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# α-POLYFLUOROALKYLBENZYL DICHLOROPHOSPHATES AS ALKYLATING AGENTS IN THE ALKYLATION OF POLYFLUORINATED PHENOLS

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Only a few examples of polyfluoroalkyl ethers of polyfluorinated phenols have been reported, and all these compounds are derivatives of primary polyfluoroalkanols [1, 2]. A general method for the synthesis of such compounds is the arylation of polyfluorinated alkali-metal alcoholates by polyfluorobenzenes.

In our previous work, we establish that α-polyfluoroalkylbenzyl dichlorophosphates alkylate primary, secondary, and tertiary polyfluorinated carbinols with the formation of the corresponding ethers:

$$4\text{-}RC_6H_4CH(CF_3)OPOCl_2 + R_FR'R''COH \xrightarrow[-HCl \atop -[PO_2Cl]]{t^\circ} 4\text{-}RC_6H_4CH(CF_3)OCR'R''R_F$$

$R_F$ = polyfluoroalkyl group; R = H, Me; R' = H, Alk; R" = H, Alk, Ar.

We may assume that this reaction is more general, and these phosphates should alkylate other fluorinated hydroxyl compounds, in particular, polyfluorinated phenols. Indeed, α-polyfluoroalkylbenzyl dichlorophosphates alkylate polyfluorinated phenols with the formation of ethers. This reaction proceeds under relatively mild conditions in the absence of solvent to give pure isomers as products in rather high yields.

Thus, heating equimolar amounts of α-trifluoromethylbenzyl dichlorophosphate (I) and pentafluorophenol (II) at 160°C for 2 h gives α-trifluoromethylbenzyl pentafluorophenyl ether (III) in 80% yield

$$\underset{(I)}{PhCH(CF_3)OPOCl_2} + \underset{(II)}{C_6F_5OH} \xrightarrow[-HCl \atop -[PO_2Cl]]{} \underset{(III)}{PhCH(CF_3)OC_6F_5}$$

Gas—liquid chromatography showed that small amounts of α-trifluoromethylbenzyl chloride (IV) were formed during the reaction.* The formation of such side products was also found in the alkylation of polyfluorinated alcohols by α-polyfluoroalkylbenzyl dichlorophosphates [3].

The reaction of (I) with substituted polyfluorophenols, 4-trifluoromethyltetrafluorophenols (V), and 4-chlorotetrafluorophenol (VI) proceeds analogously to give high yields of

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*Gas—liquid chromatography indicated that the ratio of ether (III) to chloride (IV) was 19:1.

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TABLE 1. NMR Spectral Data for α-Trifluoromethylbenzyl Polyfluorophenyl Ethers $PhCH(CF_3)OC_6F_4R$-4

| Compound | R | PMR spectrum, δ, ppm, J, Hz | | $^{19}F$ NMR spectrum, δ, ppm, J, Hz | | | |
|---|---|---|---|---|---|---|---|
| | | CH | $C_6H_5$ | $CF_3$ | $F^{2,6}$ * | $F^{3,5}$ * | R |
| (III) | F | 5,10 q, $J_{H-F}=6,1$ | 6,69–7,31 m | 0.48 d, $J_{H-F}=6,1$ | –78,05 m | –86,77m | –85,07 m* |
| (VII) | $CF_3$ | 5,31 q, $J_{H-F}=6,0$ | 6,68–7,32 m | 0,26 d, $J_{H-F}=6,1$ | –76,67 m | –64,29 m, $J_{F^{3,5}R}=21,6$ | 20,84 t $J_{F^{3,5}R}=21,6$ |
| (VIII) | Cl | 5,27 m $J_{H-F}=6,1$ | 6,77–7,42 m | 0,89 d, $J_{H-F}=6,1$ | –76,61 m | –64,44 m | – |

*The signals were assigned using the data of various workers [4-6].

