$: Cl, 14.5; N, 11.5. Found: Cl, 15.0; N, 11.2.

This material corresponds to the desired monochloride,



$[(C_2H_5)_2N]_2\overset{\overset{S}{\uparrow}}{-P-}Cl$.

The monochloride was then treated with sodium azide in the usual manner; the major product was a yellow fluid, b.p. 95–98° (0.9–1.0 mm.), n^{20}_D 1.5057. This liquid, while it was still heavily contaminated with starting chloride, had a strong azide absorption at 2140 cm.$^{-1}$.

Because of the probably extreme toxicity of these materials no further effects were made to isolate IIIb.

Reaction of O,O-Diethylphosphoryl Azide and Aniline.—A sample of diethyl phosphoryl azide (IVa) (*ca.* 45 g.) was added to 150 g. of freshly distilled aniline and the mixture was refluxed overnight. Adequate scrubbing of the reaction vapors and general ventilation precautions were taken due to the toxicity of the azide. The solution was heated at 185° for 17.5 hr., an aliquot was taken and infrared analysis indicated approximately 10% azide concentration. (This method did not differentiate between the presence of IVa or of hydrazoic acid.) The mixture was then reheated, and after a further 6.5 hr., another aliquot was taken and its infrared spectrum revealed the presence of a 3% azide concentration. The solution was then refluxed for another 17 hr. after which a trace amount of azide remained. The mixture was cooled and filtered. The reaction mass was triturated five times with aliquots of anhydrous ether and the white residual solid was dried to constant weight (29.3 g.), m.p. 280–288°. A sample was leached twice with absolute ethanol at room temperature and once with boiling ethanol. Its color whitened, but its melting point remained virtually unchanged, 280–286° (yield *ca.* 70%).

Anal. Calcd. for $C_6H_8NO_3P$: C, 41.62; H, 4.62; N, 8.09; P, 17.91. Found: C, 41.42; H, 4.62; N, 8.53; P, 18.06.

It corresponded to N-phenylphosphoramidic acid (Va).[12]

It was insoluble in either hot or cold ethanol, ether, acetone, water, or dimethylformamide (DMF). It did dissolve in both 0.5 *N* sodium hydroxide and hydrochloric acid (hot) solutions.

Reaction of Aniline and O,O-Diethylphosphorochloridate.—Freshly distilled aniline, 99.3 g. (1.07 moles) and 23.2 g. (0.133 mole) of freshly distilled diethyl phosphorochloridate (IVb) were mixed. There was an immediate and vigorously exothermic reaction. The mixture was refluxed for 40 min. with stirring, the mass then being cooled and filtered. The dry, white solid (23.8 g.) thus obtained was leached successively with water and absolute ethanol and the product remaining undissolved weighed 15.2 g. and had a m.p. 276–277°. The yield was 66%; the material corresponded to N-phenylphosphoramidic acid.

Anal. Calcd. for $C_6H_8NO_3P$: C, 41.62; H, 4.62; N, 8.09; P, 17.91. Found: C, 41.44; H, 4.39; N, 8.12; P, 17.56.

From the aniline mother liquor was obtained a further 12.8 g. of solid on the addition of ether. This solid was leached with cold ethanol. The insoluble material (2.49 g.), had a m.p. of 256–260°.

Anal. Found: C, 38.70; H, 4.36; N, 8.12; P, 18.40.

Its structure is still unknown. Its infrared spectrum shows P=O absorption, and the presence of a phenyl ring and NH_3^+.

From the combined ethanol leachings was also isolated 8.07 g. (48%) of aniline hydrochloride.

