CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKANOLS.

15. CATALYTIC PHOSPHORYLATION OF α-POLYFLUOROALKYLBENZYL ALCOHOLS BY BIS(POLYFLUOROALKYL) CHLOROPHOSPHATES

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The catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols by bis(polyfluoroalkyl) chlorophosphates is a convenient method for the synthesis of various bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) phosphates, including those having donor substituents in the benzene ring. It was shown that in the series of p-methyl-α-trifluoromethylbenzyl phosphates p-$CH_3C_6H_4CH(CF_3)OP(O)XY$ (where X, Y = Cl, CF_3CH_2O), the ability to act as O-alkylating agents with respect to polyfluorinated alcohols is a common characteristic, and the alkylating ability increases symbatically with increase in the overall electron-acceptor strength of the X and Y substituents at the phosphorus atom.

We have previously found that the reaction of α-polyfluoroalkylbenzyl dichlorophosphates with primary polyfluoroalkanols under catalytic phosphorylation conditions may serve as a convenient method for the synthesis of several symmetric bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) phosphates [1]

$$RC_6H_4CHR_FOPOCl_2 + R_F'CH_2OH \xrightarrow[-HCl]{Cat,\,t^\circ} RC_6H_4CHR_FOP(O)(OCH_2R_F')_2$$
$$R = m\text{-}CH_3,\ H,\ m\text{-}CF_3,\ m\text{-}NO_2$$

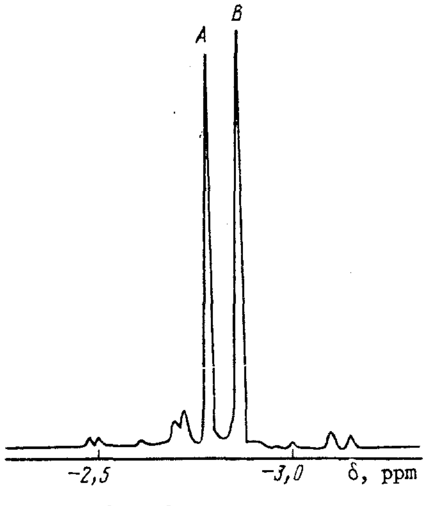

Fig. 1. $^{31}P-\{^1H\}$ NMR spectrum of the reaction mixture formed as a result of the catalytic phosphorylation of benzyl alcohol (IV) by chlorophosphate (III) after chromatography on Al_2O_3.

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TABLE 1. Catalytic Phosphorylation of α-Polyfluoroalkylbenzyl Alcohols by Bis(polyfluoroalkyl) Chlorophosphates

$$(R_FCH_2O)(R_F'CH_2O)POCl + RC_6H_4CHR_F''OH \xrightarrow{\text{Cat, }200°} (R_FCH_2O)(R_F'CH_2O)P(O)(OCHR_F''C_6H_4R)$$

R_F	R_F'	R	R_F''	Catalyst*	Time of reaction, h	Yield, %
CF_3	CF_3	H	CF_3	$CaCl_2$	3,0	83
CF_3	CF_3	H	CF_3	Mg	1,25	86
CF_3	CF_3	H	C_3F_7	Mg	3,0	88
CF_3	CF_3	H	C_4F_9	Mg	3,5	84
CF_3	CF_3	H	$CF_3OCF_2CF_2$	Mg	2,0	78
CF_3	CF_3	m-CH_3	CF_3	Mg	1,25	88
CF_3	CF_3	m-CH_3O	CF_3	Mg	1,5	82
CF_3	CF_3	m-CF_3	CF_3	Mg	2,0	88
C_3F_7	C_3F_7	H	CF_3	$CaCl_2$	4,0	84
CF_3	$H(CF_2)_6$	H	CF_3	Mg	3,0	90

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*A 0.025 mole portion of the catalyst per 1 mole of $(R_FCH_2O)(R_F'CH_2O)POCl$.

TABLE 2. Reaction of p-Methyl-α-trifluoromethylbenzyl Alcohol (XX) with Bis(2,2,2-trifluoroethyl) Chlorophosphate (I) under Catalytic Phosphorylation Conditions

$$\underset{(XX)}{p\text{-}CH_3C_6H_4CH(OH)CF_3} + \underset{(I)}{(CF_3CH_2O)_2POCl} \xrightarrow{Mg,^{*}\ t°} \underset{(XXI)}{p\text{-}CH_3C_6H_4CH(CF_3)OP(O)(OCH_2CF_3)_2} + \underset{(XXII)}{[p\text{-}CH_3C_6H_4CH(CF_3)]_2O} + \underset{(XXIII)}{p\text{-}CH_3C_6H_4CHClCF_3}$$

T, °C	Time, h	(XXI): (XXII): (XXIII) ratio†
200	0,3	55 : 23 : 22 according to $^{19}F\text{-}\{^1H\}$ NMR data
160	1.0	80 : 10 : 10 according to GLC data
120	3,5	93 : 2 : 5 according to GLC data

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*0.025 mole of Mg per mole of (I).

