CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKANOLS.

COMMUNICATION 9. PHOSPHORYLATION OF 1,1-DIHYDROPOLYFLUOROALKANOLS IN THE PRESENCE OF GROUP I METAL CHLORIDES

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We have already shown that salts of metals, in particular Group II metals, are effective catalysts for the phosphorylation of polyfluorinated alkanols by chlorides of oxygenated acids of pentavalent phosphorus [1-3]. For these reactions, salts of Group I metals have been little studied. The only representative studied, KCl, had a relatively low activity [1]. Group I metal chlorides are fairly effective as catalysts during phosphorylation of phenols with phosphorus oxychloride [4]. It was therefore interesting to carry out a systematic study of the catalytic activity of Group I metal chlorides and to clarify their possible use for the preparative synthesis of polyfluoroalkyl phosphates. At least in the case of LiCl, if we consider the known chemical similarity between lithium and magnesium, one of the most effective catalysts of the phosphorylation of polyfluorinated alkanols, a fairly high catalytic activity of lithium in the phosphorylation reaction could also be expected.

We first studied the catalytic activity of Group I metal chlorides in the phosphorylation of 1,1-dihydroperfluorobutanol by phosphorus oxychloride that we had previously chosen as a model reaction [1]. A mixture of the reagents and the catalyst in the ratio required for the preparation of neutral phosphate was heated at a bath temperature of 160°C, until no more hydrogen chloride was evolved. We found that all Group I metal chlorides do not completely dissolve in the reaction mixture (in all cases the solubility apparently even decreased in the course of the reaction), so that it was not possible to estimate their real catalytic activity. Therefore, the effectiveness of the overall process was judged from the yield and time required for the completion of the reaction.

The results are shown in Table 1. For comparison, data are also listed on the use of metallic magnesium as catalyst, which dissolves completely in the reaction mixture, and apparently converts into the corresponding chloride.

It was found that the catalytic activity of Group I met chlorides in the reaction studied decreases in the series of LiCl > RbCl > CsCl > NaCl > KCl. The highest activity is exhibited by LiCl, which although not completely soluble, is sufficiently soluble in the reaction mixture, and so in its effectiveness, LiCl is scarcely not inferior to magnesium.

Noticeably lower is the catalytic activity of RbCl and CsCl, which have also a fairly high solubility, and in the case of CsCl even complete dissolution of the catalyst is observed at the beginning of the reaction. The low effectiveness of NaCl, and in particular KCl, is clearly explained by their low solubility. For comparison, it should be noted that previously, in the course of a study on the kinetics of the preparation of phenyl dichlorophosphate during phosphorylation of phenol by excess of $POCl_3$ [4], an activity series of Group I metal chlorides was obtained: LiCl > RbCl > CsCl > KCl > NaCl. This compares well with the series obtained by us, except for the relative positions of KCl and NaCl, apparently due to their different relative solubility in different reaction media.

The results show that some Group I metal chlorides, in particular, LiCl, although somewhat inferior to the better representatives of Group II, can be successfully used for preparative purposes. In fact, if LiCl is used as catalyst, different symmetric tris(polyfluoroalkyl) phosphates and also the corresponding mono- and dichlorophosphates (see Table 1) can be obtained. Thus, depending on the conditions, we can exclusively obtain full esters (yield up to 95%) and mixtures of the latter with mono- and dichlorophosphates with appreciable predomi-

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TABLE 1. Catalytic Phosphorylation of Polyfluorinated Alkanols by Phosphorus Oxychloride

$$R_FCH_2OH+POCl_3 \xrightarrow{\text{catalyst}} \underset{(I)}{R_FCH_2OPOCl_2}+\underset{(II)}{(R_FCH_2O)_2POCl}+\underset{(III)}{(R_FCH_2O)_3PO}$$

