A Simple Preparation of Methylphosphonous Dichloride

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Methylphosphonous dichloride ($H_3C—PCl_2$), a useful starting material for the synthesis of a variety of organophosphorus compounds with $P—CH_3$ groups, is not a readily available substance. The described methods for its preparation, although quite numerous[1], lack simplicity and reliability necessary for routine large-scale laboratory work. The inherent difficulties of methylphosphonous dichloride preparation by the described methods are evidenced by the prohibitively high price of the commercial product.

In connection with a research project dealing with the synthesis and biological activity of P-methylphosphinic analogues of amino acids[2,3] we have developed a practical procedure for methylphosphonous dichloride preparation which invariably gives a 70–80% yield of pure product and is readily executed in conventional laboratory glassware. The procedure involves a combination of thermal decomposition and reduction with iron of the complex formed *in situ* from methyl iodide, aluminium chloride, and phosphorus trichloride. Due to the low melting temperature, thermal instability, and easy reduction of this complex, the preparation requires only moderate temperatures and the reaction has no tendency to run out of control at 1.5 mol scale. Larger scale preparations have not yet been tried.

$$H_3C—J + PCl_3 + AlCl_3 \longrightarrow \underset{\mathbf{1}}{[H_3C—PCl_3]^{\oplus}\ [AlCl_3J]^{\ominus}}$$

$$\underset{\mathbf{1}}{[H_3C—PCl_3]^{\oplus}\ [AlCl_3J]^{\ominus}} \xrightarrow{KCl\ /\ Fe\ (powder)} \underset{\mathbf{2}}{H_3C—P(Cl)Cl}$$

Both the thermal decomposition of alkyl iodide complexes with aluminium trichloride and phosphorus trichloride and the reduction of analogous methyl chloride complex with various metals are known from literature reports[1,4] so that there is no new chemistry in our method. What appears to be new, however, is the combination of known reactions in one effective, practical procedure, which, in our experience, by far exceeds the described methods in simplicity, reliability, and safety of operation.

Preparation of Methylphosphonous Dichloride (2):

The reaction is carried out under dry nitrogen in a 1 liter glass-reactor[5] equipped with a KPG stirrer, reflux condenser, dropping funnel, and calcium chloride filled drying-tube.

In the reactor is placed phosphorus trichloride (1.5 mol) and anhydrous aluminium chloride. (1.7 mol). The mixture is heated for 30 minutes at 60–70°, cooled in a sodium chloride/ice bath, and methyl iodide (1.5 mol) is added dropwise over 0.5 h with continous stirring. After 0.5–1 h the complex solidifies and stirring is impossible. To the solid complex is added a mixture of dry potassium chloride (1.7 mol) and iron powder (90 g). The reflux condenser is exchanged for a distillation condenser. After heating the mixture on an electric bath to the melting point, the stirrer is started, and the iodine/methylphosphonous dichloride mixture is distilled to give 225–250 g of the fraction collected at 80–170°. The mixture of iodine and methylphosphonous dichloride is fractionated (60 cm Vigreux column) two or three times to give the pure methylphosphonous dichloride as a colourless liquid; yield: 70–80%; b.p. 80–82°.

The structure was confirmed by elemental analysis, N.M.R. spectra and synthesis of the methylphosphonous acid esters.

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[4] V. G. Gruzdiev et al., *Zh. Obshch. Khim.* **37**, 450 (1967).

[5] The reactor FR 1 LF and the stirrer ST 1/5 (Quickfit catalog) were used for these syntheses.