†Ether (XXII) and chloride (XXIII) were identified by comparison with authentic samples, synthesized previously in [7, 2].

It should be noted however that benzyl phosphates containing fairly strong electron-donor substituents in the benzene ring cannot be obtained by this method, since, as we have already shown for p-methyl-α-trifluoromethylbenzyl dichlorophosphate, the corresponding starting benzyl dichlorophosphates are unstable under the catalytic phosphorylation conditions and decompose with the formation of benzyl chlorides [2]. Moreover, this method cannot be applied for the synthesis of phosphates containing nonidentical primary polyfluoroalkyl radicals.

It was found in the present investigation, that the catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols by bis(polyfluoroalkyl) chlorophosphates having both symmetric and asymmetric structures is a more general method, free of the above indicated limitations, for the synthesis of bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) phosphates.

Thus, it was found that the phosphorylation by chlorophosphates (I)-(III) of benzyl alcohols (IV)-(X), both unsbustituted and those containing acceptor (m-CH_3O and m-CF_3) or weakly donor (m-CH_3) substituents in the benzene ring, in the presence of anhydrous $CaCl_2$ or metallic magnesium as the catalyst, proceeds with the exclusive formation of the phosphorylation products – bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) phosphates (XI)-(XIX)– despite the rigorous reaction conditions (200°C)

TABLE 3. Bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) Phosphates $(R_FCH_2O)(R_F'CH_2O)P(O)(OCHR_F''C_6H_4R)$

Compound	R_F	R_F'	R_F''	R	Bp, °C (p, mm Hg)	n_D^{20}	d_{20}^4	Found/Calculated, %				Empirical formula
								C	H	F	P	
(XI)	CF_3	CF_3	CF_3	H	113,5–115 (8)	1,3942	1,4834	34,6/34,3	2,5/2,4	40,8/40,7	7,3/7,4	$C_{12}H_{10}F_9O_4P$
(XII)	CF_3	CF_3	C_3F_7	H	89–90 (0,5)	1,3784	1,5478	32,7/32,3	2,0/1,9	–	6,0/6,0	$C_{14}H_{10}F_{13}O_4P$
(XIII)	CF_3	CF_3	C_4F_9	H	87,5–88 (0,3)	1,3735	1,5780	31,5/31,6	1,8/1,8	49,8/50,0	5,5/5,4	$C_{15}H_{10}F_{15}O_4P$
(XIV)	CF_3	CF_3	$CF_3OCF_2CF_2$	H	80–81 (0,01)	1,3739	1,5499	31,3/31,4	1,6/1,9	46,0/46,1	5,7/5,8	$C_{14}H_{10}F_{13}O_5P$
(XV)	CF_3	CF_3	CF_3	*m*-CH_3	95–96 (1)	1,3976	1,4494	36,1/36,0	2,7/2,8	39,2/39,4	7,1/7,1	$C_{13}H_{12}F_9O_4P$
(XVI)	CF_3	CF_3	CF_3	*m*-CH_3O	107–108 (1)	1,4068	1,4915	34,7/34,7	2,7/2,7	37,5/38,0	6,6/6,9	$C_{13}H_{12}F_9O_5P$
(XVII)	CF_3	CF_3	CF_3	*m*-CF_3	94–95 (1)	1,3780	1,5589	32,0/32,0	1,9/1,9	46,6/46,7	6,3/6,3	$C_{13}H_9F_{12}O_4P$
(XVIII)	C_3F_7	C_3F_7	CF_3	H	98–100 (0,1)	1,3645	1,5920	31,1/31,0	1,6/1,6	52,4/52,1	5,2/5,0	$C_{16}H_{10}F_{17}O_4P$
(XIX)	CF_3	$H(CF_2)_6$	CF_3	H	132,5–133,5 (1)	1,3732	1,6273	31,3/31,3	1,8/1,7	–	4,8/4,8	$C_{17}H_{11}F_{18}O_4P$
(XXI)	CF_3	CF_3	CF_3	*p*-CH_3	97–98 (1)	1,3989	1,4474	36,0/36,0	2,8/2,8	39,2/39,4	7,1/7,1	$C_{13}H_{12}F_9O_4P$

$$(\mathrm{R_FCH_2O})(\mathrm{R_F'CH_2O})\mathrm{POCl} + \mathrm{RC_6H_4CHR_F''OH} \xrightarrow[-\mathrm{HCl}]{\text{Cat, 200°C}}$$

