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## CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKANOLS.

13. SOME AMMONIUM AND PHOSPHONIUM SALTS AS PHOSPHORYLATION CATALYSTS

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It was shown that it is possible to use a series of ammonium and phosphonium salts as effective catalysts for the preparative synthesis of tris(polyfluoroalkyl) phosphates. The effect of the structure of substituted ammonium salts on their catalytic activity was studied in the phosphorylation of 1,1-dihydroperfluorobutanol by phosphorus oxychloride. It was determined that the reaction rate is affected not only by the solubility of the salt, but also by the nature of the ion pair and the steric access of the onium center for solvation by phosphoryl compounds.

Previously it was shown that some metal and ammonium salts catalyze the phosphorylation of 1,1-dihydropolyfluoroalkanols by phosphorus(V) oxyacid chlorides [1]

$$R_FCH_2OH + CI - P \xrightarrow{O} R_FCH_2OP + HCI$$

R<sub>F</sub> is polyfluoroalkyl.

The following salts were studied as the catalyst: KCl, Mg,  $MgCl_2$ ,  $MgSO_4$ ,  $CaCl_2$ ,  $AlCl_3$ , Al, ZnCl\_2, NH\_4Cl,  $(C_2H_5)_3$ NHCl,  $(C_2H_5)_4$ NHCl. However, for most of the metal salts, their effectiveness as catalysts was limited under the conditions of catalytic phosphorylation by the relatively low solubility in the reaction media. In the present paper, we carried out an investigation of the catalytic activity of a series of substituted ammonium salts. In addition, we assumed that they would dissolve better in the reaction mixture, which would make it possible to increase their effective concentration in the solution and to increase the reaction rate.

We studied the effect of the environment at the nitrogen atom on the catalytic activity of the substituted ammonium salts in the model reaction of 1,1-dihydroperfluorobutanol with phosphorus oxychloride (Table 1). The reaction was carried out at 160°C, ensuring the

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Catalyst	Reaction time, h	Treatment method	Phosphate yield, %	Catalyst solubility*
NH4CI	12.0	A	88.8	
CH <sub>3</sub> NH <sub>3</sub> Cl	10.3	A	87.5	C - D
$(CH_3)_2NH_2Cl$	8.0	A	96.9 **	
		В	79.5	
(CII <sub>3</sub> ) <sub>3</sub> NHCl	4.7	A	87.5	c
(CII <sub>3</sub> ) <sub>4</sub> NCl	7.5	Ā	88.1	D
$(C_2II_5)_4NCl$	3,0	A	85.1 **	r c
(C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> NCl	5,8	A	93 1 **	č
C <sub>5</sub> H <sub>5</sub> NHCl	3,3	A	86.0 **	r r
$(C_6H_5)_3PC_2H_5Br$	6.9	A	92.5	c
$(C_6H_5)_3PCH_2C_6H_5Cl$	5,1	A	91.9	c
LiCl [2]	3.6	A	93.8	a di
Mg [2]	2.8	A	89.4	i

 $C_3F_7CH_2OH + POCl_3 \frac{Cat}{160} (C_3F_7CH_2O)_3PO + HCl$ 

\*i denotes significantly insoluble, p partially soluble, and c completely soluble.

\*\*The substance was contaminated by the catalyst or its decomposition products.

maximum rate of the process and good reproducibility of the results. The reproducibility was  $\pm 5\%$  for the reaction time and  $\pm 0.5\%$  for the phosphate yield.

For the case of polymethylammonium chlorides, we studied the effect of the degree of substitution at the nitrogen atom on the effectiveness of the catalyst and determined that in successively going from unsubstituted ammonium chloride to mono-, di-, and trisubstituted ammonium salts the solubility and, correspondingly, the reaction rate increase. With furthere substitution, i.e., introduction of a fourth methyl group, the solubility of the catalyst decreases, naturally causing an increase in reaction time. When we used tetraethylammonium chloride as the catalyst, we observed complete dissolution of the salt and reduction of the reaction time. However, a further increase in length of the catalyst, led to a detraalkylammonium chlorides, without worsening the solubility of the catalyst, led to a decrease in catalytic activity.

