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

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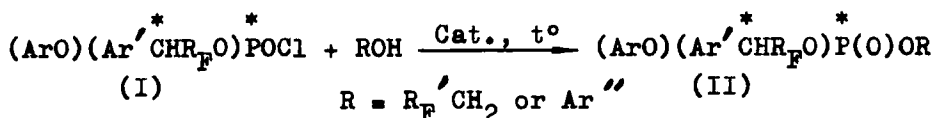
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Synthesis and Stereochemistry of some New Unsymmetrical Phosphates with α -Poly-fluoroalkylbenzyl Fragments

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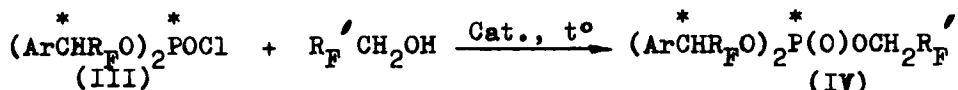
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The methods of synthesis unsymmetrical polyfluoroalkyl phosphates (II) by catalytic phosphorylation of phenols or polyfluoroalkanols by chlorophosphates (I) were elaborated



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 (1:1) 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 place in the synthesis of phosphates (IV) with pseudoasymmetrical phosphorus atom by catalytic phosphorylation of polyfluoroalkanols by chlorophosphates (III) with statistical component ratio (1:2:1)



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.