(I)—(III) (IV)—(X)

$$\rightarrow (\mathrm{R_FCH_2O})(\mathrm{R_F'CH_2O})\mathrm{P(O)(OCHR_F''C_6H_4R)}$$

(XI)—(XIX)

$R_F = R_F' = CF_3$ (I); $R_F = R_F' = C_3F_7$ (II); $R_F = CF_3$, $R_F' = (CF_2)_6H$ (III); $R = H$, $R_F'' = CF_3$ (IV); $R = H$, $R_F'' = C_3F_7$ (V); $R = H$, $R_F'' = C_4F_9$ (VI); $R = H$, $R_F'' = CF_3OCF_2CF_2$ (VII); $R = m\text{-}CH_3$, $R_F'' = CF_3$ (VIII); $R = m\text{-}CH_3O$, $R_F'' = CF_3$ (IX); $R = m\text{-}CF_3$, $R_F'' = CF_3$ (X); $R = H$, $R_F = R_F' = R_F'' = CF_3$ (XI); $R = H$, $R_F = R_F' = CF_3$, $R_F'' = C_3F_7$ (XII); $R = H$, $R_F = R_F' = CF_3$, $R_F'' = C_4F_9$ (XIII); $R = H$, $R_F = R_F' = CF_3$, $R_F'' = CF_3OCF_2CF_2$ (XIV); $R = m\text{-}CH_3$, $R_F = R_F' = R_F'' = CF_3$ (XV); $R = m\text{-}CH_3O$, $R_F = R_F' = R_F'' = CF_3$ (XVI); $R = m\text{-}CF_3$, $R_F = R_F' = R_F'' = CF_3$ (XVII); $R = H$, $R_F = R_F' = C_3F_7$, $R_F'' = CF_3$ (XVIII); $R = H$, $R_F = R_F'' = CF_3$, $R_F' = (CF_2)_6H$ (XIX).

The conditions of the catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols by bis(polyfluoroalkyl) chlorophosphates and the yields of the phosphorylation products are given in Table 1.

The data in Table 1 show that the rate of phosphorylation is maximal for α-trifluoromethylbenzyl alcohol (IV) and its m-methyl-substituted homolog (VIII), and decreases with increase in the acceptor character of the substituent in the benzene ring, which is clearly due to decrease in the nucleophilicity of the phosphorylating agent. A similar effect, i.e., decrease in the reaction rate, is also caused by chain elongation of the α-polyfluoroalkyl radical. However, in this case the reason for this decrease in rate is, probably, mainly the increase in steric hindrances, although the substantially higher rate of phosphorylation of alcohol (VII) (containing an oxygen bridge in the α-polyfluoroalkyl chain), compared with alcohols (V) and (VI), also indicates that the nature of the α-polyfluoroalkyl radical noticeably influences the rate of the reaction. The decrease in the rate of phosphorylation of alcohol (IV) when the chain length of one or two polyfluoroalkyl groups is increased in monochlorophosphates (III) and (II) is most likely also related to the influence of steric forces.

Despite the fact that in the reaction systems studied both catalysts ($CaCl_2$ and Mg) eventually dissolve completely, metallic Mg showed an appreciably higher effectiveness. We have previously observed a higher effectiveness of Mg or its salts, compared with $CaCl_2$ during the phosphorylation of α-polyfluoroalkylbenzyl alcohols by $POCl_3$ [3], polyfluoroalkyl dichlorophosphates [4] and aryl chlorophosphates [5, 6], and this is fairly general in character.

The catalytic phosphorylation of p-methyl-α-trifluoromethylbenzyl alcohol (XX) by chlorophosphate (I) is much more complex and is strongly dependent on temperature (see Table 2). At 200°C, the reaction of equimolar amounts of (I) and (XX) in the presence of Mg as catalyst leads, according to the TLC, GLC, and ^{19}F-{^1H} spectral data to a mixture of bis(2,2,2-trifluoroethyl)(p-methyl-α-trifluoromethylbenzyl) phosphate (XXI), di-p-methyl-α-trifluoromethylbenzyl ether (XXII), and p-methyl-α-trifluoromethylbenzyl chloride (XXIII); with decrease in the reaction temperature to 160°C, a decrease in the amount of the by-products (XXII) and (XXIII) formed is observed, and at 120°C, the reaction mixture consists almost exclusively of phosphate (XXI) and contains only traces of the ether and the chloride.

Phosphates (XI)-(XIX), (XXI) obtained are mobile colorless liquids, which are highly soluble in organic solvents and insoluble in water. The physical constants of bis(polyfluoroalkyl) (α-polyfloroalkylbenzyl) phospahtes and the elemental analysis data are given in Table 3.