Previously we stated an assumption concerning the mechanism of the catalytic effect of ammonium salts on the phosphorylation of polyfluoroalkanols by phosphorus acid chlorides, according to which the catalyst cation is solvated by the phosphoryl compound; as a result of ion-dipole interaction, additional polarization of the phosphoryl group appears, the effective positive charge on the phosphorus atom increases and nucleophilic substitution is facilitated [1]. It is known that the predominant type of species in solutions of tetraalkylammonium salts in 2,2,2-trifluoroethanol [3] and phosphorus oxychloride [4] are ion pairs. The obtained results on catalysis by ammonium salts under homogeneous conditions can apparently be explained both by differences in the structure of these ion pairs (characterizing the distance between the ions and, correspondingly, their polarizing ability) and by the nature of shielding of the onium center by substituents at the nitrogen atom.

From this standpoint, the higher catalytic activity of trimethylammonium chloride in comparison with dimethylammonium chloride is apparently explained by the higher polarizing ability of the ion pair of the first (weaker interaction of the cation with the anion because of a decrease in probability of formation of hydrogen bonds between them and shielding of the cation charge by methyl groups). The decrease of the catalytic activity in going from tetraethylammonium to tetrabutylammonium chloride is possibly due to further shielding of the onium center by bulkier radicals.

A comparison of trimethylammonium chloride and pyridine hydrochloride, the latter surpassing the former salt in effectiveness (both salts were completely soluble in the reaction mixture), probably indicates the significant effect of the steric factor: the planar structure of the pyridinium cation is less sterically shielded for association with the phosphoryl group than is the tetrahedral nitrogen atom in trimethylammonium chloride. Among the ammonium salts that were studied, the di- and trimethylammonium salts and also tetraalkylammonium salts containing not less than two carbon atoms in the alkyl group were found to be freely soluble. On the whole, the most active ammonium salts with respect to catalytic activity are on the level of the best inorganic catalysts, metallic magnesium and lithium chloride. In addition, however, the practical use of substituted ammonium salts for preparative purposes is apparently limited only to salts that are nonvolatile during distillation of the phosphorylation product and thermally stable under the reaction conditions and during distillation. Such salts include ammonium chloride, methylammonium chloride, and tetramethylammonium chloride. The remaining ammonium salts are either distilled together with the target product as dimethylammonium and trimethylammonium chloride and the pyridinium salt or, as in the case of tetraethyl- and tetrabutylammonium salts. In both cases, the obtained substance is contaminated and one of the main advantages of the catalytic phosphorylation method, high purity of the synthesized compounds, is lost.

In this regard, we considered the possibility of using more thermally stable phosphonium salts as the phosphorylation catalyst. In them the charges are separated by a greater distance than in ammonium salts and the onium center is more sterically accessible for iondipole solvation by phosphoryl compounds.

Indeed, it was found that the salts that were studied (ethyltriphenylphosphonium bromide and benzyltriphenylphosphonium chloride) are very effective phosphorylation catalysts (see Table 1). In addition, because of the presence of large organic radicals, these salts dissolve well in the reaction mixture and, in addition, are thermally stable under catalytic phosphorylation conditions and do not contaminate the target product during distillation of the reaction mixture. They make it possible to obtain pure tris(1,1-dihydroperfluorobutyl) phosphate in good yield and can be used for preparative purposes.

However, the phosphonium salts that were studied are nevertheless inferior in catalytic activity to the more soluble ammonium salts. In this case, a significant role is possibly played by the lower charge density on the phosphorus onium center which has as its result a weaker polarization of the phosphoryl group.

Thus, using the principle of introduction of organic radicals into the onium-type catalyst molecule, we found a series of homogeneous phosphorylation catalysts that are sufficiently effective for the preparative synthesis of polyfluoroalkyl phosphates.

