CATALYTIC PHOSPHORYLATION OF PENTAFLUOROPHENOL

WITH PHOSPHORIC ACID CHLORIDES

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The known methods for the preparation of pentafluorophenyl phosphates are the phosphorylation of pentafluorophenol (PFP) with chlorophosphates in the presence of pyridine [1] or with the corresponding imidazolides [2], and also the reaction of potassium pentafluorophenoxide with POF₂Br [3]. Without an HCl acceptor the reaction of PFP with POCl₃ requires long refluxing [4, 5]. At the same time, since the phosphorylation of ordinary phenols using chlorophosphates is catalyzed by a number of metal salts [6, 7], it seemed practical to also use this method for the synthesis of pentafluorophenyl phosphates.

We made a detailed study of the phosphorylation of PFP with POCl₃ (Table 1), and with aryl and polyfluoroalkyl chlorophosphates (Table 2), and established that the process is catalyzed by certain metal salts [8]. The reaction was run by heating a mixture of PFP, the appropriate acid chloride, and catalyst (0.5-21 h at 100-200°C, depending on the type of catalyst and the structure of the desired compound). As the catalyst under the selected experimental conditions it is possible to use metal salts with an enthalpy equivalent to that for the formation of metal fluorides from the corresponding chlorides (Δ H), or else smaller or at most equal to the corresponding value for Mg (56 kcal/mole), which is the maximum Δ H value for the studied catalysts, where the exchange of F in a perfluoroaromatic nucleus by Cl fails to occur when treatment is with metal chlorides, i.e., practically all of the members of the major subgroups of Groups I and II of the periodic system. LiCl proved to be the most active catalyst. For preparative purposes we also successfully used KC1, CaCl₂, NaCl, BaCl₂, and metallic Mg, which during reaction dissolved completely, apparently being converted to MgCl₂.

The amount of catalyst usually ranged from 0.1 to 5 mole % when based on the PFP. When preparing the full pentafluorophenyl phosphates it proved expedient to use close to equivalent ratios of the starting reactants. In the case of pentafluorophenyl dichlorophosphate (II) we used a fivefold excess of POCl₃. When preparing the monochlorophosphates the equivalent ratio of PFP to the acid chloride was predominantly 1:1.8-4.0. The yields of the desired compounds depend on their structure and are 88-94% in the case of the full phosphates, and 50-60% in the case of the pentafluorophenyl chlorophosphates. When preparing the di(pentafluorophenyl) chlorophosphate it is also possible to isolate both the neutral phosphate (I) and the dichlorophosphate (II), in which connection the total yield reaches 92%.

With our method we synthesized a number of phosphates that lack chlorine in the aromatic rings (Table 3). Even in the case of the full phosphates, which require the most drastic phosphorylation conditions, replacement of the fluorine by chlorine is not observed. The fact that the synthesized chlorophosphates can be converted to neutral phosphates that are devoid of chlorine serves as evidence that the exchange products of fluorine by chlorine are absent in the synthesized compounds. Thus, the catalytic phosphorylation of 1,1-dihydroperfluorobutanol (IX) with dichlorophosphate (II) leads to the formation of the pure pentafluorophenyl di(1,1-dihydroperfluorobutyl) phosphate (VII) in 88% yield. The reaction of dichlorophosphate (II) with n-butanol (X) in the presence of a tertiary amine also gave a pentafluorophenyl dibutyl phosphate (VIII) that was completely devoid of chlorine.

EXPERIMENTAL

The constants of the obtained compounds and their analyses are given in Table 3.

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TABLE 1. Catalytic Phosphorylation of Pentafluorophenol with POCl₃

Com- pound	n	Catalyst	PFP POCI3: catalyst mole ratio	Reaction time, h	T., °C	Yield, ơ,
(I)	3	LiCl CaCl ₂	3:1:0 3:1:0,02 3:1:0,02	49 *. † 12 21	100-220 100-220 100-220	90 89 88
(11)	1	LiCl KCl CaCl ₂	1:5:0 1:5:0,05 1:5:0,05 1:5:0,05 1:5:0,05	72 ‡ 1 4 3	118-119 106-113 106-113 106-113	73 54 60 59
(III)	2	LiCl	2:1,25:0,02	1,2	100-177	51 +30% (I) +11% (II)

 $nC_6F_5OH + POCl_3 \xrightarrow{\text{catalyst}} (C_6F_5O)_nP(O)Cl_{3-n}$ (I)-(III)

*Cf. [4].

