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## Phosphorus, Sulfur, and Silicon and the Related Elements

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## Synthesis and Thermal Transformations of 1-Polyfluoro-Alkyl-2-Trialkylsilylethyl Esters of Phosphorus Acids

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We have studied the phosphorylation of 1-polyfluoroalkyl-2-trialkylsilylethanols
(1) with phosphorus acids chlorides.

$$R_3SiCH_2CH(R_f)OH + Cl-P(O) < \xrightarrow{A \text{ or } B} R_3SiCH_2CH(R_f)OP(O) < II$$

R = alkyl, R<sub>f</sub> = polyfluoroalkyl, A = metal salt catalyst, t°, B = R<sub>3</sub>N, CH<sub>2</sub>Cl<sub>2</sub>, 20°

We have considered the possibility to use POCl<sub>3</sub>, MePOCl<sub>2</sub>, monochlorophosphates and -phosphonates as phosphorylating agents. Reaction conditions, A or B, depend on the structure of the alcohol (I) and the nature of phosphorylating agent. In certain cases, the formation of pyrophosphates (both under conditions A and B) and products of thermal decomposition of phosphonates (II) has been observed (conditions A):

Thermal stability of the esters (II) has been studied and the dependence of their stability on the bulk of the polyfluoroalkyl group and the electron-withdrawing properties of substituents at phosphorus atom has been revealed. The possible mechanism of the thermal decomposition of this type of silicon-containing phosphorus esters is proposed.