CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKANOLS.
COMMUNICATION 10. CATALYTIC PHOSPHORYLATION OF α-POLYFLUOROALKYLBENZYL ALCOHOLS BY DIARYL CHLOROPHOSPHATES

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Depending on the conditions and the character of the substituent in the benzene ring, the catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols by $POCl_3$ leads to either α-polyfluoroalkylbenzyl dichlorophosphates or to the symmetric di-α-polyfluoroalkylbenzyl ethers. The formation of these ethers as the result of the alkylation of the initial alcohols by the intermediately formed benzyl dichlorophosphates is favored by the presence of donor substituents in the benzene ring and increase in the reaction temperature [1-3].

In the case of primary polyfluorinated alcohols, the process of catalytic phosphorylation by diaryl chlorophosphates proceeds under much more rigid conditions than that by $POCl_3$ [4]. It was therefore not clear in which direction the reaction of diaryl chlorophosphates with α-polyfluoroalkylbenzyl alcohols would proceed under the conditions of catalytic phosphorylation. We were able to find that in the catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols by diaryl chlorophosphates, phosphorylation products are formed in several cases [5].

The present work deals with the study of the direction of the catalytic phosphorylation of α-polyfluroalkylbenzyl alcohols by diaryl chlorophosphates, depending on the nature of the catalyst, the character of the substituent in the benzene ring of the alcohol, length of the chain, and structure of the polyfluoroalkyl radical. For the phosphorylation we selected α-trifluoromethylbenzyl alcohol (I), its p-methyl homolog (II), α-heptafluoroporpylbenzyl alcohol (III), and α-(heptafluoro-3-oxabutyl)benzyl alcohol (IV), and we used diphenyl chlorophosphate (V) and di(m-tolyl) chlorophosphate (VI) as the phosphorylating agents.

A mixture of equimolar amounts of α-polyfluoroalkylbenzyl alcohol and diaryl chlorophosphate was heated at 200°C in the presence of catalytic amounts of anhydrous $CaCl_2$ or metallic Mg up to cessation of HCl evolution. It was found that the corresponding α-polyfluoroalkylbenzyl diaryl phosphates are formed as the main reaction products (Table 1). The catalytic activity of metallic Mg, which dissolves in the reaction and probably converts into $MgCl_2$, is somewhat higher than that of $CaCl_2$, which agrees well with the data on the relative catalytic activity of these compounds obtained in the study of the catalytic phosphorylation of phenols [6].

TABLE 1. Catalytic Phosphorylation of α-Polyfluoroalkylbenzyl Alcohols by Diaryl Chlorophosphates

$$ArCH(OH)R_F + (Ar'O)_2POCl \xrightarrow[-HCl]{\text{Catalizator, } 200°} ArCH(R_F)OP(O)(OAr')_2$$

Ar	R_F	Ar′	Catalyst*	Time of reaction, h	Yield, %
C_6H_5	CF_3	C_6H_5	$CaCl_2$	14	88
C_6H_5	CF_3	C_6H_5	Mg	2,5	93
C_6H_5	CF_3	m-$CH_3C_6H_4$	$CaCl_2$	22	87
C_6H_5	CF_3	m-$CH_3C_6H_4$	Mg	4	94
p-$CH_3C_6H_4$	CF_3	C_6H_5	$CaCl_2$	3	67
p-$CH_3C_6H_4$	CF_3	C_6H_5	Mg	0,75	85
C_6H_5	C_3F_7	C_6H_5	Mg	7	92
C_6H_5	$CF_3OCF_2CF_2$	C_6H_5	Mg	4	94

*0.025 mole of catalyst per mole of $ArCH(OH)R_F$.

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TABLE 2. α-Polyfluoroalkylbenzyl Diaryl Phosphates $ArCH(R_F)OP(O)(OAr')_2$

Ar	R_F	Ar′	mp, °C (hexane)	Found, %				Empirical formula	Calc., %			
				C	H	F	P		C	H	F	P
C_6H_5	CF_3	C_6H_5	70–71,5	59,0	4,0	13,9	7,7	$C_{20}H_{16}F_3O_4P$	58,8	4,0	14,0	7,6
C_6H_5	CF_3	m-$CH_3C_6H_4$	51–52	60,1	4,4	12,9	6,9	$C_{22}H_{20}F_3O_4P$	60,5	4,6	13,1	7,1
p-$CH_3C_6H_4$	CF_3	C_6H_5	67,5–69	59,8	4,2	13,4	7,3	$C_{21}H_{18}F_3O_4P$	59,7	4,3	13,5	7,3
C_6H_5	C_3F_7	C_6H_5	67–68	52,2	3,2	25,6	6,1	$C_{22}H_{16}F_7O_4P$	52,0	3,2	26,2	6,1
C_6H_5	$CF_3OCF_2CF_2$	C_6H_5	56,5–58	50,0	3,1	25,6	6,2	$C_{22}H_{16}F_7O_5P$	50,4	3,1	25,4	5,9