The structure of the compounds obtained was confirmed by the ^{31}P NMR spectral and mass spectral data (see Table 4). In the mass spectra of bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) phosphates the peak of the molecular ion is absent (except for the m-methoxy-substituted phosphate (XVI)), while $[M-HF]^+$, $[RC_6H_4CHR_F'']^+$ and $[M-R_F'']^+$ are the main fragmentary ions, i.e., at least two alternative types of decomposition are observed for the benzyl fragment of the molecule of the phosphates: with the cleavage of the $ArCHR_F''{-}O$ bond or $ArCH{-}R_F''$ bond. In the series of phosphates (XI)-(XIII), the relative intensity of the $[M-R_F'']^+$ ions increases, while the relative intensity of the $[C_6H_5CHR_F'']$ ions decreases symbatically with the increase in the chain length of the α-polyfluoroalkyl radical R_F''.

Phosphate (XIX), whose molecule contains two asymmetric centers – the benzyl carbon atom and the phosphorus atom, according to ^{31}P-{^1H} NMR (Fig. 1), ^{19}F NMR data and chromato-mass spectra comprises a mixture of two diastereomers A and B, formed in ~48:52 ratio, i.e., only

TABLE 4. ^{31}P NMR and Mass Spectral Data of Bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) Phosphates $(R_FCH_2O)(R_F'CH_2O)-P(O)OCHR_F''C_6H_4R$

Compound	$^{31}P-\{^1H\}$ NMR spectrum (CCl_4, δ, ppm)	Mass spectrum m/z (relative intensity, %)			
		$[M]^+$	$[M-HF]^+$	$[M-R_F'']^+$	$[RC_6H_4CHR_F'']^+$
(XI)	−2,60 s	–	400(82)	351(8)	159(100)
(XII)	−2,81 s	–	500(100)	351(37)	259(61)
(XIII)	−2,75 s	–	550(100)	351(53)	309(29)
(XIV)	−2,71 s	–	516(100)	351(29)	275(28)
(XV)	−2,41 s	–	414(96)	365(13)	173(100)
(XVI)	−2,76 s	450(63)	430(100)	381(7)	189(48)
(XVII)	−2,65 s	–	468(100)	419(13)	227(66)
(XVIII)	−2,86 s	–	600(100)	551(4)	159(35)
(XIX) *A*	−2,165 s*	–	632(34)	583(3)	159(35)
B	−2,242 s*	–	632(40)	583(5)	159(38)
(XXI)	−2,58 s	–	414(100)	365(16)	173(99)

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*In a C_6H_6 solution.

TABLE 5. PMR Spectrum (in C_6D_6) of 2,2,2-Trifluoroethyl)(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)(α-trifluoromethylbenzyl) Phosphate $C_6H_5C^*H(CF_3)-OP^*(O)(OCH_AH_BCF_3)[OCH_AH_B(CF_2)_6H]$ (XIX)

Fragment	Parameter (δ, ppm; J and Δv, Hz)	Diastereomer A	Diastereomer B
$CHCF_3$	δ	5,649 d.q	5,640 d.q
	J_{H-F}	6,3	6,3
	J_{H-P}	9,8	9,8
$H(CF_2)_6$	δ	5,316 t.t	5,339 t.t
	$^2J_{H-F}$	51,6	51,6
	$^3J_{H-F}$	5,1	5,0
$CH_AH_BCF_3$	δH_A	4,043 m	3,785 m
	δH_B	3,916 m	3,655 m
	$\Delta\nu H_AH_B$	25,6	26,2
	$J_{H_AH_B}$	12,1	12,1
	J_{H_A-F}/J_{H_B-F}	8,1/8,1	8,1/8,1
	J_{H_A-P}/J_{H_B-P}	8,1/8.1	8,1/8,1
$CH_AH_B(CF_2)_6$	δH_A	4,034 m	4,303 m
	δH_B	3,886 m	4,187 m
	$\Delta\nu H_AH_B$	29,7	23,3
	$J_{H_A-H_B}$	12,9	12,9
	$^3J_{H_A-F}/^3J_{H_B-F}$	12,9/13,0	12,8/13,0
	J_{H_A-P}/J_{H_B-P}	8,0/8,0	8,1/8,1
C_6H_5	δ	6,96—7,29 m	

differing from the statistical value. In the PMR spectrum (Table 5), the doubling of the proton signals of the CHF_3 and $(CF_2)_6H$ groups also indicates the presence of two diastereomers in the mixture. The section of the spectrum in the region of the OCH_2R_F group protons is much more complex in character. This signal represents a superposition of four multiplets: two multiplets of type ABM_3X and two of type ABM_2X (in both cases, M is the ^{19}F atom, and X is the ^{31}P atom). This character of the spectrum indicates that together with the phenomenon of the diastereomeric anisochronism (DA), which leads to doubling of signals belonging to two nonidentical OCH_2R_F groups, the phenomenon of a magnetic nonequivalency of the geminal protons is observed in each of these groups, this nonequivalency taking place for both the diastereomer A and diastereomer B. We should also note the relatively high (0.022 ppm) value of DA for a proton present in the ω-position of a fairly flexible polyfluorocarbon chain, and removed from the nearest asymmetric center, the phosphorus atom – by nine ordinary bonds. The observation of DA at such a great distance is a fairly rare phenomenon, although compounds have recently been described where the DA appears in the ^{31}P NMR spectra even when the asymmetric centers are removed from one another as much as 11 bonds distance [8].

