PREPARATION OF ACID BROMIDES OF TRI- AND PENTAVALENT PHOSPHORUS ACIDS

B. A. Arbuzov, V. K. Krupnova, and A. O. Vizel'

UDC 542.91:547.1'118

When comparing the known methods for the synthesis of the acid bromides of phosphorus acids [1-9] we found that replacing the chlorine by bromide in the corresponding acid chlorides under the influence of phosphorus tribromide can prove to be a very convenient method. Thus, it was shown previously [10] that exchange of the halogen atoms proceeds easily in the system phosphorus oxychloride – phosphorus tribromide. In addition, the acid bromides of alkyl- and arylphosphonous and phosphinous acids were obtained [5] in good yields by the exchange reaction. The possibility of applying this reaction to the acid chlorides of other phosphorus acids was not studied.

We found that PBr_3 can be used to obtain a wide gamut of acid bromides of the penta- and trivalent phosphorus acids. The reaction was run by heating a mixture of the appropriate acid chloride with PBr_3 and removal of the formed PCl_3 by distillation. The optimum reaction temperature was 170-190°C. At lower temperatures the reaction rate drops noticeably. At higher temperatures the yield decreases due to tarring. The structure and valence state of the phosphorus atom of the starting acid chlorides are retained in the formed acid bromides, which was corroborated by their ^{31}P NMR spectra.

EXPERIMENTAL METHOD

Dibromide of Phenylphosphorous Acid. In a distillation flask fitted with a Vigreux column were placed 38.4 g of the dichloride of phenylphosphorous acid and 35.5 g of PBr_3. The amount of PCl_3 that distilled at a bath temperature of 180-190° was 13.3 g. Fractional distillation of the residue gave 46.2 g (81.9%) of a product with bp. 115-116° (8 mm); n_D^{20} 1.6225. Found: Br 57.20% $C_6H_5Br_2OP$. Calculated: Br 56.34%. From [3]: bp. 120-130° (11 mm); n_D^{20} 1.6202. The reaction conditions and isolation of the products were the same in subsequent experiments.

Dibromide of Dibutylamidophosphorous Acid. From 23 g of the dichloride of dibutylamidophosphorous acid and 17.8 g of PBr_3 was obtained 25 g (78.1%) of a product with bp. 128-129° (8 mm); d_4^{20} 1.4750; n_D^{20} 1.5460. Found: Br 49.25; P 9.28%; MR 57.82. $C_8H_{18}Br_2NP$. Calculated: Br 50.1; P 9.7%, MR 57.32. δ_P^{31} −174 ppm (85% H_3PO_4).

Acid Bromide of Salicylphosphorous Acid. From 40.4 g of the acid chloride of salicylphosphorous acid and 17.8 g of PBr_3 was obtained 44.5 g (90.8%) of a product with bp. 145° (8 mm); mp. 46°. Found: Br 32.59%. $C_7H_4BrO_3P$. Calculated: Br 32.35%. δ_P^{31} − 175 ppm. From [2]: bp. 143° (9 mm).

Dibromide of Methylphosphonic Acid. From 26.6 g of the dichloride of methylphosphonic acid and 35.6 g of PBr_3 was obtained 39 g (89.6%) of a product with bp. 65-66° (9 mm); d_4^{20} 2.4230; n_D^{20} 1.5856. Found: Br 73.12%. CH_3Br_2OP. Calculated: Br 72.12%. From [11]: bp. 191-195° (728 mm); d_4^{20} 2.4278; n_D^{20} 1.5829.

Dibromide of Phenylthiophosphonic Acid. From 41.6 g of the dichloride of phenylthiophosphonic acid and 35.6 g of PBr_3 was obtained 53.1 g (89.0%) of a product with bp. 140-141° (9 mm); d_4^{20} 1.8875; n_D^{20} 1.6872. Found: Br 52.47; P 9.87%. $C_6H_5Br_2PS$. Calculated: Br 53.33; P 10.32%. From [9]: bp. 96-98° (0.3 mm); d_4^{20} 1.8866; n_D^{20} 1.6856.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR.

Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1193-1194, May, 1972. Original article submitted June 9, 1971.

CONCLUSIONS

It was shown that the acid bromides of phosphorus acids can be obtained via the exchange of chlorine by bromine in the corresponding acid chlorides under the influence of phosphorus tribromide.

LITERATURE CITED

1. G. M. Kosolapoff, Organophosphorus Compounds, New York (1950).
2. J. A. Cade and W. Gerrard, J. Chem. Soc., 1249 (1960).
3. M. Frazer, W. S. Gerrard, and J. Patel, Chem. Ind. (London), 728 (1959).
4. L. D. Quin, J. P. Gratz, and T. P. Barket, J. Org. Chem., 33, 1034 (1968).
5. W. Kuchen and W. Grünewald, Chem. Ber., 98, 480 (1965).
6. C. Weber, U. S. Patent 2,882,242, April 14, 1959; Ref. Zh., Khim., 97597 II (1960).
7. L. Maier, Angew. Chem., 71, 574 (1959).
8. L. Maier, Helv. Chim. Acta, 47, 120 (1964).
9. L. I. Mizrakh and V. P. Evdakov, Zh. Obshch. Khim., 36, 469 (1966).
10. E. Schwarzmann and J. R. Van Wazer, J. Am. Chem. Soc., 81, 6366 (1959).
11. L. Maier, Helv. Chim. Acta, 46, 67 (1963).