Catalytic synthesis of α-trichloromethylbenzyl esters of phosphorus acids

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Reactions of α-polyfluoroalkylbenzyl alcohols $ArCHR_FOH$ with phosphorus acid chlorides are catalyzed by some metals or their salts to afford the corresponding esters.[1–5] However, in attempting to carry out noncatalytic phosphorylation of α-trichloromethylbenzyl alcohol $PhCH(CCl_3)OH$ (**1**) with different phosphorylating agents, among them acid chlorides, trichlorostyrene $PhCCl{=}CCl_2$ was the only reaction product.[6]

We demonstrated that, as in the case of α-polyfluoroalkylbenzyl alcohols, under certain conditions, catalytic phosphorylation makes it possible to obtain different ester chlorides and complete esters of phosphorus acids containing α-trichloromethylbenzyl fragments:

$$\underset{\mathbf{1}}{PhCH(CCl_3)OH} + \underset{\mathbf{2a–e}}{RR'P(O)Cl} \xrightarrow{Mg,\ \Delta} \underset{\mathbf{3a–e}}{RR'P(O)OCH(CCl_3)Ph}$$

R = CF_3CH_2O, R′ = Cl (**a**); R = Me, R′ = Cl (**b**);
R = R′ = CF_3CH_2O (**c**); R = R′ = PhO (**d**);
R = R′ = Ph (**e**)

Thus, when alcohol **1** is phosphorylated with excess (two-fold excess is optimum) acid dichlorides **2a,b** in the presence of metallic magnesium* as a procatalyst, ester chlorides **3a,b** are formed. Esters **3c—e** were obtained by catalytic phosphorylation of **1** with equimolar amounts of acid monochlorides **2c—e**. The conditions of catalytic phosphorylation and the yields of α-trichloromethylbenzyl esters of phosphorus acids are given in Table 1.

* In the course of the reaction, magnesium dissolves and converts to $MgCl_2$.

Table 1. Catalytic phosphorylation of α-trichloromethylbenzyl alcohol with phosphorus acid chlorides

Initial acid chloride	Reaction temperature/°C	Duration of the reaction/h	Yield of **3** (%)
2a	140	25.5	61
2b	140	6.0	71
2c	180	7.5	84
2d	180	16.5	86
2e	180	14.0	90

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