FIRST EXAMPLE OF THE CATALYTIC PHOSPHORYLATION OF TERTIARY POLYFLUORINATED ALCOHOLS

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UDC 542.97:547.1'118

The phosphorylation of primary α,α-dihydropolyfluoroalkyl alcohols and secondary α-polyfluoroalkylbenzyl alcohols by phosphorus acid chlorides in the presence of metal salts as catalysts may be used for the synthesis of various phosphate esters containing primary and secondary polyfluoroalkyl groups [1]. On the other hand, the catalytic phosphorylation of tertiary α,α-dialkyl-ω-hydropolyfluoroalkyl alcohols by $POCl_3$ and diphenyl chlorophosphate did not lead to the formation of the corresponding phosphorylation products.

However, the use of dichlorophosphates or dichlorophosphonates permitted us to apply catalytic phosphorylation for the first time for the synthesis of phosphorus acid esters containing tertiary polyfluoroalkyl groups.

$$\underset{(I)}{H(CF_2)_4CMe_2OH} + \underset{(IIa-d)}{RPOCl_2} \xrightarrow[-HCl]{CaCl_2,\ t^\circ} \underset{(IIIa-d)}{H(CF_2)_3CMe_2OP(O)(Cl)R}$$

R = CF_3CH_2O (a), C_6H_5O (b), CH_3 (c), C_6H_5 (d).

A mixture of 10.4 g (0.04 mole) 1,1-dimethyl-2,2,3,3,4,4,5,5-octafluoropentanol (I), 13.0 g (0.06 mole) 2,2,2-trifluoroethyl dichlorophosphate (IIa), and 111 mg (1 mmole) anhydrous $CaCl_2$ was heated for 52 h at 140°C and then fractionated in vacuum to yield 11.6 g (66%) (2,2,2-trifluoroethyl) (1,1-dimethyl-2,2,3,3,4,4,5,5-octafluoropentyl) chlorophosphate (IIIa), bp 74.5-75° (1 mm), n_D^{20} 1.3590, d_4^{20} 1.6119. Found: C 24.3; H 2.1; Cl 8.3; F 47.3; P 7.0%, MR, 60.17. Calculated for $C_9H_9ClF_{11}O_3P$: C 24.5; H 2.1; Cl 8.0; F 47.4; P 7.0%, MR 60.88. $^{31}P-\{^1H\}$ NMR spectrum (ppm): 2.14 s.

Etheroacid chlorides (IIIb-d) were obtained by analogy. The structures of these compounds were supported by elemental analysis and PMR and $^{31}P-\{^1H\}$ NMR spectroscopy.

LITERATURE CITED

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0568-5230/85/3404-0875$09.50