CATALYTIC PHOSPHORYLATION OF SILICON-CONTAINING ALCOHOLS

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The phosphorylation of primary silicon-containing alcohols is usually carried out using acid chloride derivatives of phosphorus acids in the presence of tertiary amines [1, 2]. We have found that the introduction of a strongly electron-withdrawing polyfluorinated group into the α-position of ω-(trimethylsilyl)alkanols permits the phosphorylation of these secondary alcohols using diphenyl chlorophosphate by catalytic phosphorylation, which we proposed previously for the phosphorylation of primary polyfluoroalkanols [3]. Metallic magnesium may also be used as the procatalyst

$$\underset{\text{(Ia—c)}}{Me_3Si(CH_2)_nCHR_FOH} + (PhO)_2POCl \xrightarrow[-HCl]{Mg,\ t^\circ} \underset{\text{(IIa—c)}}{Me_3Si(CH_2)_nCHR_FOP(O)(OPh)_2}$$

n = 1, $R_F = C_4F_9$ (a); n = 2, $R_F = C_3F_7$ (b); n = 3, $R_F = CF_3$ (c).

A mixture of 0.011 mole (Ia)-(Ic), 0.010 mole diphenyl chlorophosphate, and 0.25 mmole magnesium was heated for several hours until HCl was no longer released. The reaction mixture was dissolved in 10 ml pentane and subjected to chromatography on 2 g alumina using pentane as an eluent. The eluate was evaporated and the residue was distilled in vacuum. The reaction conditions, the yields, and ^{31}P NMR spectra of the phosphates obtained are given in Table 1.

TABLE 1

Starting alcohol	Reaction temp., °C	Time, h	Yield of (II), %†	$^{31}P-\{^1H\}$ NMR spectrum, δ, ppm
(Ia)	140	15	51	−12,8
(Ib)	160	12	66	−11,8
(Ic)	160	4	50	−12,8

*The syntheses of alcohols (Ia)-(Ic) will be published separately.

†The yields of (IIa)-(IIc) were 95-100% as indicated by ^{31}P NMR spectroscopy.

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