## EXPERIMENTAL

Phosphorus oxychloride was purified by bidistillation, bp 107°C. 1,1-Dihydroperfluorobutanol was distilled over sulfuric acid and then over phosphoric anhydride, bp 96°C. The ammonium salts (analytical-purity or pure) were additionally purified by recrystallization, after which they had constants agreeing with the literature ones: NH\_Cl, sublimed above 335°C (from water) (cf. [5]), CH<sub>3</sub>HN<sub>3</sub>Cl, mp 226-228°C (chloroform) (cf. [6]), (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub>Cl, mp 169-171°C (chloroform-hexane) (cf. [7]), (CH<sub>3</sub>)<sub>3</sub>NHC1, mp 276-278°C (chloroform) (cf. [7]),  $(CH_3)_4NC1$ , decomposed above 320°C (from water) (cf. [8]), and  $(C_2H_5)_4NC1$ , decomposed above 180°C (from water) (cf. [9]). The  $(C_4H_9)_4NCl$  was obtained by neutralization of a solution of  $(C_4H_9)_4NOH$  by hydrochloric acid with subsequent evaporation in a desiccator over sulfuric acid at room temperature before the beginning of crystallization, mp 74-76°C (from water) (cf. [10]). Pyridine hydrochloride was generated directly into the reaction mixture by adding phosphorus oxychloride and 1,1-dihydroperfluorobutanol to a weighed amount of pyridine. The pyridine was dried with KOH and distilled over KOH, bp 115.4°C, np<sup>20</sup> 1.5095. Benzyltriphenylphosphonium chloride was synthesized from triphenylphosphine and benzyl chloride according to [11], mp 334-339°C with decomposition. The preparation of ethyltriphenylphosphonium bromide is described below. Before use, the ammonium and phosphonium salts were dried in vacuo at room temperature over phosphoric anhydride.

<u>Preparation of Ethyltriphenylphosphonium Bromide.</u> A solution of 10.5 g (0.04 mole) of triphenylphosphine and 4.9 g (0.045 mole) of ethyl bromide in 40 ml of alcohol was heated for 7 h at the boiling point, 2.2 g (0.02 mole) of ethyl bromide was added, the whole was heated for 7 h, then 2.2 g (0.02 mole) of ethyl bromide was added and the whole was again heated for 7 h. The solution was evaporated to a volume of 20 ml and cooled, and 20 ml of ether was added dropwise. The resulting precipitate was filtered and dried in air and then

in vacuo over phosphoric anhydride. We obtained 14.0 g (94.2%) of ethyltriphenylphosphonium bromide, mp 210-211°C (cf. mp 203-205°C [12], 207-209°C [13], and 209-210.5°C [14]).

<u>General Method for Catalytic Phosphorylation of 1,1-Dihydroperfluorobutanol by Phosphorus Oxychloride.</u> A mixture of 17.0 g (0.085 mole) of 1,1-dihydroperfluorobutanol, 3.8 g (0.025 mole) of phosphorus oxychloride, and 0.002 mole of the catalyst was heated at bath temperature 160°C with a reflux condenser, equipped with a bubble counter, until hydrogen chloride was no longer evolved. Hydrogen chloride and excess 1,1-dihydroperfluorobutanol were removed in vacuo with an aspirator with heating to 100°C. Then the reaction mixture was treated by two methods.

<u>Method A.</u> The residue was distilled in vacuo. We obtained tris(1,1-dihydroperfluorobutyl) phosphate, bp 78-80°C (0.5 mm),  $n_D^{20}$  1.3105 (cf. [1]).

<u>Method B.</u> To the residue was added 20 ml of a mixture of abs. benzene with abs. ether (1:1 by volume) and the precipitate was filtered and washed with 20 ml of the same mixture. The filtrate was passed through a column filled with aluminum oxide (neutral, Brockmann activity grade II), with column diameter 25 mm and adsorbent-bed height 25 mm. Elution was carried out with 50 ml of abs. ether. The solvent was removed and the residue was distilled in vacuo.

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