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SHORT COMMUNICATIONS

New Synthesis of Tetraphenylphosphonium Halides

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A number of methods for preparation of tetrarylphosphonium halides are known, the main of which are based on the reactions of triarylphosphine and phenyl halide in the presence of aluminum halide and of triarylphosphine oxide with arylmagnesium halide followed by subsequent treatment of the reaction mixture with hydrohalic acid [1]. Also, the reaction of pentaphenylphosphorane with appropriate acid should be noted [2].

We have developed a new procedure for preparation of tetraphenylphosphonium halides by reaction of pentaphenylphosphorane with dihalotriphenylphosphoranes. In such a way, using pentaphenylphosphorane (**I**) and dihalides **IIa** and **IIb** as starting compounds, we have synthesized tetraphenylphosphonium chloride and bromide **IIIa** and **IIIb** in 92 and 95% yield, respectively:

$$\mathrm{Ph_5P + Ph_3PHlg_2 \rightarrow 2Ph_4PHlg}$$

$$\mathrm{Hlg = Cl}\ (\mathbf{a}),\ \mathrm{Br}\ (\mathbf{b}).$$

The reactions were carried out by heating the reactants in an aromatic hydrocarbon. The process also occurs at room temperature, but at a lower rate.

The synthesis of antimony and bismuth compounds of the general formula Ar_4EX (E = Sb, Bi) by the same procedure was reported by us in [3–9]. We have now demonstrated that the arylation of triaryldihalo derivatives of the 5th Group elements with their pentaaryl compounds is also applicable to phosphorus(V) derivatives.

Tetraphenylphosphonium chloride (IIIa). A mixture of 1 g (2.18 mmol) of pentaphenylphosphorane–cyclohexane solvate, 0.73 g (2.18 mmol) of dichlorodiphenylphosphorane, and 15 ml of toluene was kept for 1 h at 90°C. The solvent was distilled off, and the residue was recrystallized from water. Yield 1.5 g (92%), mp 262°C (published data [1]: mp 265°C; no depression of the melting point was observed on mixing with an authentic sample).

Tetraphenylphosphonium bromide (IIIb) was synthesized in a similar way from compound **I** and dibromotriphenylphosphorane. Yield 95%, mp 285°C (published data [1]: mp 287°C).

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