+The data given in [9] that reaction is complete in 14 h at 70-170° are apparently explained by the fact that the process is catalyzed by traces of metal salts, which are possibly present in the system either as natural impurities or due to dissolving of the glass, as was observed in a number of cases during the phosphorylation of phenols was $POCl_3$ [7]. +Cf. [5].

<u>Phosphorylation of Pentafluorophenol with $POCl_3$.</u> A mixture of 18.4 g (0.1 mole) of PFP,* $POCl_3$, and catalyst was heated until the HCl evolution ceased. Vacuum distillation gave pentafluorophenyl phosphates (I)-(III). The mole ratios of the reactants, the reaction conditions, and the yields are given in Table 1.

Phosphorylation of Pentafluorophenol with Aryl and Polyfluoroalkyl Phosphates. A mixture of 9.2 g (0.05 mole) of PFP, the appropriate chlorophosphate, and catalyst was heated until the HCl evolution ceased. Vacuum distillation gave pentafluorophenyl phosphates (IV)-(VII). The mole ratios of the reactants, the reaction conditions, and the yields are given in Table 2.

Pentafluorophenyl Di(1,1-dihydroperfluorobutyl) Phosphate (VII).† A mixture of 13.6 g (0.045 mole) of dichlorophosphate (II), 20.0 g (0.1 mole) of alcohol (IX), and 0.085 g (0.002 mole) of LiCl was heated for 40 min at 160°. Vacuum distillation gave 24.8 g (88%) of phosphate (VII).

Pentafluorophenyl Dibutyl Phosphate (VIII). With stirring, to 5.9 g (0.08 mole) of alcohol (X) and 8.1 g (0.08 mole) of Et_3N in 40 ml of abs. benzene was added in drops at $\sim 20^{\circ}$ a solution of 12.0 g (0.04 mole) of dichlorophosphate (II) in 20 ml of abs. benzene and the mixture was let stand overnight. The precipitate was filtered, while the solution

TABLE 2. Catalytic Phosphorylation of Pentafluorophenol with Aryl- and Polyfluoroalkyl Chlorophosphates

 $C_{6}F_{5}OH + (RO)_{n}P(O)Cl_{3-n} \xrightarrow{catalyst} (RO)_{n}P(O)(OC_{6}F_{5})Cl_{2-n} (IV)-(VII)$

Com- pound	n	R	Cat- a lyst	PFP:POCl ₃ , catalyst mole ratio	Reaction time, h	T., °C	Yield, %
(IV) (V) (VI) (VII)	1 2 1 2	$\begin{array}{c} C_6H_5\\ C_6H_5\\ CF_3CH_2\\ C_3F_7CH_2\end{array}$	NaCl Mg BaCl ₂ LiCl	$\begin{array}{c} 1:2:0.02\\ 1:1:0.02\\ 1:2:0.001\\ 1:1:0.02\\ \end{array}$	2 4 2,5 0,7	190–220 130–210 150–169 105–195	62 94 57 92

*In the preparation of phosphate (I) the charge of PFP was 27.6 g (0.15 mole). +Also see the described phosphorylation of PFP with polyfluoroalkyl chlorophosphates (Table 2).