Reaction of O,O-Diethyl N-Phenylphosphoramidate and Aniline.—O,O-Diethyl N-phenylphosphoramidate (IVc) was first prepared as follows. To 11.2 g. of aniline (0.120 mole) cooled in ice was added 10.4 g. (0.060 mole) of diethyl phosphorochloridate with stirring. After half of the latter had been added the mixture solidified. However, the remaining chloride was added, and the mass was manually stirred. The mass was extracted with two 200-ml. portions of benzene and the benzene was stripped under vacuum. An oil remained which gradually solidified. This substance was washed with 20 ml. of ether. It weighed 4.27 g. (31%

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[10] All melting points and boiling points are uncorrected.

[11] This substance proved to be a virulent and highly dangerous anticholinesterase.

[12] Goldwhite and Saunders, *loc. cit.*, report the melting point of Va as 267–271° (dec.). We found the melting points of all of our samples of this compound varied markedly with the rate of heating. Samples of Va prepared by any of our methods did not depress the melting points of a sample of Va (kindly provided by Professor Saunders) prepared by Goldwhite and Saunders' technique, and the infrared spectra of our samples and that of Saunders were identical.

yield), m.p. 97°. After recrystallization from either benzene or ether it had a m.p. 95–96°, reported[13] m.p. 94–95°.

Anal. Calcd. for $C_{10}H_{16}NO_3P$: C, 52.40; H, 7.05; N, 6.12; P, 13.50. Found: C, 52.30; H, 6.47; N, 5.92; P, 13.54.

To 1.56 g. (6.5 mmoles) of IVc was added 14.97 g. (0.161 mole) of aniline. The clear solution was refluxed for 11 min. by which time a white precipitate had formed. The mixture was cooled and filtered. The residue was leached with ether and washed with benzene. This treatment left 830 mg. (71% yield) of material, m.p. 274–276°. This did not depress the melting point of a sample of Va.

Anal. Calcd. for $C_6H_8NO_3P$: C, 41.62; H, 4.62; N, 8.09; P, 17.91. Found: C, 41.51; H, 4.77; N, 8.93; P, 17.42.

Some further experiments were run on this cleavage. Thus 3.0 g. of IVc was dissolved in 40 ml. of aniline in a sealed ampoule, and maintained at 75.0 (+0.1)° for 72 hr. There was no indication of any precipitation of Va and after work-up (*i.e.*, mixing the liquor with a large volume of ether followed by repeated extraction of the ethereal liquor with hydrochloric acid), 55% of IVc was recovered unchanged. Again 5.0 g. (21.9 mmoles of IVc and 12.2 g. (0.131 mole) of aniline were dissolved in 100 ml. of benzene and refluxed for 72 hr. On work-up analogous to the reaction just described, 52% of IVc was again recovered without the detection of any Va. When this last experiment was performed in refluxing toluene (at 110°), 31.8% of Va separated out after 170 hr. When similar quantities of reactants (5.0 g. of IVc and 12.2 g. of aniline) were refluxed in solution in 100 ml. of xylene (at 138°) for 24 hr., 1.17 g. (31%) of Va deposited. When 5.0 g. of IVc was refluxed in 100 ml. of xylene for 520 hr., in the absence of aniline, no Va could be detected. From these aminolysis data, the half-life of the aniline-induced scission of IVc is (very roughly) 12.5 days at 110°, and 21 hr. at 138°.

Reaction of Aniline and Triethyl Phosphate.—To 65.2 g. (0.7 mole) of aniline was added 18.2 g. (0.1 mole) of redistilled triethyl phosphate. The mixture was refluxed for 2 hr. After such refluxing the material appeared to be in two phases. Upon cooling the lower bronze-colored phase solidified. This was filtered off and washed with eight 25-ml. portions of ether. It was ground up and releached with three 100-ml. portions of ether. The residual material, m.p. 164–172°, weighed 21.3 g. It was recrystallized from hot water and then possessed a m.p. of 177–178°. It corresponded to dianilinium orthophosphate (A), reported[14] m.p. 180°.

