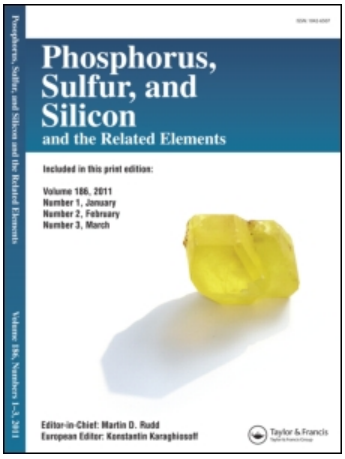

Phosphorus, Sulfur, and Silicon and the Related Elements

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Catalytic Phosphorylation of Silapolyfluoroalkanols

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CATALYTIC PHOSPHORYLATION OF SILAPOLYFLUOROALKANOLS

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O-Aryl-O-(α-perfluoroalkyl-ω-trialkylsilyl)methylphosphonates (II) have been prepared by catalytic phosphorylation of silapolyfluoroalkanols (I) with O-arylmethylphosphonochloridates.

$$R_3Si(CH_2)_nCH(R_F)OH + Cl\text{-}P(O)(Me)OAr \xrightarrow{Mg,\ t^0} R_3Si(CH_2)_nCH(R_F)OP(O)(Me)OAr$$

(I) (II)

n = 1,3; R = Me, Pr, $CF_3CH_2CH_2$; R_F = CF_3, C_4F_9; Ar = Ph, 4-t-BuC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2,6-$Me_2C_6H_3$.

According to NMR and GC, the esters II are the mixtures of two diastereomers. A diastereomer ratio differs substantially from statistic one in some cases. We have examined the influence of the distance between silicon atom and reaction site, the nature of R and R_F groups, and a type of phosphorylating agent upon the diastereoselectivity. The maximum stereoselectivity was found for II (n = 1, R_F = $CF_3CH_2CH_2$), with diastereomer ratio being 91:9. The observed diastereoselectivity is unusually high and seems to be due to the tendency of silicon to form coordination bonds. The possible mechanism of the phosphorylation is discussed.

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