Thus, the catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols by bis(polyfluoroalkyl) chlorophosphates is a simple and convenient method of synthesis, by which most diverse bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) phosphates can be obtained, also including (by the corresponding selection of the reaction conditions) compounds having donor substituents in the benzene ring.

With regard to the by-products formed together with phosphate (XXI) in the reaction of p-methyl-substituted alcohol (XX) with acid chloride (I), we have previously in some cases observed the presence of benzyl ethers among the reaction products, for example, during the study of the catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols by $POCl_3$ [7] or by $R_FCH_2OPOCl_2$ [4]. It was found that ethers are obtained as a result of the alkylation of the starting alcohols by the corresponding benzyl chlorophosphate formed in these reactions [2, 4].

It can be assumed that also in the present case the formation of benzyl ether proceeds by a similar scheme, whereby the completely esterified phosphate (XXI) acts as the alkylating agent. To verify this supposition, we studied the reaction of alcohol (XX) with phosphate (XXI) at the temperature at which the catalytic phosphorylation reaction is carried out.

In fact, at 200°C, phosphate (XXI) vigorously alkylates benzyl alcohol (XX) (the reaction is completed even after 1.5 h), as a result of which, according to the TLC and GLC data, together with several unidentified compounds, ether (XXII) is obtained. At 160°C, the alkylation proceeds at a considerably lower rate, but in this case the reaction is practically unaccompanied by the formation of by-products, and the ether can be isolated in a pure state. Finally, at 120°C the alkylation process is so much slowed down that even a 40 h long reaction of (XX) with (XXI) leads according to the GLC data, only to traces of the ether

$$\underset{(XX)}{p\text{-}CH_3C_6H_4CH(CF_3)OH} + \underset{(XXI)}{p\text{-}CH_3C_6H_4CH(CF_3)OP(O)(OCH_2CF_3)_2} \xrightarrow{t^\circ} \underset{(XXII)}{[p\text{-}CH_3C_6H_4CH(CF_3)]_2O}$$

When the alcohol and phosphate were heated separately, the formation of the ether was not observed even at 200°C, but while alcohol (XX) in general does not change under these temperature conditions, phosphate (XXI) completely decomposes after 7 h (fairly rapidly for polyfluoroalkyl esters of phosphorus acid*) whereby, according to the TLC data, several of the decomposition products were identical with compounds obtained together with the ether obtained during the alkylation of alcohol (XX) at 200°C.

The ability of phosphate (XXI) to act as an alkylating agent with respect to a polyfluorinated alcohol, and also a similar ability which we previously discovered in the case of p-methyl-α-trifluoromethylbenzyl dichlorophosphate (XXIV) [2] and (2,2,2-trifluoroethyl)(p-methyl-α-trifluoromethylbenzyl) chlorophosphate (XXV) [4] indicates that the tendency to participate in the O-alkylation reactions, in general not characteristic for polyfluoroalkyl esters of phosphorus acids, in the series of p-methyl-α-trifluoromethylbenzyl phosphates is more or less general in character.

$$p\text{-}CH_3C_6H_4CH(CF_3)OP(O)XY$$
$$X = Y = OCH_2CF_3\ (XXI);\ X = Y = Cl\ (XXIV);\ X = Cl,$$
$$Y = OCH_2CF_3\ (XXV);\ X = Y = OC_6H_5\ (XXVI)$$

At the same time, the alkylation conditions are substantially dependent on the nature of the alkylating agent. Thus, dichlorophosphate (XXIV) alkylates alcohol (XX) even at 95°C [2], monochlorophosphate (XXV) at 120°C [4], while the completely esterified phosphate (XXI) displays an alkylating action with respect to this alcohol only at a temperature of ≥160°C. In the case of diphenyl (p-methyl-α-trifluoromethylbenzyl) phosphate (XXVI), the alkylation reaction was not observed, even at 200°C [5].

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*In the case of bis(2,2,2-trifluoroethyl)(α-trifluoromethylbenzyl) phosphate (XI) unsubstituted in the benzene ring, no indications of the thermal decomposition were observed, according to the TLC and GLC data, even under more rigorous conditions (200°C, 10 h).

