XXX.—*Some Interactions of Nitrogen Chlorophosphide.*

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CHLOROPHOSPHIDE of nitrogen was carefully and at length examined by Gladstone at the request of its discoverer, Liebig; and, about the same time, Gerhardt examined the interaction in which it is formed. Since that date, the only work which has been done with it, excepting Wichelhaus' confirmatory determination of its high vapour-density, is that of Hofmann, who studied the interaction of aniline and chlorophosphide of nitrogen. My object in resuming the investigation of chlorophosphide of nitrogen was, if possible, to elucidate its formation and to examine in more detail its reaction with amines. As my work proceeded, other issues suggested themselves. I endeavoured to displace the chlorine-atoms by cyanogen-groups; and as the efforts which had been made to remove, by the action of sodium and potassium. the chlorine, and to isolate the radicle of phosphorus and nitrogen, had not given very definite results, I tried the action of zinc ethide, expecting by this means to displace the chlorine by ethyl, and thus to form compounds of which the reduction products would have been interesting. But to work with this substance one has to meet the difficulty of its preparation, and as Gladstone found the yield is but small.

My method of preparation was a slight modification of that given by Gladstone (*Jour. Chem. Soc.*, **3**, 135). Instead of attaching receivers directly to the flask in which the ammonium chloride and the phosphorus pentachloride are heated by a Bunsen burner, a straight condenser was first fixed to the flask in order to return to the sphere of action any unaltered vaporised pentachloride, and to condense the chlorophosphide of nitrogen, which would otherwise have been carried over by the evolved hydrogen chloride, and would, in part, have been lost. The chlorophosphide of nitrogen was purified by driving over with steam. The objection to this method of purification is that the steam decomposes some of the product; but in its favour is the fact that it is less trouble than to extract with anhydrous ether. The yield was somewhat variable; but in no case was it large. The maximum yields I obtained amounted to 10 grams of chlorophosphide of nitrogen from 100 grams of phosphorus pentachloride and 200 grams of ammonium chloride; whereas the theoretical yield calculated from the equation—

$$3PCl_5 + 3NH_3 = P_3N_3Cl_6 + 9HCl,$$

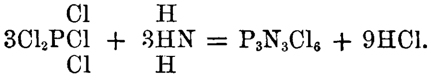
would be 41 grams. Gladstone states that his yield was uniformly about 6 per cent. of the pentachloride used.

The smallness of the yield is most probably explained by the following experiments. I found that when dry ammonia gas is passed through a dry tube over melted chlorophosphide of nitrogen, a reaction takes place, which results in the transformation of the greater part of the latter substance into a greyish-white infusible powder, and in the volatilisation of the smaller portion on to the cooler part of the tube, where it remains unaltered; this same greyish-white infusible substance is also obtained when chlorophosphide of nitrogen and ammonium chloride are heated in a sealed tube at a temperature of 150° for an hour or more; at the end of which time mere traces only of chlorophosphide of nitrogen remain. The following equation represents the reaction:—

$$P_3N_3Cl_6 + 3NH_3 = \underset{\text{Phospham.}}{P_3N_3(NH)_3} + 6HCl.$$

The greyish-white infusible substance is readily characterised as phospham. This easy transformation of chlorophosphide of nitrogen into phospham renders the view distinct that the molecule of phospham is not PN(NH) but is $P_3N_3(NH)_3$, just as chlorophosphide of nitrogen is not $PNCl_2$ but is $P_3N_3Cl_6$.

The production in the first instance of chlorophosphide of nitrogen receives a simple explanation in terms of the following equation :—



$$3\mathrm{Cl_2}\overset{\mathrm{Cl}}{\underset{\mathrm{Cl}}{\mathrm{PCl}}} + 3\overset{\mathrm{H}}{\underset{\mathrm{H}}{\mathrm{HN}}} = \mathrm{P_3N_3Cl_6} + 9\mathrm{HCl}.$$

Gerhardt (*Ann. Chim. Phys.*, **18**, 205), who investigated the action of phosphorus pentachloride on ammonium chloride, concluded that the formation of phosphorus nitrogen chloride,* occurring as it does in small quantities, was accidental. But the above-mentioned action of ammonia would lead to another conclusion. And, indeed, not only does ammonia react with phosphorus nitrogen chloride, but also amines generally appear to remove the chlorine. Hofmann (*Ber.*, **17**, 1909) found that by dissolving phosphorus nitrogen chloride in aniline, and warming the solution on a water-bath, the whole solidified; and from the solid mass, by extracting the aniline hydrochloride and the unaltered aniline by hydrochloric acid and water, he obtained a white, solid substance, which, after crystallisation from glacial acetic acid, gave on analysis numbers corresponding to the constitution

$$P_3N_3(NH{\cdot}C_6H_5)_6.$$

I repeated this experiment, using somewhat larger quantities of substances. There was formed the white substance which Hofmann described, and together with it a viscid dark-coloured oil, which was separated by digestion with cold alcohol, after treating the solid mass with hydrochloric acid and water. This oily substance is extremely soluble in alcohol, ether, and benzene, and appears to be unaltered by boiling with a large quantity of water for 10 hours. All attempts to crystallise it were futile; and after standing for two months it shows no signs of crystallisation. This resinous matter was formed in every case from the action of phosphorus nitrogen chloride on the amines which I used.

