### INORGANIC SYNTHESES

The residue is nearly colorless and solidifies to a crystalline mass on cooling. The yield is approximately 90%. *Anal.*\* Calcd. for  $(C_2H_5O)_2PONH_2$ : P, 20.2; N, 9.1. Found: P, 20.7, 21.7; N, 8.8, 8.7.

# Properties

Diethyl monoamidophosphate forms colorless, needlelike crystals, which melt at 46 to 47°. It is very soluble in water, alcohol, acetone, ether, carbon tetrachloride, and a number of other organic solvents but insoluble in hexane. It is very hygroscopic and liquefies when exposed to moist air.

# References

ATHERTON, OPENSHAW, and TODD: J. Chem. Soc., 1945, 660.
STEINBERG: J. Org. Chem., 15, 637 (1950).

# 27. DIETHYL MONOCHLOROPHOSPHATE

 $(C_2H_5O)_2POH + Cl_2 \rightarrow (C_2H_5O)_2POCl + HCl$ 

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Diethyl monochlorophosphate has been prepared by the reaction of triethyl phosphate with phosphorus(V) oxychloride, by treating diethyl phosphite with sulfuryl chloride,<sup>1</sup> from diethyl phosphite and carbon tetrachloride in the presence of a tertiary amine,<sup>2</sup> from ethanol and phosphoryl chloride in a medium of pyridine and benzene,<sup>3</sup> and by the chlorination of diethyl phosphite.<sup>4,5</sup> The last procedure is simple and gives good yields.

# Procedure

One hundred thirty-eight grams of diethyl phosphite (1.0 mol) is placed in a three-necked flask, equipped with a close-fitting stirrer, gas inlet and outlet tubes, and a thermometer, and then cooled in an ice-salt bath. The gas outlet tube is

\* Analytical data are furnished by the checkers.

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connected to a drying tube to prevent access of moist air. Since hydrogen chloride is generated, the experiment must be conducted in a *hood*.

Chlorine is slowly conducted into the diethyl phosphite with constant stirring and at such a rate that the temperature does not exceed  $5^{\circ}$ . When the liquid acquires a light yellow color from free chlorine, in from 2 to 3 hours, the chlorine flow is stopped and the product is transferred to a distilling flask. A short fractionating column is attached, and this column is connected to a condenser and a receiver.

When vacuum is applied, the liquid bubbles vigorously as the free chlorine and hydrogen chloride escape. After this boiling subsides, heating is started. With a pressure of 20 mm., distillation begins at 100 to 110°. The vapor temperature is 103.0 to 104.5°. When the distillation is complete, the temperature in the flask rises rapidly to 150°, with the pressure increasing to about 35 mm., indicating decomposition. The distillation is stopped when this occurs. The yield of diethyl monochlorophosphate is 80 to 90%. Anal.\* Calcd. for  $C_4H_{10}O_3CIP$ :  $P_2O_5$ , 41.5; Cl, 20.6. Found:  $P_2O_5$ , 41.2, 41.0; Cl, 21.6, 21.5.

# Properties

Diethyl monochlorophosphate is a colorless liquid of irritating, unpleasant odor, with boiling point 89° (at 15 mm.),  $n_{\rm D}^{25}$ , 1.4150. It fumes in moist air and reacts vigorously with water. It reacts with ammonia to give ethylamidophosphate and with amines to give substituted ethylamidophosphates.<sup>5</sup>

#### References

- 1. ATHERTON, HOWARD, and TODD: J. Chem. Soc., 1948, 1106.
- 2. STEINBERG: J. Org. Chem., 15, 637 (1950).
- 3. MASTIN, NORMAN, and WEILMUENSTER: J. Am. Chem. Soc., 67, 1663 (1945).
- HARDY and KOSOLAPOFF: U.S. patent 2409039 (Oct. 8, 1946); cf. Chem. Abstracts, 41, 1233<sup>b</sup> (1947).
- 5. McCombie, Saunders, and Stacey: J. Chem. Soc., 1945, 380.
  - \* The analytical data are furnished by the checkers.