B.—To 10 ml. of refluxing aniline was carefully added 2.0 g. of 4-amino-2-chloropyrido(3,2-d)pyrimidine (VII) and the heating was continued for 30 minutes. After cooling, the product was treated with 10 ml. of 50% ethanol containing a little sodium hydroxide, and filtered. The solid was recrystallized from ethanol to yield 0.6 g. of tan needles, m.p. 168–170°. A mixed melting point of this product with that of III prepared by method A was 168–170°.

**2,4-Bis-(dimethylamino)-pyrido(3,2-d)pyrimidine (II).**—This product was prepared from 2,4-dichloropyrido(3,2-d)-pyrimidine (VI) and dimethylamine by three different procedures. The products were identical as judged by ultraviolet absorption spectra, melting points and mixed melting points.

A.—A mixture of 2 g. of VI and 30 ml. of a 20% solution of dimethylamine in alcohol was heated in a sealed tube at 150° for 8 hours. The solution was evaporated to dryness on the steam-bath and the residue dissolved in 20 ml. of 2 *N* sodium hydroxide at 40°. After chilling overnight at 4°, the precipitate was collected, washed with water and dried at room temperature. The crude product was extracted with 100 ml. of boiling hexane (Skellysolve B). The solution gave 1.7 g. of product, m.p. 61–63°. Recrystallization from a small amount of pentane (Skellysolve A) raised the m.p. to 65–66°.

*Anal.* Calcd. for $C_{15}H_{15}N_5$: C, 60.9; H, 6.89; N, 32.3. Found: C, 61.39; H, 6.48; N, 32.6.

B.—A mixture of 1 g. of VI and 30 ml. of 20% alcoholic dimethylamine was heated on the steam-bath until dry. The residue was worked up as in method A and gave 0.9 g. of product, m.p. 61–63°.

C.—A mixture of 1.5 g. of VI and 75 ml. of 20% aqueous dimethylamine was heated on the steam-bath until dry (8 hours). The residue was worked up as in method A and gave 1.1 g. of product, m.p. 60–63°.

The reaction of dimethylamine with the dichloro compound was studied, by means of spectrophotometric observations, at lower temperatures and with more dilute dimethylamine solutions. No evidence was obtained for the formation of a 2-chloro-4-dimethylamino derivative.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

# Preparation of Some Hexaalkyl-phosphorous, Phosphoric and Phosphorothioic Triamides[1]

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*sec*-Aliphatic amines react readily with phosphorus trichloride to form hexaalkyl-phosphorous triamides, $(R_2N)_3P$. These phosphorous triamides are easily converted to the corresponding phosphoric triamides, $(R_2N)_3PO$, by oxidation with dilute hydrogen peroxide; or to the corresponding phosphorothioic triamide, $(R_2N)_3PS$, by sulfurization with elemental sulfur. Each of these three types of amides was prepared, using diethyl-, di-*n*-propyl- and di-*n*-butylamines. At temperatures of about 150°, the phosphorous triamides also react with benzyl mercaptan with the evolution of secondary amine to form S-benzyl-N,N′-tetraalkyl-phosphorodiamidothioite esters, $(R_2N)_2PSCH_2C_6H_5$.

Previous work in this Laboratory has shown that primary aliphatic or aromatic amines react with phosphorus pentasulfide to give phosphorodiamidodithioic acids, $(RNH)_2P(S)SH$, or phosphorothioic triamides, $(RNH)_3PS$, depending on mole ratios and reaction conditions.[3a] Phosphorus pentoxide gives similar results with primary aromatic amines, but in very low yields.[3b]

Secondary aliphatic amines, however, react with phosphorus pentasulfide to form N-dialkyl-phosphoroamidotrithioic acids, $R_2NP(S)(SH)_2$, N,N,N′-trialkyl-phosphorodiamidodithioic acids, $R_2N(RNH)P(S)SH$, or N,N′,N″-trialkyl-phosphorothioic triamides, $(RNH)_3PS$, depending again upon mole ratios and reaction conditions.[3c]

Since the reaction of secondary amines with phosphorus pentasulfide did not yield phosphorodiamidodithioic acids or hexaalkyl-phosphorothioic triamides, it was of interest to prepare these compounds by other methods.

Michaelis[4] has reported the preparation of a few phosphoric and phosphorothioic triamides by treating secondary aliphatic amines with phosphoric trichloride or phosphorothioic trichloride and also by the oxidation or sulfurization, respectively, of the corresponding phosphorous triamides. However, Michaelis was not able to purify his products by distillation and the analytical results, when given, are not satisfactory.

Therefore, attempts were made to repeat Michaelis' work. Using the amine with either phosphoric or phosphorothioic trichloride, we found that the crude product was contaminated with chlorine compounds which could not be removed without decomposing the product. However, the reaction of excess secondary aliphatic amines with phosphorus trichloride to form the phosphorous triamides gave satisfactory results, if anhydrous conditions were maintained. The hexaalkyl-phosphorous triamides of diethyl-, di-*n*-propyl- and di-*n*-butylamines were obtained in good yields as water-white, slightly oily liquids. They could be distilled under reduced pressure without decomposition. Treatment of the phosphorous triamides with either hydrogen peroxide or elemental sulfur gave the corresponding phosphoric or phosphorothioic triamides in fair yields (25–80%). They are colorless to light yellow oils and, with the exception of hexa-*n*-butyl-phosphorothioic triamide, were purified by distillation. The latter was purified by crystallization.