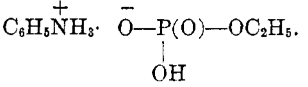
Anal. Calcd. for $C_{12}H_{17}N_2O_4P$: C, 50.75; H, 6.04; N, 9.86; P, 10.84. Found: C, 50.33; H, 5.72; N, 9.74; P, 10.63.

It did not depress the melting point of an authentic sample prepared by the reaction of 86% orthophosphoric acid in ethanolic solution with aniline in the same solvent.

When acetone was added to the mother liquid after (A) had crystallized, a small quantity of material, m.p. 192–195°, separated. This may be monoanilinium orthophosphate.

Anal. Calcd. for $C_6H_{10}NO_4P$: C, 37.71; H, 5.27; N, 7.33; P, 16.21. Found: C, 39.70; H, 5.16; N, 7.62; P, 17.81.

Inasmuch as the experiment had shown that neither Va, nor N,N′,N″-triphenyl phosphoric triamide, was formed—the main fact of relevance to the present discussion—no further effort was made to establish the identity of the higher melting point salt. We did establish that a sample of the crude reaction product, on treatment with base, followed by ether extraction and treatment of the ethereal solution with ethereal picric acid, afforded a picrate, m.p. 183–185°, which did not depress the melting point of an authentic sample of aniline picrate, m.p. 185° (reported[15] m.p. 182° dec.). We also prepared the monoanilinium salt of the monoethyl ester of orthophosphoric acid, *i.e.*



$C_6H_5\overset{+}{N}H_3\cdot\ \overset{-}{O}—\underset{\displaystyle OH}{\underset{|}{P}}(O)—OC_2H_5$. This had a m.p. of 145–146°.

Anal. Calcd. for $C_8H_{14}NO_4P$: N, 6.39; P, 14.13. Found: N, 7.1; P, 14.70.

Some Miscellaneous Aminolyses.—(a) When compound IVc was refluxed in an excess of morpholine for 4 hr. and the solvent was then removed, an oil was obtained which resisted all efforts towards purification. Its infrared spectrum suggested it could be the morpholine salt of N-morpholinophosphoramidic acid (VI).

(b) The phosphoramidate (IVd) was synthesized by treating morpholine and IVb in ethereal solution under reflux. Substance IVd was obtained as a liquid, b.p. 137° (11 mm.), in 56% yield.

Anal. Calcd. for $C_8H_{18}NO_4P$: C, 43.00; H, 8.14; N, 6.28; P, 13.86. Found: C, 42.80; H, 7.86; N, 6.10; P, 13.50.

When this material was refluxed in an excess of morpholine an oil was obtained whose infrared spectrum again suggested it was a salt of compound VI.

(c) Because of this suggestion of nitrogen–phosphorus bond cleavage, the following experiment was run. A mixture of 5.0 g. of IVc and 66.0 g. of redistilled *p*-chloroaniline was heated with vigorous stirring. When the temperature of the fluid reached 166° its color darkened, at 177° it became black and by 183° the solution appeared a dark blue-black. The mixture was maintained at 185° for 2 hr. and filtered hot. A gray-blue solid (8.25 g.) was obtained. This was leached with ether to remove uncharged *p*-chloroaniline and 4.08 g. (90.3% yield) of insoluble blue-gray material, m.p. 282–292°, remained. This was leached repeatedly with ethanol, in which it was insoluble, and after such treatment it was obtained as a fine white powder, m.p. 288–294° dec. It corresponds to N-(*p*-chlorophenyl)phosphoramidic acid (Vb), reported[5a] d.p. 268–270°.

Anal. Calcd. for $C_6H_7ClNO_3P$: C, 34.69; H, 3.37; N, 6.75; P, 14.94. Found: C, 35.05; H, 3.81; N, 7.06; P, 15.66.

We ascribe the difference of 20° in our observed melting point and that reported to variation in rates of heating. Our melting points were all taken at fast heating rates (≃ 3°/min.), and the greater the heating rate, the higher the melting point in this instance.

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