Inorganic Syntheses, Volume VII
Edited by Jacob Kleinberg

collected as product. This fraction weighs 403 g., 96% of theory based on the dimethylamine used. Redistillation through an 18-in. Vigreux column yields the pure product (b.p. 45° at 1 mm.) in 88 to 95% yield. *Anal.* Calcd. for $(CH_3)_2NPOCl_2$: P, 19.1; N, 8.7; Cl, 43.7. Found: P, 19.1; N, 8.7; Cl, 43.5.

Properties

(Dimethylamido)phosphoryl dichloride is a water-white liquid with the following physical constants: b.p. 45° at 1 mm.; 88° at 18 mm.; 90 to 91° at 22 mm.; 194 to 195° at 760 mm.; sp. gr., 1.369 $\frac{15.5}{15.5}$; n_D^{25}, 1.4610. It is very reactive toward water, alcohol, and amines. On long standing, some precipitation of dimethylammonium chloride is noted.

References

1. T. Götz: German patent 855,248 (1952); cf. *C.A.*, **48**, 11481 (1954).
2. A. Michaelis: *Ann.*, **326**, 179 (1903).

21. BIS(DIMETHYLAMIDO)PHOSPHORYL CHLORIDE

(Tetramethylphosphorodiamidic Chloride)

$$(CH_3)_2NPOCl_2 + 2(CH_3)_2NH \rightarrow [(CH_3)_2N]_2POCl + (CH_3)_2NH\cdot HCl$$

Submitted by E. N. Walsh* and A. D. F. Toy*
Checked by M. L. Nielsen† and T. J. Morrow†

Bis(dimethylamido)phosphoryl chloride has been prepared by the reaction of phosphorus(V) oxychloride with

* Victor Chemical Works, Division of Stauffer Chemical Company, Chicago Heights, Ill.
† Monsanto Chemical Company, Dayton, Ohio.

the calculated quantity of dimethylamine,[1] by the reaction of hexamethylphosphoramide with phosphorus(V) oxychloride,[2] and by the action of dimethylamine on (dimethylamido)phosphoryl dichloride.[3] The procedure described here is a modification of the preparation using (dimethylamido)phosphoryl dichloride as the starting material.

Procedure

In a 3-l. three-necked flask equipped with a stirrer, thermometer, gas-inlet tube with a ½-in. bottom opening, and a reflux condenser equipped with a soda-lime drying tube at the top, are put 400 g. (2.47 mols) of (dimethylamido)phosphoryl dichloride (synthesis 20) and 1250 ml. of carbon tetrachloride. Dimethylamine, 222.3 g. (4.94 mols), is condensed in a 500-ml. distilling flask containing a boiling chip. This distillation flask is then attached to a safety bottle, which is connected to the gas-inlet tube of the reactor. With stirring, the dimethylamine is distilled into the reactor under the surface of the liquid. The temperature of the reaction is maintained below 45° by means of an ice-salt bath. Dimethylammonium chloride separates immediately. When the addition of dimethylamine is complete (in about 4 hours), the reaction mixture, a thick suspension of dimethylammonium chloride in the carbon tetrachloride solution of the desired product, is held at 45° for one more hour. It is then cooled and filtered through a sintered-glass funnel. The dimethylammonium chloride is washed free of product with a total of 500 ml. of carbon tetrachloride. The filter cake may be freed of solvent under reduced pressure and used as a reagent for the preparation of (dimethylamido)phosphoryl dichloride. The filtrate is placed in a distillation apparatus equipped for fractionation and distillation under reduced pressure. An 18-in. Vigreux column is inserted in the still, and ice-cooled water is circulated through the condenser. The major portion of the carbon tetrachloride is removed by distillation at atmospheric pres-

sure to a liquid temperature of 80°. The pressure is then reduced gradually to 40 mm. to remove the last trace of solvent. The pressure is reduced further to 1 mm., and after removal of a small forerun (10–20 g.) consisting primarily of (dimethylamido)phosphoryl dichloride, the fraction boiling at 64 to 67° at 1 to 2 mm. is collected as product. This weighs about 400 g. (95% yield). Redistillation through an 18-in. Vigreux column results in a yield of 377 g. (86%) of pure product. *Anal.* Calcd. for $[(CH_3)_2N]_2POCl$: P, 18.2; N, 16.4; Cl, 20.8. Found: P, 18.2; N, 16.2; Cl, 20.8.

Properties

Bis(dimethylamido)phosphoryl chloride is a water-white liquid having the following physical constants: b.p., 63° at 1 mm.; 97 to 98° at 4 mm.; 102° at 6 mm.; n_D^{25}, 1.4642; sp. gr., 1.177 $^{15.5}_{15.5}$.

References

1. 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.*, **1949**, 2921.
2. P. Lester: U.S. patent 2,678,335 (1954); cf. *C.A.*, **49**, 6300 (1954).
3. J. E. Gardiner and B. A. Kilby: *J. Chem. Soc.*, **1950**, 1769.

22. OCTAMETHYLPYROPHOSPHORAMIDE

$$2[(CH_3)_2N]_2POCl + H_2O + 2(C_2H_5)_3N \rightarrow [(CH_3)_2N]_2OPOPO[N(CH_3)_2]_2 + 2(C_2H_5)_3N\cdot HCl$$

Submitted by A. D. F. Toy* and E. N. Walsh*
Checked by M. L. Nielsen† and T. J. Morrow†

Octamethylpyrophosphoramide has been prepared by the action of $[(CH_3)_2N]_2POCl$ on $[(CH_3)_2N]_2OPOC_2H_5$ or

* Victor Chemical Works, Division of the Stauffer Chemical Company, Chicago Heights, Ill.
† Monsanto Chemical Company, Dayton, Ohio.