- 4. R. Hunt and S. T. Reid, J. Chem. Soc. Perkin Trans. 1, 1972, 2527.
- 5. Y. Toki, J. Chem. Soc. Perkin Trans. 2, 1977, 1240.
- 6. A. K. Chibisov, V. A. Kuz'min, G. P. Roitman, I. I. Levkoev, and A. V. Karyakin, Izv. Akad. Nauk SSSR, Ser. Fiz., <u>34</u>, 1288 (1970).
- 7. N. M. Émanuél' and D. G. Knorre, Course in Chemical Kinetics [in Russian], Moscow (1974), p. 116.
- 8. R. Scheerer and M. Grätzel, J. Am. Chem. Soc., 99, 865 (1977).
- 9. A. P. Tomilov, S. G. Mairanovskii, M. Ya. Fioshin, and V. A. Smirnov, Electrochemistry of Organic Compounds [in Russian], Khimiya, Leningrad (1968).

PREPARATION OF O-(POLYFLUOROALKYL) ALKYLCHLOROPHOSPHONATES AND O-(POLYFLUOROALKYL) ARYL CHLOROPHOSPHATES BY CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKANOLS

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The full polyfluoroalkyl esters of alkylphosphonic and aryl phosphoric acids can be obtained by the catalytic phosphorylation of polyfluoroalkanols with the dichlorides of these acids [1, 2]. At the same time, the corresponding ester-acid chlorides are difficultly available; information exists only on the O-(fluoroalkyl) alkylchlorophosphonates, which are formed by treating the mixed alkyl fluoroalkyl esters of alkylphosphonic acids with PCl_s [3]. Taking into account the fact that the ester-acid chlorides of phosphorus acids, which contain polyfluoroalkyl groups, can be used as phosphorylating agents to synthesize the unsymmetrical esters of these acids, we examined on the example of 1,1-dihydroperfluoroamyl alcohol (I) the possibility of using the catalytic phosphorylation method to obtain such ester-acid chlorides directly from polyfluorinated alcohols and the dichlorides of phosphorus acids.

As study objects we selected the readily available methylphosphonic dichloride (II) and phenyl dichlorophosphate (III). In order to hinder the formation of the full esters, a double excess of the phosphorylating agent was used. As catalysts we used the salts of the Group II metals of the periodic system, which proved to be best for the catalytic phosphorylation of polyfluoroalkanols [1, 2].

In the case of acid chloride (II) it proved that the magnesium and calcium salts, which are readily soluble in the reaction mixture, have approximately the same efficiency. Thus, when (I) is heated with excess (II) at 100°C in the presence of 1-4 mole% of either MgSO₄ or CaCl₂ we isolated O-(1,1-dihydroperfluoroamy1) methylchlorophosphonate in 59-65% yield (see [4]), together with 10-17% of 0,0-di(1,1-dihydroperfluoroamy1) methylphosphonate (V). As regards BaCl₂, which is practically insoluble in the reaction mixture, then its catalytic activity proved to be exceedingly low and reaction is not complete even after 15 h at 100°, while the yield of (IV) is only 29%.

$$\begin{array}{c} C_4F_9CH_2OH + CH_3POCl_2 \xrightarrow[-HCl]{-HCl} & CH_3P(O)Cl(OCH_2C_4F_9) + & CH_3P(O)(OCH_2C_4F_9)_2 \\ (I) & (II) & (IV) & (V) \end{array}$$

In a similar manner, when (I) is heated with excess (III) in the presence of CaCl₂ at 120° the main product is 0-(1,1-dihydroperfluoroamy1) phenyl chlorophosphate (VI). Besides (VI), we also isolated 0,0-di(1,1-dihydroperfluoroamy1) phenyl phosphate (VII) from the reaction mixture.

