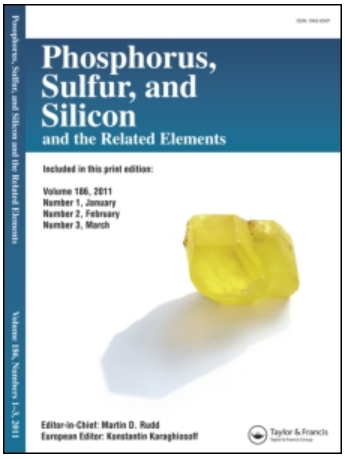

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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

Martin I. Kabachnik[a]; Leonid S. Zakharov[a]; Evgenii I. Goryunov[a]; Mikhail A. Kurykin[a]; Galina N. Molchanova[a]; Svetlana A. Kal'fa[a]; Pavel V. Petrovskii[a]; Tatyana M. Shcherbina[a]; Anna P. Laretina[a]
[a] Nesmeyanov Institute of Organoelement Compounds, the Russian Academy of Sciences, Moscow, Russia

To cite this Article Kabachnik, Martin I. , Zakharov, Leonid S. , Goryunov, Evgenii I. , Kurykin, Mikhail A. , Molchanova, Galina N. , Kal'fa, Svetlana A. , Petrovskii, Pavel V. , Shcherbina, Tatyana M. and Laretina, Anna P.(1996) 'Catalytic Methods for Synthesis of (Polyfluoroalkyl)-Arylchlorophosphates and Unsymmetrical Bis(Polyfluoroalkyl)Arylphosphates and Their Stereochemistry', Phosphorus, Sulfur, and Silicon and the Related Elements, 111: 1, 111
To link to this Article: DOI: 10.1080/10426509608054740
URL: http://dx.doi.org/10.1080/10426509608054740

Phosphorus, Sulfur, and Silicon, 1996, Vol. 111, p. 111
Reprints available directly from the publisher
Photocopying permitted by license only

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

MARTIN I. KABACHNIK, LEONID S. ZAKHAROV, EVGENII I. GORYUNOV, MIKHAIL A. KURYKIN, GALINA N. MOLCHANOVA, SVETLANA A. KAL'FA, PAVEL V. PETROVSKII, TATYANA M. SHCHERBINA, AND ANNA P. LARETINA

Nesmeyanov Institute of Organoelement Compounds, the Russian Academy of Sciences, ul. Vavilova 28, Moscow, 117334 Russia

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

$$\begin{matrix} ArOH + R_FCHROPOCl_2 \\ R_FCHROH + ArOPOCl_2 \end{matrix} \xrightarrow{Cat., t^o} ArOP(O)(Cl)OCHRR_F \quad (I)$$

Ar = C_6H_5, 2,6-$(CH_3)_2C_6H_3$, 4-ClC_6H_4, napht-1-yl; $R_F = CF_3$, n-C_6F_{13}, cyclo-C_6F_{11}; R = H, CH_3

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

$$\underset{(I)}{ArOP(O)(Cl)OCHRR_F} + R'_FCH_2OH \xrightarrow{Cat.,t^o} \underset{(II)}{ArO(R'_FCH_2O)P(O)OCHRR_F}$$

$R'_F = CF_3$, n-C_4F_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.

This research was made possible in part by Grant No. MSF 000 from the International Science Foundation.