Thus, the alkylating ability of p-methyl-α-trifluoromethylbenzyl phosphates decreases in the series (XXIV) > (XXV) > (XXI) ≫ (XXVI), i.e., it changes symbatically with decrease in the overall acceptor strength of substituents X and Y at the phosphorus atom.* This agrees with the scheme proposed by us [7] for the alkylation of α-polyfluoroalkylbenzyl aclohols by α-polyfluoroalkylbenzyl phosphates, including the heterolysis of the C–OP bond of the phosphate. It is natural that the occurrence of this heterolysis should be facilitated with increase in the acceptor strength of substituents X and Y. The initial α-polyfluoroalkylbenzyl alcohols (IV)-(X), (XX) [11, 5, 1] and also the monochlorophosphate (II) [12] were obtained by known methods.

The symmetrical chlorophosphate (I) was synthesized by catalytic phosphorylation of 2,2,2-trifluoroethanol (XXVII) by $POCl_3$; in addition to (I), considerable amounts of 2,2,2-trifluoroethyl dichlorophosphate (XXVIII) and tris(2,2,2-trifluoroethyl) phosphate (XXIX) were isolated from the reaction mixture

$$\underset{(XXVII)}{CF_3CH_2OH} + POCl_3 \xrightarrow[-HCl]{CaCl_2,\ t^\circ} \underset{(XXVIII)}{CF_3CH_2OPOCl_2} + \underset{(I)}{(CF_3CH_2O)_2POCl} + \underset{(XXIX)}{(CF_3CH_2O)_3PO}$$

The asymmetric chlorophosphate (III) was obtained by phosphorylation of 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptan-1-ol (XXX) by an excess of dichlorophosphate (XXVIII) in the presence of metallic magnesium as catalyst at 140°C. This is the first instance of the use of the catalytic phosphorylation method for the synthesis of monochlorophosphates of this type. Bis(2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl)(2,2,2-trifluoroethyl) phosphate (XXXI) was obtained as a by-product

$$\underset{(XXX)}{H(CF_2)_6CH_2OH} + \underset{(XXVIII)}{CF_3CH_2OPOCl_2} \xrightarrow[-HCl]{Mg,\ 140^\circ} \underset{(III)}{CF_3CH_2OP(O)(Cl)OCH_2(CF_2)_6H} + \underset{(XXXI)}{CF_3CH_2OP(O)[OCH_2(CF_2)_6H]_2}.$$

The ratio between (III) and (XXXI) is dependent on the excess of the phosphorylating agent used: at a double excess this ratio is equal to 4.5:1, but when a triple excess of (XXVIII) is used, it changes to 8.6:1. In both cases the excess dichlorophosphate is regenerated from the reaction mixture in close to quantitative yield, and in a state fairly pure for repeated use.

EXPERIMENTAL

The PMR and ^{19}F NMR spectra were run on a Bruker WP-200 SY spectrometer, using as standards TMS (internal) and CF_3COOH (external); the ^{31}P NMR spectra were recorded on Bruker HX-90 and Bruker WP-200SY spectrometers in a pulse regime with noise suppression of the spin–spin interactions of the phosphorus nuclei with protons (85% H_3PO_4 – external standard). The chromatographic separation was carried out on a Varian apparatus with an SE-54 capillary column 15 m long, using an AT-800 ionic trap from the firm Finnigan MAT, and helium as carrier gas; the samples were introduced directly into the column, and the column temperature was raised from 60 to 230°C at a rate of 4 deg/min. The TLC was carried out on Silufol UV-254 plates.

Catalytic Phosphorylation of 2,2,2-Trifluoroethanol (XXVII) by $POCl_3$. A mixture of 200 g (2 moles) of (XXVII), 191 g (1.25 moles) of $POCl_3$ and 2.78 g (25 mmoles) of anhydrous $CaCl_2$ was boiled for 3.5 h and fractionated under vacuum on a Widmer column. Yield, 85.9 g (32%) of (XXVIII), bp 46-46.5°C (20 mm), n_D^{20} 1.3830, d_4^{20} 1.6228. Found: C 11.1; H 1.1; Cl 32.5; F 25.7; P 14.2% $C_2H_2Cl_2F_3O_2P$. Calculated: C 11.1; H 0.9; Cl 32.7; F 26.3; P 14.3%. PMR spectrum (δ, ppm): 4.705 d.q (J_{H-F} = 7.8, J_{H-P} = 11.0 Hz). ^{19}F NMR spectrum (δ, ppm): 2.079 t (J_{H-F} = 7.8 Hz). $^{31}P-\{^1H\}$ NMR spectrum (δ, ppm): 7.931 s.

