

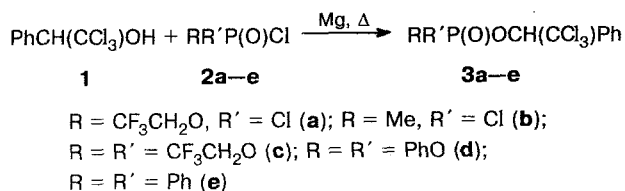
# Catalytic synthesis of $\alpha$ -trichloromethylbenzyl esters of phosphorus acids

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Reactions of  $\alpha$ -polyfluoroalkylbenzyl alcohols  $\text{ArCHR}_F\text{OH}$  with phosphorus acid chlorides are catalyzed by some metals or their salts to afford the corresponding esters.<sup>1–5</sup> However, in attempting to carry out noncatalytic phosphorylation of  $\alpha$ -trichloromethylbenzyl alcohol  $\text{PhCH}(\text{CCl}_3)\text{OH}$  (**1**) with different phosphorylating agents, among them acid chlorides, trichlorostyrene  $\text{PhCCl}=\text{CCl}_2$  was the only reaction product.<sup>6</sup>

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



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  $\alpha$ -trichloromethylbenzyl esters of phosphorus acids are given in Table 1.

\* In the course of the reaction, magnesium dissolves and converts to  $\text{MgCl}_2$ .

**Table 1.** Catalytic phosphorylation of  $\alpha$ -trichloromethylbenzyl alcohol with phosphorus acid chlorides

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

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