Hofmann considered that if this compound, $P_3N_3(NH{\cdot}C_6H_5)_6$, were heated with hydrochloric acid, it might lose 3 mols. of aniline and be converted into the corresponding phospham-derivative, $P_3N_3(NC_6H_5)_3$. But I found that when heated in a sealed tube with strong hydrochloric acid, it remained unaltered at a temperature of 150°, and

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* This name seems preferable to "chlorophosphide of nitrogen."

when the temperature was raised to 250°, it was completely decomposed into phosphoric acid, ammonium chloride, and aniline. Thus—

$$P_3N_3(NH{\cdot}C_6H_5)_6 + 12H_2O + 9HCl = 3NH_4Cl + 6C_6H_5{\cdot}NH_2,HCl + 3H_3PO_4.$$

I next used, instead of aniline, orthotoluidine. On mixing together the phosphorus nitrogen chloride and the orthotoluidine the mixture gets warm; and on heating on the water-bath it finally solidifies. Instead of at first treating the solid mass with hydrochloric acid, I used ether to remove the excess of orthotoluidine, fearing lest the hydrochloric acid might be the cause of the production of the resinous substance. After filtering off the ethereal extract, a white solid remained, but its ready solubility in water proved it to be orthotoluidine hydrochloride. The ethereal extract gave a residue, after the removal of the free orthotoluidine, of a viscid oil, similar to that obtained when aniline was used. Thus at 100°, no product of the type $P_3N_3R_6$ was formed. But when the orthotoluidine and the phosphorus nitrogen chloride were heated at temperatures of 150° or 250°, such a substance was produced together with the resin; so that on extracting the solid mass with ether, and with hydrochloric acid and water, a white substance remained, which could be crystallised in slender needles from hot alcohol. Its melting point is 241—242°. The formula $P_3N_3(NH{\cdot}C_6H_4{\cdot}CH_3)_6$ requires 12·17 per cent. of nitrogen; I found 12·16.

When phenylhydrazine was used, there was, at a temperature of 100°, formed in addition to the viscid oil, a crystallisable substance which I extracted as in the previous instance. It was crystallised from alcohol. Its melting point was 200°. The constitution, $P_3N_3(NH{\cdot}NH{\cdot}C_6H_5)_6$, requires 11·97 per cent. of phosphorus and 27·03 per cent. of nitrogen; my analysis gave 12·15 per cent. of phosphorus and of nitrogen 27·27.

The reaction with piperidine and phosphorus nitrogen chloride is very rapid. So much heat is evolved that the piperidine begins to boil. The reaction is completed by warming on a water-bath. The products are here again a viscid oil, in much smaller quantity than in the other instances, and a crystallisable compound. The latter can with difficulty be crystallised from alcohol. On heating, it decomposed before melting.

The formula $P_3N_3(NC_5H_{10})_6$ would require—

		Found.
Phosphorus	14·08 per cent.	14·3
Nitrogen	19·89 ,,	19·8

Diphenylamine and diamylamine do not at ordinary temperatures react with phosphorus nitrogen chloride.

Attempts were made to prepare cyanogen-derivatives of phosphorus nitrogen chloride by dissolving it in alcohol and heating the solution with silver cyanide at a 100° for several hours. But the phosphorus nitrogen chloride was entirely decomposed, and prussic acid was set free. On evaporating the alcohol a thick oil with a strongly acid reaction was obtained. It readily gave off ammonia when warmed with baryta-water, and otherwise reacted as a mixture of acid ammonium salts. It showed Gladstone's test for azophosphoric acid; for on adding a drop of ferric chloride to the ammoniacal solution of the acid, the liquid became brown, and no trace of precipitate was formed. But on applying this test to a solution of ammonium phosphate, I obtained exactly the same result.

Previous efforts which had been made to remove the chlorine and to isolate the radicle had not yielded very definite results. I found that sodium or sodium amalgam acts very slowly on a benzene solution of phosphoric nitrogen chloride; so I mixed it with dry zinc-dust, exhausted the tube, and heated the mixture. Much gas was evolved smelling of cyanogen. The phosphorus nitrogen chloride was entirely decomposed, and the phosphorus remained behind in combination with the zinc. I next tried the action of zinc ethide on the phosphorus nitrogen chloride; but at ordinary temperatures the substances do not react.

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