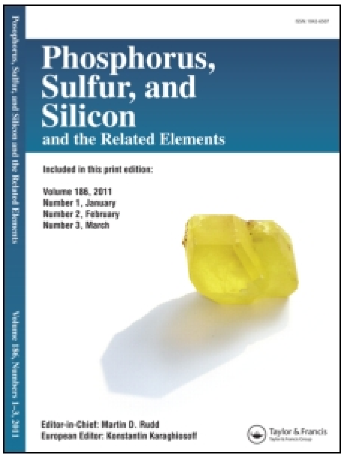

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Reactions of Tris(Perfluoroalkyl)Difluorophosphoranes and Their Derivatives with Nucleophilic Reagents

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REACTIONS OF TRIS(PERFLUOROALKYL)DIFLUOROPHOSPHORANES AND THEIR DERIVATIVES WITH NUCLEOPHILIC REAGENTS

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This paper is concerned with the reactions of $(R_f)_3PF_2$ and $(R_f)_3PO$ with N-, O-, C-nucleophiles and fluoride ion. Either the replacement of one or two perfluoroalkyl radicals by different functional groups or the addition of reagent to electrophilic phosphorus occurs. These phosphinic oxides and phosphoranes readily add fluoride-ion with the expansion of phosphorus coordination: the former produces phosphoranes of a new type $(R_f)_3P(F)O^-Cs^+$, while the latter stable substituted fluorophosphates of general formula $M^+[(R_f)_3PF_3]^-$. Based on these salts it was possible to synthesize aryldiazonium tris(perfluoroalkyl)trifluorophosphates, whose thermal decomposition leads to the formation of substituted fluorobenzenes with high yields. The reaction is a convenient modification of the Shieman method. The approaches of the synthesis of phosphoranes containing simultaneously both perfluoroalkyl groups and nonfluorinated radicals are developed due to the reactions of tris(perfluoroalkyl)difluorophosphoranes with the lithium-organic compounds. The replacement of either fluorine atom or perfluoroalkyl radical by the nonfluorinated group depends on the lithium reagent nature:

$$(R_f)_2PF_2(Ar) \xleftarrow{ArLi} (R_f)_3PF_2 \xrightarrow{AlkLi} (R_f)_3PF(Alk)$$

A number of bis(perfluoroalkyl)phosphinic and perfluoroalkylphosphonic amides and esters are obtained by the action of N- and O-nucleophiles on tris(perfluoroalkyl)phosphinic oxides. As a result of the presence of strong electron-acceptor substituents in the phosphorus atom these products are of practical value.