R_F	Catalyst	Molar amounts			Bath temperature, °C	Time, h	Yield		
		R_FCH_2OH	$POCl_3$	catalyst			(I)	(II)	(III)
C_3F_7	LiCl	0,085	0,025	0,002	160	3,6	–	–	93,8
C_3F_7	NaCl	0,085	0,025	0,002	160	19–20	–	–	91–92
C_3F_7	KCl	0,085	0,025	0,002	160	31–34			91–22
C_3F_7	RbCl	0,085	0,025	0,002	160	9	–	–	87,5
C_3F_7	CsCl	0,085	0,025	0,002	160	15	–	–	85,5
C_3F_7	Mg	0,085	0,025	0,002	160	2,8	–	–	89,4
HCF_2CF_2	LiCl	0,1	0,03	0,001	160	2,5	–	–	91,6
C_4F_9	LiCl	0,1	0,03	0,001	170	2,0	–	–	95,6
$H(CF_2)_4$	LiCl	0,15	0,05	0,001	190–200	4,5	–	–	93,0
C_3F_7	LiCl	0,2	0,125	0,002	150–170	1,5	20,4	60,3	6,8
C_4F_9	LiCl	0,2	0,125	0,002	150–155	1,5	20,3	60,4	7,4
C_4F_9	LiCl	0,2	0,6	0,002	140	2,5	67,2	12,1	12,8

TABLE 2. Catalytic Phosphorylation of Polyfluorinated Alkanols by Dichlorophosphates and Dichlorophosphonates

$$R_FCH_2OH+RPOCl_2 \xrightarrow{\text{catalyst}} \underset{(IV)}{RPO(OCH_2R_F)_2}+\underset{(V)}{RPO(Cl)OCH_2R_F}$$

R_F	R	Catalyst	Molar amounts			Bath temperature, °C	Time, h	Yield, %	
			R_FCH_2OH	$RPOCl_2$	catalyst			(IV)	(V)
CF_3	$C_3F_7CH_2O$	LiCl	0,042	0,02	0,0002	165–185	7,6	92,3	–
CF_3	PhO	LiCl	0,22	0,1	0,005	160–170	8,0	95,2	–
C_4F_9	PhO	LiCl	0,105	0,05	0,001	180	4	97,0	–
C_4F_9	PhO	LiCl	0,05	0,15	0,001	185–190	0,7	11,9	72,6
CF_3	Me	LiCl	0,22	0,1	0,005	160	4	85,0	–
HCF_2CF_2	Me	LiCl	0,41	0,2	0,004	150–175	2,5	89,8	–
$H(CF_2)_4$	Me	LiCl	0,205	0,1	0,002	170–195	2,5	96,8	–
$H(CF_2)_4$	Me	LiCl	0,1	0,2	0,002	160–170	1,5	26,7	64,1

TABLE 3. Catalytic Phosphorylation of Polyfluorinated Alkanols by Diphenyl Chlorophosphate

$$R_FCH_2OH+(PhO)_2POCl \xrightarrow{\text{catalyst}} R_FCH_2OPO(OPh)_2$$

R_F	Catalyst	Molar amounts			Bath temperature, °C	Time, h	Yield, %
		R_FCH_2OH	$(PhO)_2POCl$	catalyst			
CF_3	LiCl	0,11	0,1	0,005	150–170	17,5	95,7
HCF_2CF_2	LiCl	0,22	0,2	0,01	200	12,5	91,5
C_4F_9	LiCl	0,0502	0,05	0,001	180–200	19	95,4

nance of one of them (up to 60-67%) at an overall yield of 87-92%.

Lithium chloride can be successfully employed for the preparative synthesis of polyfluoroalkyl esters of oxygenated acids of pentavalent phosphorus. Polyfluorinated alkanols are readily phosphorylated in the presence of LiCl by polyfluoroalkyl dichlorophosphates, aryl dichlorophosphates, and alkyl dichlorophosphonates (Table 2). If an equivalent amount or a slight excess of the polyfluorinated alkanol is used, the corresponding full esters, i.e., mixed phosphates and phosphonates, are obtained in good yields. If a 2-3-fold excess of the phosphorylating agent is used, the corresponding ester-chlorides can be obtained: aryl polyfluoroalkyl chlorophosphates and O-polyfluoroalkyl alkyl chlorophosphonates. The yield of the ester-chlorides increases and that of full esters decreases, if an excess of the phosphorylating agent is used.