TABLE 3. Data of (^1H, ^{19}F, ^{31}P) NMR Spectra of α-Polyfluoroalkylbenzyl Diaryl Phosphates $ArCHR_FOP(O)(OAr')_2$*

Compound	Ar	R_F	Ar′	PMR (δ, ppm; J, Hz)			^{19}F NMR (δ, ppm) CF_3CH	$^{31}P-\{^1H\}$ NMR, (δ, ppm)
				$POCHR_F$	aromatic proton	$\underline{CH_3}C_6H_4$		
(VII)	C_6H_5	CF_3	C_6H_5	5,78 d.q. $J_{H-F}=6,6$, $J_{H-P}=10,3$	6,79–7,58 m	–	1,82 d $J_{H-F}=6,5$ Hz	–12,30 s
(VIII)	C_6H_5	CF_3	m-$CH_3C_6H_4$	5,84 d.q $J_{H-F}=6,5$, $J_{H-P}=10,5$	6,46–7,51 m	2,06 s 2,25 s	1,82 d $J_{H-F}=6,6$ Hz	–12,33 s
(IX)	p-$CH_3C_6H_4$	CF_3	C_6H_5	5,77 d.q $J_{H-F}=6,6$, $J_{H-P}=10,3$	6,86–7,51 m	2,30 s	1,85 d $J_{H-F}=6,6$ Hz	–12,53 s
(X)	C_6H_5	C_3F_7	C_6H_5	5,99 d.d.d $J_{H-F}=7,6$, $J_{H-F}=15,5$. $J_{H-P}=9,8$†	6,70–7,58 m	–	–	–12,70 s
(XI)	C_6H_5	$CF_3OCF_2CF_2$	C_6H_5	5,81 d.d.d $J_{H-F}=7,6$, $J_{H-F}=14,6$, $J_{H-P}=9,8$†	6,62–7,52 m	–	–	–12,63 s

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*In a CCl_4 solution.

†Identification of SSCC J_{H-P} was carried out by comparison with the data of ^{31}P NMR spectrum.

When a donor substituent (the p-Me group) is introduced into the benzene ring of α-trifluoromethylbenzyl alcohol, the phosphorylation reaction becomes markedly accelerated, but even in this case no ethers are formed. p-Methyl-α-trifluoromethylbenzyl chloride is formed (according to TLC data) as the only side product in this reaction, which leads to a certain decrease in the yield of diaryl benzyl phosphate.

When the chain length of polyfluoroalkyl radical is increased, as in the phosphorylation of α-polyfluoroalkylbenzyl alcohols by $POCl_3$ [2], a decrease in the reaction rate is observed, probably as the result of increase in the steric hindrances. In this case, alcohol (IV), whose polyfluoroalkyl group has, apparently, a less marked acceptor character [7], is phosphorylated somewhat more rapidly than alcohol (III).

Thus, in contrast to the case of $POCl_3$, in the reaction of the catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols by diaryl chlorophosphates no ethers are formed, irrespective of the structure of the alcohol and reaction conditions. This can be explained by the lower alkylating ability of the diaryl benzyl sulfates, compared with that of benzyl dichlorophosphates, most probably because of the appreciably lower value of the effective positive charge on the P atom, and hence the lower ability of the C—O—P of the benzylic fragment of the molecule to undergo heterolysis.

The α-polyfluoroalkylbenzyl diaryl phosphates obtained (Table 2) are colorless crystalline compounds, soluble in most organic solvents. The structure of these compounds was confirmed by the NMR spectral data (Table 3). In the PMR spectrum of phosphate (VIII) a nonequivalency of the m-Me group protons of the aroxyl radicals is observed, which is probably due to their diastereotopic character [2].

The initial alcohols (I)-(III) were synthesized by known methods [2]. Alcohol (IV) was obtained from $CF_3OCF_2CF_2COOH$ according to the following scheme:

$$CF_3OCF_2CF_2COOH \xrightarrow{C_6H_5MgBr} \underset{(XII)}{CF_3OCF_2CF_2COC_6H_5} \xrightarrow{NaBH_4} \underset{(IV)}{CF_3OCF_2CF_2CH(OH)C_6H_5}$$

The structure of ketone (XII) is confirmed by the data of IR and ^{19}F NMR spectra. In the ^{19}F NMR spectrum,* the value of the long-range spin—spin coupling constants of fluorine atoms in CF_3OCF_2 fragment (9 Hz) is nearly equal to the $^4J_{F-F}$ constant for fluorine atoms present at the 1,3-positions of the normal perfluoropropyl radical (9-10 Hz) [9], but is somewhat lower than a similar constant on the CF_3NCF_2 grouping (∿14-16 Hz) [9, 10]. Additional broadening of the $CF_3OCF_2\underline{CF_2}$ group signal is due to the spin—spin coupling with the benzene ring protons.

