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Catalytic Methods for Synthesis of (Polyfluoroalkyl)-Arylchlorophosphates and Unsymmetrical Bis(Polyfluoroalkyl)Arylphosphates and Their Stereochemistry

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CATALYTIC METHODS FOR SYNTHESIS OF (POLYFLUOROALKYL)-ARYLCHLOROPHOSPHATES AND UNSYMMETRICAL BIS(POLY-FLUOROALKYL)ARYLPHOSPHATES AND THEIR STEREOCHEMISTRY

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Catalytic methods for the synthesis of (polyfluoroalkyl)arylchlorophosphates (I) have been developed

Ar =
$$C_6H_5$$
, 2,6-(CH₃)₂C₆H₃, 4-ClC₆H₄, napht-1-yl; $R_F = CF_3$, n-C₆F₁₃, cyclo-C₆F₁₁; $R = H$, CH₃

The chloridates (I) were found to react with 1,1-dihydropolyfluoroalkanols to give unsymmetrical bis(polyfluoroalkyl)arylphosphates (II) under catalytic phosphorylation conditions.

ArOP(O)(Cl)OCHRR_F + R'_FCH₂OH
$$\xrightarrow{\text{Cat.,to}}$$
 ArO(R'_FCH₂O)P(O)OCHRR_F
(I)
(II)
$$R'_{F} = CF_{3}, \text{ n-C}_{4}F_{9}$$

It has been shown that in the case of chlorophosphates (I, $R = CH_3$) (which are the statistical mixtures of two diastereomers), the nucleophilic substitution of chlorine atoms by primary polyfluoroalkyl groups proceeds stereoselectively, and in the phosphates (II) the diastereomers ratio differs essentially from statistical one.

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