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Catalytic Phosphorylation of Silapolyfluoroalkanols

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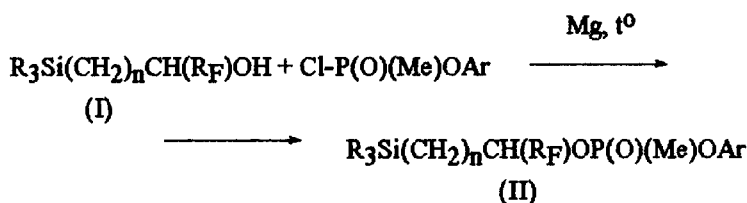
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CATALYTIC PHOSPHORYLATION OF SILAPOLYFLUOROALKANOLS

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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.



$n = 1, 3$; $\text{R} = \text{Me, Pr, CF}_3\text{CH}_2\text{CH}_2$; $\text{R}_F = \text{CF}_3, \text{C}_4\text{F}_9$; $\text{Ar} = \text{Ph, 4-}t\text{-BuC}_6\text{H}_4, \text{4-MeOC}_6\text{H}_4, \text{4-ClC}_6\text{H}_4, \text{2,6-Me}_2\text{C}_6\text{H}_3$.

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 ($n = 1, \text{R}_F = \text{CF}_3\text{CH}_2\text{CH}_2$), 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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