It is known that catalytic phosphorylation of polyfluorinated alkanols by diaryl chlorophosphates usually proceeds slowly, and the most widely used Group I metal salts are not sufficiently active as catalysts [1]. We found, however, that in this case LiCl has a high catalytic activity, so that the corresponding diaryl polyfluoroalkyl phosphates can be obtained in good yields.

TABLE 4. Properties of Polyfluoroalkyl Esters of Phosphorus Acids Compound

Compound	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	Found/Calculated, %					Empirical formula
				C	H	F	P	Cl	
$(HCF_2CF_2CH_2O)_3PO$	133(7)	1,3452	1,6555	24,66 24,56	1,85 2,06	51,67 51,80	7,02 7,04	–	$C_9H_9F_{12}O_4P$
$C_2F_7CH_2OPOCl_2$ (cp. [2])	48–49(6)	1,3560	Literature data [2]: bp 58–59(12), n_D^{20} 1,3560						
$(C_3F_7CH_2O)_2POCl$ (cp. [2])	83–84(6)	1,3243	Literature data [2]: bp 89–90(9), n_D^{20} 1,3246						
$(C_3F_7CH_2O)_3PO$ (cp. [1])	78–79(1)	1,3101	Literature data [1]: bp 96(2,5), n_D^{20} 1,3102						
$C_4F_9CH_2OPOCl_2$	79(17)	1,3510	1,7341	16,17 16,35	0,75 0,55	46,91 46,61	8,48 8,44	19,49 19,33	$C_5H_2Cl_2F_9O_2P$
$(C_4F_9CH_2O)_2POCl$	67–68(1)	1,3240	1,7558	20,72 20,67	1,00 0,70	58,99 58,92	5,27 5,34	5,79 6,11	$C_{10}H_4ClF_{18}O_3P$
$(C_4F_9CH_2O)_3PO$	89–91(1)	1,3115	1,7683	22,76 22,69	0,70 0,76	64,47 64,59	4,25 3,90	–	$C_{15}H_6F_{27}O_4P$
$(H(CF_2)_4CH_2O)_3PO$ (cp. [1])	126(0,5)	1,3334	Literature data [1]: bp 154(2), n_D^{20} 1,3636						
$C_3R_7CH_2OPO(OCH_2CF_3)_2$	105(20,5)	1,3152	1,6512	21,73 21,64	1,70 1,36	55,60 55,62	6,77 6,97	–	$C_8H_6F_{13}O_4P$
$PhOPO(OCH_2CF_3)_2$	125–126(9)	1,4062	1,4451	35,43 35,52	2,71 2,68	34,35 33,71	8,87 9,16	–	$C_{10}H_9F_6O_4P$
$PhOPO(OCH_2C_4F_9)_2$	108(0,5) (comp. [5])	1,3631	Literature data [5]: bp 129–130(2), n_D^{20} 1,3636						
$PhO(Cl)P(O)OCH_2C_4F_9$	57–58(0.5) (comp. [5])	1,4068	Literature data [5]: bp 111–113(2), n_D^{20} 1,4048						
$MePO(OCH_2CF_3)_2$	70–71(8)	1,3386	1,4807	23,05 23,09	2,59 2,71	43,89 43,83	11,95 11,91	–	$C_5H_7F_6O_3P$
$MePO(OCH_2CF_2CF_2H)_2$	114–115(6)	1,3578	1,5520	25,87 25,94	2,68 2,80	47,88 46,90	9,51 9,56	–	$C_7H_9F_8O_3P$
$MePO(OCH_2(CF_2)_4H)_2$	89–90(0,5)	1,3424	1,6927	24,56 25,21	1,77 1,73	57,77 58,00	5,94 5,91		$C_{11}H_9F_{16}O_3P$
$Me(Cl)P(O)OCH_2(CF_2)_4H$	99(5,5)	1,3675	1,6334	21,92 21,94	1,89 1,84	45,37 46,27	9,36 9,43	10,39 10,79	$C_6H_6ClF_8O_2P$
$CF_3CH_2OPO(OPh)_2$	113–114(1)	1,4890	1,3304	50,50 50,62	3,80 3,64	16,95 17,16	9,17 9,32	–	$C_{14}H_{12}F_3O_4P$
$HCF_2CF_2CH_2OPO(OPh)_2$	132(0,5)	1,4855	1,3642	48,96 49,46	3,64 3,60	20,88 20,87	8,49 8,50	–	$C_{15}H_{13}F_4O_4P$
$C_4F_9CH_2OPO(OPh)_2$	128(0,7)	1,4420	1,4653	42,62 42,34	2,49 2,51	34,60 35,46	6,47 6,42	–	$C_{17}H_{12}F_9O_4P$