Various attempts were then made to prepare the tetraalkyl-phosphorodiamidodithioic acids, but without success. During this work, it was found that at temperatures of 140–150°, benzyl mercaptan reacted smoothly with the phosphorous triamides to form S-benzyl-N,N′-tetraalkyl-phosphorodia-

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[1] Nomenclature used is from the report of the A.C.S. Committee on Nomenclature: *Chem. and Eng. News*, **30**, 4515 (1952).

[2] Lubrizol Corp., Cleveland 17, Ohio.

[3a] A. C. Buck, J. D. Bartleson and H. P. Lankelma, THIS JOURNAL, **70**, 744 (1948).

[3b] A. C. Buck and H. P. Lankelma, *ibid.*, **70**, 2398 (1948).

[3c] G. Wise and H. P. Lankelma, *ibid.*, **74**, 529 (1952).

[4] A. Michaelis, *Ann.*, **326**, 129 (1903).

TABLE I

| Compound | R | Yield, % | B.p., °C. | Mm. | $n^{20}D$ | Formula | Nitrogen, % Calcd. | Nitrogen, % Found | Phosphorus, % Calcd. | Phosphorus, % Found |
|---|---|---|---|---|---|---|---|---|---|---|
| Type A[a] $(R_2N)_3P$ | $C_2H_5$ | 66.81 | 120–122 | 10 | 1.4578 | $C_{12}H_{30}N_3P$ | 17.00 | 16.88 | 12.55 | 12.41 |
| | $n$-$C_3H_7$ | 90 | 101–103 | 0.15 | 1.4721 | $C_{18}H_{42}N_3P$ | 12.68 | 12.56 | 9.36 | 9.42 |
| | $n$-$C_4H_9$ | 67 | 140–142 | .1 | 1.4700 | $C_{24}H_{54}N_3P$ | 10.12 | 9.90 | 7.46 | 7.31 |
| Type B $(R_2N)_3PO$ | $C_2H_5$ | 22.6 | 105–110 | .3 | 1.4650 | $C_{12}H_{30}N_3PO$ | 15.95 | 15.85 | 11.8 | 11.54 |
| | $n$-$C_3H_7$ | 53.4 | 131–135 | .05 | 1.4630 | $C_{18}H_{42}N_3PO$ | 12.1 | 11.89 | 8.93 | 8.91 |
| | $n$-$C_4H_9$ | 57.2 | 153–157 | .06 | 1.4635 | $C_{24}H_{54}N_3PO$ | 9.74 | 9.66 | 7.2 | 7.08 |
| Type C $(R_2N)_3PS$ | $C_2H_5$ | 83.5 | 121–122 | .12 | 1.5052 | $C_{12}H_{30}N_3PS$ | 15.1 | 14.92 | 11.1 | 10.95 |
| | $n$-$C_3H_7$ | 79 | 108–112 | .01 | 1.4783 | $C_{18}H_{42}N_3PS$ | 11.56 | 11.56 | 8.52 | 8.56 |
| | $n$-$C_4H_9$ | 45 | M.p. 19–20 | | 1.4869 | $C_{24}H_{54}N_3PS$ | 9.39 | 9.21 | 6.94 | 6.85 |

[a] Type A, N,N′,N″-hexaalkyl-phosphorous triamides; type B, N,N′ N″-hexaalkyl-phosphoric triamides; type C, N,N′,-N″-hexaalkyl-phosphorothioic triamides.

midothioite esters, $(R_2N)_2PSCH_2C_6H_5$, liberating one mole of secondary amine. This reaction is shown by the equation

$$(R_2N)_3P + C_6H_5CH_2SH \longrightarrow R_2NH + (R_2N)_2PSCH_2C_6H_5$$

These phosphorodiamidothioite esters, like the amides, could be sulfurized readily to the phosphorodiamidodithioate esters, $(R_2N)_2P(S)SCH_2C_6H_5$.

## Experimental

**Starting Materials.**—The phosphorus trichloride, commercial grade, was purified by distillation.

All of the secondary amines were supplied by Sharples Chemicals, Inc. They were further purified by distillation, after drying over potassium hydroxide.

The benzyl mercaptan, Eastman Kodak Co., was used without purification.

1. **Preparation of N,N′,N″-Hexaalkyl-phosphorous Triamides.**—The preparation of N,N′,N″-hexa-*n*-propyl-phosphorous triamide is illustrative. A solution of 355 g. (3.2 moles) of di-*n*-propylamine in 500 ml. of diethyl ether (or ligroin) was stirred at 5° while a solution of 55 g. (0.4 mole) of phosphorus trichloride in 150 ml. of ether was slowly added over a two-hour period of 5–10°. After warming to room temperature, the mixture was stirred and refluxed for four hours and cooled to room temperature. The amine hydrochloride was filtered off and washed well with ether. Filtrate and washings were combined and freed of volatile material *in vacuo*. If any amine hydrochloride precipitated at this point, it was filtered off; the crude product was purified by distillation.

