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A PREPARATIVE METHOD FOR ALKYLHALOPHOSPHINES

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Abstract—CH_3PCl_2, $(CH_3)_2PCl$ and $(CH_3)(C_2H_5)PBr$ were prepared by the reaction of the corresponding thiophosphoryl derivatives with tributylphosphine. The method appears to be of general applicability and gives 60–70 per cent yields.

RECENT publications(1–6) have described the preparation of alkylhalophosphines. BURG and SLOTA,(1) KOMKOV *et al.*(2) and PARSHALL(3) prepared dimethylchlorophosphine.

The method reported in this paper consists of simply removing sulfur from alkylthiophosphoryl halides by the use of tributylphosphine according to the following equation.†

$$R_nP(S)X_{3-n} + (C_4H_9)_3P \rightarrow R_nPX_{3-n} + (C_4H_9)_3PS \quad (X = Cl,Br;\ n = 1, 2) \quad (1)$$

EXPERIMENTAL

Apparatus and materials. Nuclear magnetic resonance (n.m.r.) of ^{31}P nucleus was used throughout this work for the qualitative and quantitative analysis of the reaction products. A 16·2 Mc/s r.f. unit was used with a magnetic field of about 9395 G. Chemical shifts are reported in p.p.m. relative to 85% H_3PO_4 as a standard. The accuracy is ± 1 p.p.m.

Tributylphosphine was used as received from Anderson Chemical Company. It was found to be of sufficient purity for the purpose of the present investigation. Thionophosphonic and thionophosphinic halides were prepared in this laboratory. $CH_3P(S)Cl_2$ was prepared by the sulphur reduction of $CH_3PCl_4{\cdot}AlCl_3$ in the presence of dry KCl as reported by KOMKOV *et al.*(8) $(CH_3)_2P(S)Cl$ was obtained by the cleavage of tetramethyldiphosphine disulphide (n.m.r. chemical shift = −35 p.p.m. in $CHCl_3$) with chlorine. The latter compound was prepared according to the method of REINHARDT *et al.*(9) The chlorine cleavage proceeded almost quantitatively. $(CH_3)(C_2H_5)P(S)Br$ was obtained by the reaction of $CH_3P(S)Br_2$ and C_2H_5MgBr to give $[(CH_3)(C_2H_5)PS]_2$ (n.m.r. chemical shift = −44 p.p.m. in $CHCl_3$) and its cleavage with bromine.(10)

The reaction of tributylphosphine with thionophosphinic or thionophosphonic halides was carried out in a round bottom reaction flask equipped with a thermometer well. A 12 in. Widmer fractionating column with a variable reflux distillation head made it possible to distill off the pure reaction

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† KÖHLER(7) stated that phenyldichlorophosphine had a greater affinity for sulphur than phosphorus trichloride. This reasoning followed to its extreme would indicate reaction (1) to be feasible.

(1) A. B. BURG, P. J. SLOTA, JR., *J. Amer. Chem. Soc.* **80**, 1107 (1958).
(2) I. P. KOMKOV, K. V. KARAVANOV, S. Z. IVIN *J. Gen. Chem. U.S.S.R.* **28**, 2992 (1958).
(3) G. W. PARSHALL, *J. Inorg. Nucl. Chem.* **12**, 372–373 (1960).
(4) K. ISSLEIB, W. SEIDEL, Ber. **92**, 2681 (1959).
(5) M. SANDER, *Ber. Dtsch. Chem. Ges.* **93**, 1220 (1960).
(6) L. MAIER, *Angew. Chem.* **71**, 574–5 (1959).
(7) H. KÖHLER, *Ber. Dtsch. Chem. Ges.* **13**, 463 (1880).
(8) I. P. KOMKOV, S. Z. IVIN, K. V. KARAVANOV, *J. Gen. Chem. U.S.S.R.* **28**, 2990 (1958).
(9) H. REINHARDT, D. BIANCHI and D. MÖLLE, *Ber. Dtsch. Chem. Ges.* **90**, 1656 (1957).
(10) L. MAIER, *Angew. Chem.* **71**, 575 (1959).

product as the reaction proceeded. The entire apparatus was flushed with dry nitrogen prior to use and during the reaction oxygen and moisture were prevented from entering the system by means of a dry nitrogen lock.