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Com-	Formula	bp, °C (p, mm	20	20 7		F ound /	ca lcu laten	- <u>0</u> /v		Empirica 1
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(1)	(CeH5O) 3PO [4]	138-139 (1) mp, 47,5-49,0) (from hexane)	I	1	35,98 36,27	1	<u>48,12</u> 47,81	<u>1</u> -	5,43 5,20	C ₁₈ F ₁₅ O ₄ P
(11)	C ₆ F ₅ OP (O) Cl ₂ [5]	103 (14).	1,4526	1,7722	24,14 23,95	I	$\frac{31,12}{31,57}$	23,94 23,56	$\frac{10,28}{10,29}$	C ₆ Cl ₂ F ₅ O ₂ P
(111)	(C ₆ F ₅ O) ₂ P (O) Cl [5]	88-90 (1)	1,4509	1,8006	32,19 32,13	l	42,42 42,36	$\frac{8,14}{7,90}$	6,88 6,91	C ₁₂ ClF ₁₀ O ₃ P
(N)	(C ₆ F ₅ O)P(O) (OC ₆ H ₅)Cl	95-96 (1)	1,4925	1,5741	$\frac{40,22}{40,19}$	$\frac{1,23}{1,40}$	$\frac{26,29}{26,49}$	9,93 9,89	8,49 8,64	C ₁₂ H ₅ ClF ₅ O ₃ P
(<u>)</u>	(C ₆ F ₅ O)P(O) (OC ₆ H ₅) ₂ [1]	152-153 (1) mp, 63-65 (from hexane)		ł	52,08 51,94	$\frac{1,87}{2,42}$	21,99 22,82	1	7,61	C ₁₈ H ₁₀ F ₅ O ₄ P
(VI)	(CeF5O) P (O) (OCH2CF3) Cl	117-118 (13)	1,4070	1,7283	26,23	0,45 0,55	41,85	9,73 9,73	8,47 8,50	C ₈ H ₂ ClF ₈ O ₃ P
(i11)	$(G_6F_5O)P(O)$ (OCH ₂ G ₃ F ₇) ₂	84-85 (1)	4,3537	1,7587	<u>26,71</u> 26,77	0,71	57,29	. 1	4,87	$C_{14}H_4F_{19}O_4P$
(IIII)	(C ₆ F ₅ O) P (O) (OC4H ₈) 2 [5]	128-129 (1)	1,4300	1,2881	44,73 44,69	<u>4,83</u> <u>4,82</u>	25,01 25,25)	8,15 8,23	C ₁₄ H ₁₈ F ₅ O ₄ P

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was washed with water $(5 \times 10 \text{ ml})$ and dried over MgSO₄. Distillation gave 13 g (87%) of phosphate (VIII).

CONCLUSIONS

A new method was developed for the preparation of pentafluorophenyl phosphates, which consists in the catalytic phosphorylation of pentafluorophenol with $POCl_3$, or with aryl and polyfluoroalkyl phosphates, in the presence of the salts of the metals of Groups I and II of the periodic system.

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CHROMIUM AND IRON COMPLEXES WITH HETEROCYCLIC LIGANDS

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Heterocyclic chromium tricarbonyl π complexes are formed with much greater difficulty than the isosteric arenechromium tricarbonyls. In condensed heterocycles [1, 2], and also in the 2- and 3-phenylthiophenes [3], the chromium exhibits the π type of coordination only with the benzene ring. When the heterocycle is condensed with Cr(CO)₆ the thiophenechromium tricarbonyl π complexes are obtained in low yield [3-5]. A higher yield of the thiophenechromium tricarbonyls is obtained by using chromium complexes with p-donor ligands, like, for example, acetonitrile [6], γ -picoline [7], or pyridine [8].

The insertion of electron-donor substituents into an aromatic ring raises the electron density of the latter and facilitates the formation of π complexes with Group VI metal [7, 9]. It seemed of interest to ascertain the effect of such a strong electron-donor substituent as CpFe(CO)₂ [9] on the ability of the thiophene ring to form complexes with Cr.

By condensing $Cr(CO)_6$ with the heterocyclic cyclopentadienyliron dicarbonyl σ derivatives (I) and (II) [10] we respectively obtained compounds (III) and (IV) in relatively high yield, in which compounds the heterocycle is linked by a σ bond to the Fe atom and exhibits the π type of coordination with the Cr atom.



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