2. **Preparation of N,N′,N″-Hexaalkyl-phosphoric Triamides.**—The preparation of N,N′,N″-hexa-*n*-propyl-phosphoric triamide is illustrative. A solution of 16.6 g. (0.05 mole) of N,N′,N″-hexa-*n*-propyl-phosphorous triamide in 200 ml. of acetone was stirred at 5°, while 18 g. (0.053 mole, 6% excess) of 10% hydrogen peroxide was added slowly over a period of a half-hour at 5–10°. The solution was then stirred for three hours at 50–60°, poured into water and extracted with diethyl ether. The ether layer was washed twice with water, dried over magnesium sulfate and freed of volatile material *in vacuo*. The crude product was purified by distillation.

3. **Preparation of N,N′,N″-Hexaalkyl-phosphorothioic Triamides.**—The preparation of N,N′,N″-hexa-*n*-propyl-phosphorothioic triamide is illustrative. A solution of 33.1 g. (0.1 mole) N,N′,N″-hexa-*n*-propyl-phosphorous triamide in 200 ml. of ligroin was stirred at 20° and 3.2 g. (0.1 mole) of sulfur was added over a ten-minute period at 20–25°, with cooling. The solution was stirred and refluxed for two hours, filtered to remove any unreacted sulfur and freed of volatile materials under vacuum. The crude product was purified by distillation. The *n*-butyl homolog could not be distilled and was purified by crystallization from ligroin, cooling with a Dry Ice–acetone-bath.

Three triamides of each of the preceding types were prepared. The yields, boiling points and analytical data for these are summarized in Table I.

4. **Reaction of Benzyl Mercaptan with N,N′,N″-Hexa-*n*-propyl-phosphorous Triamide.**—Thirty-three and one-tenth grams (0.1 mole) of N,N′,N″-hexa-*n*-propyl-phosphorous triamide was stirred and heated while slowly adding 13.4 g. (0.1 mole) of benzyl mercaptan. About one-half of the mercaptan was added in 30 min. while heating to 150°, when the mixture began to distil. The remaining mercaptan was added in about 15 min., with stirring. The mixture was finally stirred for 1.5 hr. at 150–160°. The distillate was identified as di-*n*-propylamine by the urea which it formed on treatment with α-naphthyl isocyanate (m.p. 93–94°, lit. 93°). A total yield of 9 g. (90%) of di-*n*-propylamine was obtained and the residue weighed 35 g. after drying at 45° (12 mm.). This weight represents a 100% yield as the S-benzyl-N,N′-tetra-*n*-propylphosphorodiamidothioite ester, $[(n\text{-}C_3H_7)_2N]_2PSCH_2C_6H_5$. As the product could not be distilled without decomposition and also could not be crystallized, the product was analyzed without further purification.

*Anal.* Calcd. for $C_{19}H_{35}N_2PS$: N, 7.91; P, 8.78. Found: N, 8.09; P, 8.66.

5. **Reaction of Benzyl Mercaptan with N,N′,N″-Hexa-*n*-butyl-phosphorous Triamide.**—When 20.75 g. (0.05 mole) of N,N′,N″-hexa-*n*-butyl-phosphorous triamide and 6.2 g. (0.05 mole) of benzyl mercaptan were treated in the same manner as in 4 (above), decomposition of the mixture occurred on heating to a pot temperature of 200°. However, repeating the experiment under a pressure of 100 mm. and at 145–150° for one hour and then for one hour at 70° (10 mm.) gave 20 g. of a yellow liquid as residue. This amount represents a 100% yield of the S-benzyl-N,N′-tetra-*n*-butyl-phosphorodiamidothioite ester, $[(n\text{-}C_4H_9)_2N]_2PSCH_2C_6H_5$. This ester also decomposed on attempted distillation and was, therefore, analyzed without further purification.

*Anal.* Calcd. for $C_{23}H_{43}N_2PS$: N, 6.85; P, 7.56. Found: N, 6.93; P, 7.40.

6. **Preparation of S-Benzyl-N,N′-tetra-*n*-butyl-phosphorodiamidodithioate.**—Sulfurization of 8.2 g. (0.02 mole) of crude S-benzyl-N,N′-tetra-*n*-butyl-phosphorodiamidothioite with 0.8 g. (0.025 mole) of sulfur in 50 ml. of ligroin, by the procedure given in 3, yielded 8.5 g. of the dithioate ester after taking off the solvent under a vacuum. Since the corresponding thioite ester could not be distilled, no attempt was made to distil this product. It, also, could not be crystallized. This 8.5 g. represents a 96% yield as the dithioate ester, $[(n\text{-}C_4H_9)_2N]_2P(S)SCH_2C_6H_5$, and it was analyzed without further purification. The product was a yellow oil, $n^{20}D$ 1.5931.

*Anal.* Calcd. for $C_{23}H_{43}N_2PS_2$: N, 6.33. Found: N, 6.36.

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