EXPERIMENTAL

Phosphorylation of 1,1-Dihydropolyfluoroalkanols by Phosphorus Acid Chlorides. A mixture of a polyfluoroalkanol, a phosphorus acid chloride, and the catalyst (purified by recrystallization from water and dried by calcination) was heated until no more hydrogen chloride was evolved. The products were isolated by distillation. The catalyst, molar amounts of the reagents and of the catalyst, the bath temperature, time required up to the conclusion of the reaction, and the yields of the products are listed in Tables 1-3; the physical constants and analyses of the new compounds are listed in Table 4.

CONCLUSIONS

1. In the preparation of tris(1,1-dihydroperfluorobutyl) phosphate by phosphorylation of 1,1-dihydroperfluorobutanol with phosphorus oxychloride, the relative catalytic activity of Group I metal chlorides was studied, and it was shown that the catalytic activity decreases in the series LiCl > RbCl > CsCl > NaCl > KCl.

2. The high effectiveness of LiCl as catalyst for the phosphorylation of polyfluorinated alkanols by phosphorus oxychloride, polyfluoroalkyl dichlorophosphates, aryl dichlorophosphates, diaryl chlorophosphates, and alkyl dichlorophosphonates was shown. Lithium chloride catalyst can thus be used for the preparative synthesis of polyfluoroalkyl esters and ester-chlorides of phosphoric and alkylphosphonic acids.

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INTERCONVERSIONS OF CLUSTERS IN THE Pd(O), CO, P(n-Alk)$_3$ SYSTEM

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In the first papers on the synthesis of carbonylphosphine clusters $M_n(CO)_x(PPh_3)_y$, (M_n), M = Pd (n = 3), Pt (n = 3, 4), the existence in solution of equilibria of the type $3M_1 \rightleftharpoons M_3$ [1, 2] and of transition $Pt_3 \rightarrow Pt_4$ [2] was observed. Carbonyltrialkylphosphine clusters $Pd_{10}(CO)_{12}(PAlk_3)_6$ (Ia, b), $Pd_{10}(CO)_{14}[P(n\text{-}Bu)_3]_4$ (II), $Pd_4(CO_5)(PAlk_3)_4$ (IIIa, b), (Pd_{10}, Pd_4), Alk = n-Bu(Bu) (a), Et (b) were obtained by reducing $Pd(OAc)_2$ by carbon monoxide [3-6]. The composition of the compounds depends on the acitidy of themedium and on the Pd^{2+}:$PAlk_3$ ratio.

To search for the paths of formation of one compound from another inside the family of clusters, in the present work, we studied the interconversions of compounds (I), (II), and (III), and proposed a simple, and apparently general, method for increasing the polynuclearity of carbonylphosphine clusters by binding phosphine into a protonated or another form.

DISCUSSION OF RESULTS

The transition (IIIa) → (Ia) is possible not only as the result of the reaction (1)

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