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TABLE 1. NMR Spectral Data for 1,1-Dihydroperfluoroamy1 Esters RP(0)(OCH₂C₄F₉)X

Com- pound	R	x	PMR spectrum (8, ppm)*			³¹ P NMR
			CH ₃ P	P—OCH ₂ C ₄ F ₉	C ₆ H ₅ O—P	(\$, ppm)
(IV)	СН₃	CI	2,08 d $J_{\text{H-P}}=18,0 \text{ Hz}$	4,73 m $J_{\text{H}-P}=9,0,$ $J_{\text{H}-F}=13,4 \text{ Hz}$	-	-42,32
(V)	CH3	C ₄ F ₉ CH ₂ O	1,60 d J _{H-P} =18,3 Hz	$J_{H-F} = 13,4 \text{ Hz}$ 4,60 m $J_{H-P} = 8,6,$ $J_{H-F} = 13.4 \text{ Hz}$	-	-33,71 *
(VI)	C ₆ H ₅ O	Cl	-	4,78 m $J_{\text{H}-P}=9,0,$	7,38 †	+0,74
(VII)	C ₆ H ₅ O	C₄F9CH2O	-	$J_{H-F} = 13,0 \text{ Hz}$ 4,62 m $J_{H-P} = 7,9,$ $J_{H-F} = 13,0 \text{ Hz}$	7,30 †	+7,97

*In CCl₄ solution.

+Narrow, poorly resolved multiplet.

(I) +C₆H₅OPOCl₂
$$\xrightarrow{\text{CaCl}_{2, 120^{\circ}}}$$
 C₆H₅OP(O)Cl(OCH₂C₄F₉) + C₆H₅OP(O)(OCH₂C₄F₉)₂
(III) (VI) (VII)

Ester-acid chlorides (VI), and especially (IV), are easily hydrolyzed liquids. Their structure and that of full esters (V) and (VII) was confirmed by the elemental analysis and NMR spectral data (Table 1); the employed excess phosphorylating agents can be recovered from the reaction mixture.

EXPERIMENTAL

The PMR spectra were taken on a Perkin-Elmer R-20 instrument relative to HMDS as the internal standard, while the ³¹P NMR spectra were taken on a Bruker HX-90 spectrometer under pulse conditions, with noise suppression of the spin-spin couplings of the phosphorus nuclei with the protons, relative to 85% H₃PO₄.

<u>Catalytic Phosphorylation of 1,1-Dihydroperfluoroamyl Alcohol (I) with Excess Methyl-phosphonic Dichloride (II).</u> a) A mixture of 37.5 g (0.15 mole) of (I), 40 g (0.3 mole) of (II), and 180 mg (1.5 mmoles) of anhydrous MgSO₄ was heated at 100° for 3 h and then fractionally distilled in vacuo. We obtained 20 g (100%) of (II) and 30.7 g (59%) of (IV), bp 104-105° (45 mm); $n_D^{2^\circ}$ 1.3480; $d_4^{2^\circ}$ 1.6283. Found: C 20.8; H 1.5; Cl 10.4; P 8.9%; MR 45.56. C₆H₅ClF₉O₃P. Calculated: C 20.8; H 1.4; Cl 10.2; P 8.9%; MR 45.56. The still residue was dissolved in CHCl₃ and chromatographed on an Al₂O₃ column (eluant = CHCl₃), the solvent was removed, and the residue was sublimed in vacuo to give 7.4 g (17%) of (V), mp 28-29°. Found: 23.5; H 1.4; P. 5.2%. C₁₁H₇F₁₈O₃P. Calculated: C 23.6; H 1.3; P 5.5%.

b) A mixture of 37.5 g (0.15 mole) of (I), 40 g (0.3 mole) of (II), and 670 mg (6 mmoles) of anhydrous $CaCl_2$ was heated at 100° for 3 h and then fractionally distilled in vacuo to give 16.3 g (82%) of (II) and 33.7 g (65%) of (IV). The still residue was worked up the same as before to give 4.4 g (10%) of (V).

c) A mixture of 37.5 g (0.15 mole) of (I), 40 g (0.3 mole) of (II), and 30 mg (0.15 mmole) of $BaCl_2$ was heated at 100° for 15 h and then fractionally distilled in vacuo to give 15 g (29%) of (IV). The still residue was worked up the same as before to give 5.7 g (13%) of (V).