In addition, 118.5 g (34%) of (I) was isolated, bp 59-60°C (9 mm), n_D^{20} 1.3445, d_4^{20} 1.6054. Found: C 17.3; H 1.5; Cl 12.2; F 40.6; P 10.9%. $C_4H_4ClF_6O_3P$. Calculated: C 17.1; H 1.4; Cl 12.6; F 40.6; P 11.0%. PMR spectrum (δ, ppm): 4.581 d.q (J_{H-F} = 8.0, J_{H-P} = 9.0 Hz). ^{19}F NMR spectrum (δ, ppm): 1.144 t (J_{H-F} = 8.0 Hz). $^{31}P-\{^1H\}$ NMR spectrum (δ, ppm): 4.942 s. The other product isolated was compound (XXIX), yield 34.0 g (8%), bp 82-83°C (11 mm), n_D^{20} 1.3200, d_4^{20} 1.5941 (cf. [13]). PMR spectrum ($CDCl_3$, δ, ppm): 4.426 d.q (J_{H-F} = 8.1, J_{H-P} = 8.1 Hz). ^{19}F NMR spectrum ($CDCl_3$, δ, ppm): –1.004 t (J_{H-F} = 7.9 Hz). $^{31}P-\{^1H\}$ NMR spectrum (δ, ppm) = –2.979 s. Mass spectrum, m/z (rel. intensity, %): $[M + 1]^+$ 345 (29) [M + 1 – HF] 325 (96).

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*The σ^Φ constants for the Cl, OCH_2CF_3 and OC_6H_5 substituents are 0.93 [9], 0.51-0.60 [10] and –0.06 [9], respectively.

Catalytic Phosphorylation of 2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptan-1-ol (XXX) by 2,2,2-Trifluoroethyl Dichlorophosphate (XXVIII). a) A mixture of 8.68 g (0.04 mole) of (XXVIII), 6.64 g (0.02 mole) of (XXX) and 6 mg (0.25 mmole) of Mg was heated for 1.25 h at 140°C and then was fractionated in vacuo. Yield, 5.6 g (55%) of (III), bp 85-86°C (1 mm), n_D^{20} 1.3400, d_4^{20} 1.7519. Found: C 21.2; H 1.0; Cl 6.8; F 55.2; P 6.0%. $C_9H_5ClF_{15}O_3P$. Calculated: C 21.1; H 1.0; Cl 6.9; F 55.6; P 6.0%. PMR spectrum ($CDCl_3$, δ, ppm): 4.437 d.q (CH_2CF_3, J_{H-F} = 7.7, J_{H-P} = 9.5 Hz), 4.575 d.t ($CH_2(CF_2)_6$, J_{H-F} = 13.0, J_{H-P} = 8.8 Hz), 6.010 t.t ($(CF_2)_6H$, $^2J_{H-F}$ = 51.9, $^3J_{H-F}$ = 5.1 Hz). $^{31}P-\{^1H\}$ NMR spectrum (δ, ppm): 5.101 s. Mass spectrum, m/z (rel. intensity, %): $[M + 1]^+$ 515 (10) (^{37}Cl), 513 (21) (^{35}Cl), $[M + 1 - HF]^+$ 495 (10) (^{37}Cl), 493 (34) (^{35}Cl). In addition, 4.2 g (97%) of (XXVIII) was also isolated, bp 68-70°C (45 mm). The still residue was dissolved in 5 ml of ether and the solution was chromatographed on 4 g of Al_2O_3 (eluent: ether), the solvent was evaporated from the eluate, and the residue was distilled under vacuum. Yield 2.0 g (25%) of (XXXI), bp 143-144°C (1 mm), n_D^{20} 1.3287, d_4^{20} 1.7871. Found: C 23.4; H 1.0; P 3.4%. $C_{16}H_8F_{27}O_4P$. Calculated: C 23.8; H 1.0; P 3.8%. PMR spectrum (C_6D_6, δ, ppm): 3.960 d.q (CH_2CF_3, J_{H-F} = 7.9, J_{H-P} = 8.9 Hz), 4.233 d.t ($CH_2(CF_2)_6$, J_{H-F} = 12.9, J_{H-P} = 8.4 Hz), 5.383 t.t $(CF_2)_6H$, $^2J_{H-F}$ = 51.6, $^3J_{H-F}$ = 5.1 Hz). $^{31}P-\{^1H\}$ NMR spectrum (δ, ppm): −3.276 s.

b) A mixture of 13.0 g (0.06 mole) of (XXVIII), 6.64 g (0.02 mole) of (XXX) and 6 mg (0.25 mmoles) of Mg was heated for 2 h at 140°C, and then treated as in the preceding case. Yield 6.4 g (62%) of (III) and 1.2 g (15%) of (XXXI); in addition, 8.4 g (97%) of (XXVIII) was also isolated.

Bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) Phosphates (XI)-(XIX). A mixture of 0.01 mole of α-polyfluoroalkylbenzyl alcohol, 0.01 mole of bis(polyfluoroalkyl) chlorophosphate and 0.25 mmole of the corresponding catalyst was heated for several hours at 200°C, then was cooled, dissolved in 10 ml of ether, and the solution was chromatographed on 4 g of Al_2O_3 (eluent: ether), the solvent was evaporated from the eluate. Distillation of the residue under vacuum gave bis(polyfluoroalkyl)(α-polyfluoroalkylbenzyl) phosphates (XI)-(XIX), the physical constants of which are given in Table 3.

Bis(2,2,2-trifluoroethyl)(p-methyl-α-trifluoromethylbenzyl) Phosphate (XXI). A mixture of 1.9 g (0.01 mole) of (XX), 2.8 g (0.01 mole) of (I) and 6 mg (0.25 mmole) of Mg was heated for 3.5 h at 120°C, and then was treated as in the preceding case. Yield, 3.2 g (74%) of (XXI).

Alkylation of p-Methyl-α-trifluoromethylbenzyl Alcohol (XX) by Bis(2,2,2-trifluoroethyl)(p-methyl-α-trifluoromethylbenzyl) Phosphate (XXI). A mixture of 0.48 g (2.5 mmoles) of (XX) and 1.1 g (2.5 mmoles) (XXI) was heated for 15 h at 160°C. The mixture was then cooled, dissolved in 5 ml of ether and chromatographed on 4 g of Al_2O_3 (eluent: ether). the solvent was removed from the eluate, and the residue was distilled under vacuum. Yield, 0.5 g (56%) of (XXII), bp 112-114°C (1 mm), mp 24-29°C, cf. [7].

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BORYLATION OF α-HYDROXYALKYLPHOSPHINE OXIDES IN THE PRESENCE OF STRONG BASES

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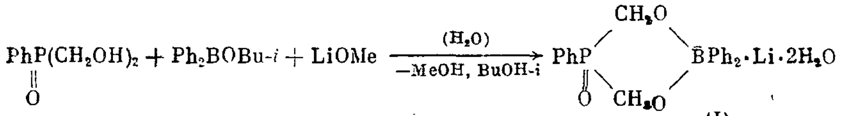
Lithium (sodium) 2,2,5-triphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinanes, forming crystals with two molecules of water, are produced when bis(hydroxymethyl)phenylphosphine oxide is reacted with isobutyl diphenylborate in the presence of metallic sodium or lithium (sodium) alcoholate.

The reaction of bis(α-hydroxyalkyl)phosphine oxides (sulfides) with isobutyl diphenylborate has been accomplished only in the presence of amines [1-3]. It was therefore suggested that amines act catalytically in the borylation reaction of α-hydroxyalkyl derivatives of tetracoordinated phosphorus. The catalytic action of organic bases was demonstrated using the example of primary, secondary, tertiary, functionally substituted amines and ammonia [4]. Amines subsequently undergo reaction with the borylation product, giving the corresponding ammonium oxaborataphosphorinanes.

In the present work, alkali metal alcoholates were used as the reagents catalyzing the borylation of α-hydroxyalkyl derivatives of tetracoordinated phosphorus.

The reaction of bis(hydroxymethyl)phenylphosphine oxide with i-BuOBPh$_2$ in the presence of LiOMe in acetone proceeds at ~20°C, leading to the formation of lithium 2,2,5-triphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinane (I) in 67% yield. It should be emphasized that bis(hydroxymethyl)phenylphosphine oxide does not react with boric ester in the presence of an alcoholate of amine, even on heating. Since the reactions were not carried out in anhydrous solvents, and the reaction mixtures were processed without protection from atmospheric moisture, compound (I) and also (II)-(IV) described below crystallize with two molecules of water.



(I)

The structure of (I) was confirmed by IR and PMR spectroscopy. There are signals in the PMR spectra of the phenyl and methylene protons only, and also signals of protons of water, with the integral intensity of all the signals corresponding to the ascribed structure. In the IR spectra, absorption of the water of crystallization is observed in the region of 1600-1700 cm^{-1}, while the absorption of hydroxyl (3100-3600 cm^{-1}) and B^{III}O (1300-1350 cm^{-1}) groups is absent. The ^{31}P NMR spectra also conform with structure (I).

In this reaction, not only an alcoholate can be used, but also for example metallic Na or NaOH. Thus a Na-salt of boratophosphorinane (II) is formed.

Boratophosphorinane (II) was also obtained by the action of MeONa in acetone on dipropylammonium 2,2,5-triphenyl-5-oxo-1,3,2,5-dioxaborataphosphorinane, which confirms the structure of (II)

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