EXPERIMENTAL

The PMR and ^{19}F NMR spectra were run on a Perkin—Elmer R-20 spectrometer (using HMDS as internal standard in the PMR spectra and CF_3COOH as the external standard in the ^{19}F NMR spectra). The ^{31}P NMR spectra were run on a Bruker HX-90 apparatus in a pulse regime, with a noise suppression of the spin—spin coupling with protons (using 85% H_3PO_4 as external standard). In the ^{19}F and ^{31}P NMR spectra, the chemical shifts into the strong field are negative in value. The IR spectra were run on a UR-20 spectrophotometer. The TLC was carried out on Silufol UV-254 plates.

1-Phenyl-2,2,3,3,5,5,5-heptafluoro-4-oxapenta-1-one (XII). A solution of 92 g (0.4 mole) of $CF_3OCF_2CF_2COOH$ in 100 ml of absolute ether was added dropwise at −40°C in the course of 1 h, with vigorous stirring, to a solution of a Grignard reagent prepared from 157 g (1 mole) of bromobenzene and 26.4 g (1.1 g-at) of Mg in 400 ml of absolute ether. The mixture was heated to ∿20°C, boiled for 2 h, treated as usual and distilled in vacuo, collecting the fraction boiling at 65-85°C (12 mm). For the final purification, the distillate was dissolved in an equal volume of absolute pentane and was passed through a column with Al_2O_3 (using 2 g of Al_2O_3 per g of distilate), and eluted with pentane. The solvent was evaporated and the residue was distilled in vacuo on a Widmer column. Yield, 104 g (90%) of (XII), bp 85-86°C (32 mm), n_D^{20} 1.4028, d_4^{20} 1.4498. Found: C 41.4; H 1.6; F 45.6%. $C_{10}H_5F_7O_2$. Calculated: C 41.14; H 1.7; F 45.8%. IR spectrum: 1711 cm^{-1} (C=O). ^{19}F NMR spectrum (δ, ppm, J, Hz): +21.53 t (CF_3, $^4J_{F-F} = 9.0$), −9.27 q.t (OCF_2, $^3J_{F-F} = 1.8$, $^4J_{F-F} = 9.0$), −38.25 br. s (OCF_2-CF_2). Semicarbazone, mp 92.5-94°C (hexane—CCl_4). Found: C 37.8; H 2.2; N 12.1%. $C_{11}H_8F_7N_3O_2$. Calculated: C 38.0; H 2.3; N 12.1%.

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*The signals were assigned according to [8].

α-(Heptafluoro-3-oxabutyl)benzyl Alcohol (IV). A solution of 8.2 g (0.215 mole) of $NaBH_4$ in 80 ml of water was added dropwise to a solution of 124.7 g (0.43 mole) of (XII) in 375 ml of MeOH. The mixture was stirred for 4 h at ~20°C, and left to stand overnight. Excess of $NaBH_4$ was decomposed by 30% H_2SO_4, the mixture was diluted by an equal volume of water, and extracted by ether (4 × 200 ml). After distillation in vacuum, 120 g (96%) of (IV) were obtained, bp 109.5-110°C (33 mm), n_D^{20} 1.4053, d_4^{20} 1.4643. Found: C 41.1; H 2.4; F 45.6%. $C_{10}H_7F_7O_2$. Calculated: C 41.1; H 2.4; F 45.5%.

Diaryl Chlorophosphates. a) A mixture of 216 g (2 moles) of m-cresol, 191 g (1.25 moles) of $POCl_3$, and 2.78 g (25 mmoles) of anhydrous $CaCl_2$ was heated for 3 h, with gradual increase in temperature from 150 to 210°C. The mixture was then filtered, and the filtrate was fractionated in vacuo. Yield, 173.6 g (59%) of (VI), bp 149-150°C (0.5 mm), n_D^{20} 1.5451, d_4^{20} 1.2382. Found: C 56.5; H 4.7; Cl 12.2; P 10.5%. $C_{14}H_{14}ClO_3P$. Calculated: C 56.7; H 4.8; Cl 12.0; P 10.4%. $^{31}P-\{^1H\}$ NMR spectrum (ppm): −6.47 s.

b) Compound (V) was obtained in a similar way from phenol and $POCl_3$ in the presence of anhydrous $CaCl_2$, yield 64%, bp 129-131°C (1 mm), n_D^{20} 1.5503, d_4^{20} 1.2993: cf. [11].

α-Polyfluoroalkylbenzyl Diaryl Phosphates. A mixture of 0.01 mole of α-polyfluoroalkylbenzyl alcohol, 0.01 mole of diaryl chlorophosphate, and 0.25 mmole of the catalyst was heated for a few hours at 200°C up to cessation of evolution of HCl, and then dissolved in a minimal amount of absolute ether, and passed through a column with 6 g of Al_2O_3 with elution by ether. After the removal of the solvent in vacuo, α-polyfluoroalkylbenzyl diaryl phosphates were obtained.

CONCLUSIONS

Irrespective of the structure of the alcohol and the reaction conditions, catalytic phosphorylation of α-polyfluoroalkylbenzyl alcohols by diaryl chlorophosphates leads exclusively to α-polyfluoroalkylbenzyl diaryl phosphates.

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