Catalytic Phosphorylation of 1,1-Dihydroperfluoroamyl Alcohol (I) with Excess Phenyl Dichlorophosphate (III). A mixture of 20 g (0.08 mole) of (I), 34 g (0.16 mole) of (III), and 350 mg (3.2 mmoles) of anhydrous CaCl₂ was heated at 120° for 2 h and then fractionally distilled in vacuo to give 17.0 g (100%) of (III) and 21.5 g (63%) of (VI), bp 111-113° (2 mm); np²⁰ 1.4048; d4²⁰ 1.5694. Found: C 30.9; H 1.6; Cl 8.5; P 7.2%. C₁₁H₇ClF₉O₃P. Calculated: C 31.1; H 1.7; Cl 8.4; P 7.3%. The still residue was dissolved in CHCl₃ and chromatographed on an Al₂O₃ column (eluant = CHCl₃), the solvent was removed, and the residue was vacuum-distilled to give 5.5 g (22%) of (VII), bp 129-130° (2 mm); np²⁰ 1.3636; d4²⁰ 1.6277. Found: C 30.3; H 1.3; F 53.6; P 4.8%. C₁₆H₉F₁₈O₄P. Calculated: C 30.1; H 1.4; F 53.6; P. 4.8%.

CONCLUSIONS

A new method was developed for the synthesis of O-(polyfluoroalkyl) alkylchlorophosphonates and O-(polyfluoroalkyl) aryl chlorophosphates, which consists in phosphorylating polyfluoroalkanols with an excess of the dichlorides of the corresponding phosphorus acids in the presence of salts of the Group II metals.

LITERATURE CITED

- M. I. Kabachnik, N. N. Godovikov, V. V. Pisarenko, and L. S. Zakharov, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1972</u>, 1667.
- 2. L. S. Zakharov, V. V. Pisarenko, N. N. Godovikov, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., <u>1971</u>, 2503.
- 3. Kh. R. Raver and G. I. Abramtseva, USSR Inventor's Certificate No. 203,680, Aug. 31, 1966; Byull. Izobr., No. 21, 29 (1967).
- M. I. Kabachnik, L. S. Zakharov, E. I. Goryunov, I. Yu. Kudryavtsev, A. P. Kharchenko, V. F. Zabolotskikh, G. D. Novikova, K. N. Bil'dinov, and A. I. Nikitina, USSR Inventor's Certificate No. 556,148, July 12, 1976; Byull. Izobr., No. 16, 68 (1977).

EPR SPECTRA OF 2-ARYLPOLYFLUOROISOPROPYL RADICALS

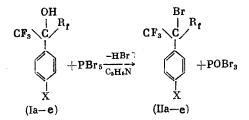
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We established that 2-bromo-2-arylpolyfluoropropanes when heated or subjected to photolysis in the presence of di-tert-butyl peroxide form substituted benzyl radicals, which we studied by the EPR method.

The starting compounds were synthesized from the corresponding alcohols, which were obtained as described in [1, 2] (Table 1).



 $R_{f} = CF_{3}, X = H (a); R_{f} = CF_{3}, X = F (b); R_{f} = CF_{3}, X = MeO (c);$ $R_{f} = CF_{3}, X = CF_{3}CONH (d); R_{f} = CF_{2}CI, X = F (e)$

The reactions of (Ia), (Ib), and (Ie) were run in refluxing benzotrifluoride (BTF), while those of the more active (Ib) and (Id) were run in CH₂Cl₂.

The hyperfine structure of the EPR spectra of the radicals (III), formed from the bromides (II) (Table 2), testifies to the fact that the distribution of the electron density in them is essentially the same as is characteristic for benzyl radicals. The hyperfine coupling (HFC) constants with the nuclei of the benzene rings are very close to those observed in the spectra of benzyl radicals that contain the corresponding substituents at the end [3].

As a result, the insertion of bulky fluoroalkyl groups as substituents on the benzene C atom evidently does not prevent the radical from retaining the planar structure that is characteristic for the unsubstituted benzyl radical, even if an o-F atom is present (radical (IIIf)).

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