Bis(1-perfluoroalkylethyl)chlorophosphates as phosphorylating agents. The first examples of stereoselective substitution of the Cl atom at the pseudoasymmetric phosphorus atom

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We have previously shown that the catalytic phosphorylation of 1-(perfluoroalkyl)ethanols $\mathrm{MeCHR_FOH}$ with phosphorus oxychloride carried out at a definite ratio of the reactants mainly affords phosphoryl monochlorides $(\mathrm{MeCHR_FO})_2\mathrm{POCl}$ (**1**). The P atom in these compounds is pseudoasymmetric, and they exist as mixtures of three diastereomers, namely, the racemic form and two *meso*-forms (**A** and **B**); these forms are always present in the ratio 2 : 1 : 1, respectively.[1,2]

We found that these phosphoryl chlorides phosphorylate primary polyfluoroalkanols $\mathrm{R_F'CH_2OH}$ (**2a—c**) to give nonsymmetric phosphates **3a—f** in 88—96 % yields.

$$\underset{\mathbf{1a,\,b}}{(\mathrm{MeCHR_FO})_2\mathrm{POCl}} + \underset{\mathbf{2a-c}}{\mathrm{R_F'\,CH_2OH}} \xrightarrow{120-140\ ^{\circ}\mathrm{C,\ Mg}} \underset{\mathbf{3a-f}}{(\mathrm{MeCHR_FO})_2\mathrm{P(O)OCH_2R_F'}}$$

1: $\mathrm{R_F} = \mathrm{CF_3}$ (**a**), *cyclo*-$\mathrm{C_6F_{11}}$ (**b**)

2: $\mathrm{R_F'} = \mathrm{CF_3}$ (**a**), $\mathrm{C_2F_5}$ (**b**), *n*-$\mathrm{C_6F_{13}}$ (**c**)

3: $\mathrm{R_F} = \mathrm{CF_3}$ (**a—c**), *cyclo*-$\mathrm{C_6F_{11}}$ (**d—f**);
$\mathrm{R_F'} = \mathrm{CF_3}$ (**a, d**), $\mathrm{C_2F_5}$ (**b, e**), *n*-$\mathrm{C_6F_{13}}$ (**c, f**)

The P atom in phosphates **3** remains pseudoasymmetric; according to ^{31}P NMR data, these compounds also exist as mixtures of three diastereomers (Table 1), but the ratio of the latter is determined by the structures of the starting reagents. For example, substitution of the Cl atom in compound **1a** occurs nonstereoselectively irrespective of the chain length of the $\mathrm{R_F'}$ radical in the alcohol to be phosphorylated, and the ratio of diastereomers in compounds **3a—c** remains virtually statistical. Phosphoryl chloride **1b** reacts with 2,2,2-trifluoroethanol **2a** in a similar way; however, when alcohols **2b,c** undergo catalytic phosphorylation with this phosphoryl chloride, the process becomes stereoselective, and the ratio of the two *meso*-forms in the resulting phosphates **3e,f** differs significantly from the statistical value (see Table 1).

Table 1. Parameters of $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra and the diastereomeric composition of phosphates **3a—f**

Compound	δ[a] (content of a diastereomer in the mixture (%))		
	rac-form	*meso*-form **A**	*meso*-form **B**
3a[b]	−3.176 s (50)	−3.805 s (26)	−3.859 s (24)
3b[b]	−3.119 s (50)	−3.805 s (26)	−3.890 s (24)
3c[c]	−3.181 s (50)	−3.919 s (26)	−3.960 s (24)
3d[c]	−4.504 s (50)	−4.852 s (24)	−5.268 s (25)
3e[c]	−4.711 s (51)	−5.106 s (19)	−5.368 s (30)
3f[c]	−4.854 s (49)	−5.152 s (20)	−5.608 s (30)

[a] Obtained on a Bruker WP-200SY spectrometer using 85 % $\mathrm{H_3PO_4}$ as the external standard. [b] In $\mathrm{C_6D_6}$. [c] In a $\mathrm{C_6D_6}$—$\mathrm{CDCl_3}$ mixture.

Thus, we have found the first examples of the stereoselective substitution of the chlorine atom in phosphoryl chlorides that contain a pseudoasymmetric P atom.

This study was financially supported by the International Science Foundation (Grant No. MSF 000).

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Received July 7, 1994

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1683—1684, September, 1994.