Preparation of CH_3PCl_2. In a reaction flask 44·4 g (0·28 mole) of $CH_3P(S)Cl_2$ and 65·3 g (0·32 mole) of $(C_4H_9)_3P$ (16 per cent excess) were mixed giving a homogeneous, yellowish mixture and a slight evolution of heat. When the reaction mixture was heated to 120°C noticeable boiling occurred and a 20·4 g (62·5 per cent yield) fraction of clear, colourless product was collected at 79–80°C and 747 mm Hg. The reaction temperature was gradually raised to 190°C during the course of the product removal. The n.m.r. chemical shift of CH_3PCl_2 obtained was −191·0 p.p.m.; literature value = −191·2 p.p.m.(11)

Preparation of $(CH_3)_2PCl$. Two layers were formed upon mixing 184·2 g (1·43 mole) of $(CH_3)_2$-$P(S)Cl$ (n.m.r. chemical shift = −87·3 p.p.m.) and 343 g (1·70 mole) of $(C_4H_9)_3P$ (19 per cent excess). Reaction was first noticed at 118°C and became rapid at 130°C at which temperature the two layers became miscible. The reaction temperature was raised to 170°C during the distillation and 89 g (58 per cent yield) of $(CH_3)_2PCl$ distilled over at 73–74°C and 749 mm Hg. In experiments with a 5 per cent excess of tributylphosphine a 60 per cent yield of $(CH_3)_2PCl$ was obtained. N.m.r. chemical shift = −96·0 p.p.m.; literature value = −93·0 p.p.m.(3)

The dimethylchlorophosphine had the same physical properties as found by BURG and SLOTA.(1) It slowly deposited a white, waxy solid upon standing in the liquid state. However, it could be stored in the solid state with numerous meltings and resolidifications for sample removal without noticeable decomposition.

Preparation of $(CH_3)(C_2H_5)PBr$.(*†) Two layers were formed when 14·5 g (0·078 mole) of $(CH_3)(C_2H_5)P(S)Br$ (n.m.r. chemical shift = −85 p.p.m.) and 22·0 g (0·1 mole) of $(C_4H_9)_3P$ came into contact. A homogeneous mixture was obtained between 130°C and 140°C where reaction began, and 8·5 g (70 per cent yield) of $(CH_3)(C_2H_5)PBr$ (n.m.r. chemical shift = −98·5 p.p.m.) distilled over at 128–129°C and 720 mm Hg. The reaction temperature was allowed to reach 220°C during the distillation. The colourless liquid fumed strongly in the air. (Found: C, 23·04; H, 5·4; Br, 51·36. Calcd. C, 23·25; H, 5·2; Br, 51·56%)

DISCUSSION

Alkylhalophosphines have been previously prepared by the cleavage of dimethylamino–dimethylphosphine with hydrogen chloride,(1,4) the aluminothermic reduction of alkyltetrachloro- and dialkyltrichlorophosphine–aluminum chloride adducts,(2) the reduction of the same type of adducts with phenyldichlorophosphine or tributylphosphine and the reaction of tetramethyldiphosphine disulphide with phenyldichlorophosphine,(3) the chlorination of dialkyl phosphonites or alkyl phosphinites with phosphorus trichloride,(5) and the catalytic reaction of alkyl halides with red phosphorus at elevated temperatures.(6)

In the latter method a mixture of mono- and disubstituted halo-phosphines was obtained which was sometimes difficult to separate. This was the case with methyldichlorophosphine and dimethylchlorophosphine which had close boiling points. This mixture could easily be separated by reaction with sulphur to produce thiophosphoryl compounds which were fractionated and then desulphurized with tributylphosphine.

The work reported in this paper indicates that the removal of sulphur from alkylthiophosphoryl halides by tributylphosphine may be a general method for the preparation of alkylhalophosphines.

It was found that the use of excess tributylphosphine made very little difference in the yields obtained. If anything, a large excess of tributylphosphine tended to lower

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* $(CH_3)(C_2H_5)PBr$ was also prepared by the cleavage of $(CH_3)(C_2H_5)P$–$P(C_2H_5)(CH_3)$ with bromine.(10)

† Dimethylbromophosphine has also been prepared by this procedure in this laboratory. However, due to its rather unusual physical characteristics a future communication will deal with its preparation and properties.

(11) N. MULLER, P. C. LAUTERBUR, J. GOLDENSON, *J. Amer. Chem. Soc.* **78**, 3557 (1956).

the yield, probably due to solubility effects. Thus, a 2–5 per cent excess of the reagent was sufficient.

Several methods were used to increase the yields. For example, yields of $(CH_3)_2PCl$ were increased to almost 70 per cent by allowing the reaction temperature to reach 200–220°C during the removal of the product. At the higher reaction temperatures some of the tributylphosphine passed over into the product and formed a separate phase. However, in general the purity of the products obtained was between 97 and 100 per cent as indicated by n.m.r. measurements.

Nuclear magnetic resonance measurements showed that the reaction residue after atmospheric distillation still contained considerable amounts of product. Thus, the yield could be increased to almost 80 per cent in some cases by a second distillation of the residue under reduced pressure. The above fact strongly suggests that the lower yields at atmospheric pressure were due in large part to a solubility effect of the residual tributylphosphine sulphide and any excess tributylphosphine.

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