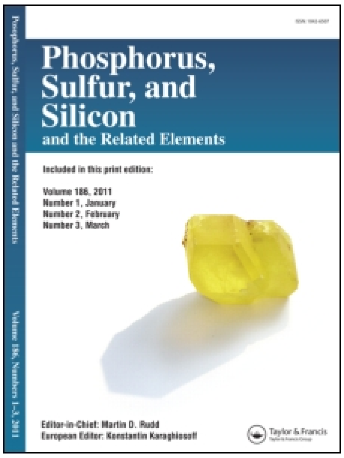

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis and Stereochemistry of some New Unsymmetrical Phosphates with α-Poly-fluoroalkylbenzyl Fragments

M. I. Kabachnik[a]; L. S. Zakharov[a]; E. I. Goryunov[a]; P. V. Petrovskii[a]; T. M. Shcherbina[a]
[a] A. N. Nesmeyanov Institute of Organo-Element Compounds, USSR Academy of Sciences, Moscow, USSR

To cite this Article Kabachnik, M. I. , Zakharov, L. S. , Goryunov, E. I. , Petrovskii, P. V. and Shcherbina, T. M.(1987) 'Synthesis and Stereochemistry of some New Unsymmetrical Phosphates with α-Poly-fluoroalkylbenzyl Fragments', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 3, 689

To link to this Article: DOI: 10.1080/03086648708079183

URL: http://dx.doi.org/10.1080/03086648708079183

Synthesis and Stereochemistry of some New Unsymmetrical Phosphates with α-Poly-fluoroalkylbenzyl Fragments

M.I.Kabachnik*, L.S.Zakharov, E.I.Goryunov, P.V.Petrovskii,
T.M.Shcherbina
A.N.Nesmeyanov Institute of Organo-Element Compounds,
USSR Academy of Sciences, Vavilov Str. 28, Moscow, USSR.

The methods of synthesis unsymmetrical polyfluoroalkyl phosphates (II) by catalytic phosphorylation of phenols or polyfluoroalkanols by chlorophosphates (I) were elaborated

$$\underset{\text{(I)}}{(ArO)(Ar'\overset{*}{C}HR_FO)\overset{*}{P}OCl} + ROH \xrightarrow{\text{Cat., t°}} \underset{\text{(II)}}{(ArO)(Ar'\overset{*}{C}HR_FO)\overset{*}{P}(O)OR}$$

$$R = R_F{}'CH_2 \text{ or } Ar''$$

The stereochemistry of this reaction was studied by NMR and GLC. Where as all parent chlorophosphates (I) were equilibrium mixtures of diastereomers with statistical ratio (I:I) in the case of phosphates (II), on the contrary, essential prevalence (20-30%) of one of the two diastereomers was observed.

Preferable formation of the definite diastereomer (namely one of the two meso-forms) also takes plase in the synthesis of phosphates (IV) with pseudoasymmetrical phosphorus atom by catalytic phosphorylation of polyfluoroalkanols by chlorophosphates (III) with statistical component ratio (I:2:I)

$$\underset{\text{(III)}}{(Ar\overset{*}{C}HR_FO)_2\overset{*}{P}OCl} + R_F{}'CH_2OH \xrightarrow{\text{Cat., t°}} \underset{\text{(IV)}}{(Ar\overset{*}{C}HR_FO)_2\overset{*}{P}(O)OCH_2R_F{}'}$$

In all cases the stereoselectivity is of general nature and is due to both intertransformation of diastereomers of the parent chlorophosphates (I) or (III), and different interaction rates of these diastereomers with nucleophiles.