α-trifluoromethylbenzyl 4-trifluoromethyltetrafluorophenyl ether (VII) and α-trifluoromethylbenzyl 4-chlorotetrafluorophenyl ether (VIII), respectively. As in the case of phenol (II), gas–liquid chromatographic analysis of the reaction mixture indicated the presence of slight amounts of benzyl chloride (IV)

$$\text{(I)} + \underset{\text{(V), (VI)}}{4\text{-}RC_6F_4OH} \xrightarrow[-[PO_2Cl]]{-HCl} \underset{\text{(VII), (VIII)}}{4\text{-}RC_6F_4OCH(CF_3)Ph}$$

$$R = CF_3\text{(V), (VII); Cl (VI), (VIII).}$$

These ethers may be separated from the reaction mixture by distillation in vacuum or by chromatography on alumina. α-Trifluoromethylbenzyl ethers of polyfluorophenols are colorless, clear liquids with a pleasant odor which are highly soluble in organic solvents. The ether structures were confirmed by PMR and $^{19}F$ NMR spectroscopy (Table 1). The $^{19}F$ NMR spectrum of the fluorine atoms at C-3 and C-5 of the polyfluorophenyl ring of ether (VIII) is a multiplet characteristic for the AA' part of an AA'XX' spin system. In the case of the two other ethers, the multiplet of the corresponding fluorine atoms is complicated due to coupling with the fluorine atoms of the substituent at C-4 of the polyfluorophenyl ring. The line broadening observed in the $^{19}F$ NMR spectra of ethers (III), (VII), and (VIII) for the signals of the α-trifluoromethyl groups and fluorine atoms at C-2 and C-6 of the polyfluorophenyl ring is a consequence of long-range coupling of the fluorine atoms of these fragments through six bonds ($^6J_{F-F} \leqslant 1.6$ Hz). Similar coupling was found previously for 2,2,2-trifluoroethyl pentafluorophenyl ether [4].

## EXPERIMENTAL

The PMR and $^{19}F$ NMR spectra were taken on a Perkin–Elmer R-20 spectrometer. The internal standard for the PMR spectra was HMDS (0.05 ppm), and the internal standard for the $^{19}F$ NMR spectra was $CF_3CO_2H$.

The gas–liquid chromatographic analysis was carried out on a Khrom-4 chromatograph using a 2-m glass column packed with 0.75% polyethylene glycol adipate on Chromosorb W (100/120 mesh), a flame-ionization detector, and 30 ml/min helium carrier gas flow rate. The sample was injected directly into the column. The column temperature was raised from 80 to 230°C at 8 deg/min. The calculations were calculated using a Kent Chromalog 2 electronic integrator.

α-Trifluoromethylbenzyl Pentafluorophenyl Ether (III). A mixture of 44 g (0.15 mole) (I) and 27.6 g (0.15 mole) (II) was heated for 2 h at 160°C. The filtrate was distilled in vacuum to yield 41.3 g (80%) (III), bp 82-83°C (2 mm), $n_D^{20}$ 1.4568, $d_4^{20}$ 1.5005.

α-Trifluoromethylbenzyl 4-Trifluoromethyltetrafluorophenyl Ether (VII). A mixture of 2.93 g (0.01 mole) (I) and 2.34 g (0.01 mole) (V) was heated for 2 h at 160°C and, upon cooling, was treated with $CCl_4$ and filtered. The filtrate was subjected to chromatography on a column packed with 3 g alumina with $CCl_4$ as the eluent to yield 3.3 g (84%) (VII), bp 76.5-77°C (1 mm), $n_D^{20}$ 1.4440, $d_4^{20}$ 1.5417.

α-Trifluoromethylbenzyl 4-Chlorotetrafluorophenyl Ether (VIII). A mixture of 2.93 g (0.01 mole) (I) and 2.0 g (0.01 mole) (VI) was heated for 2 h at 160°C and then treated as in the synthesis of (VII) to yield 2.3 g (64%) (VIII), bp 101-102°C (1.5 mm), $n_D^{20}$ 1.4803, $d_4^{20}$ 1.5172.

The elemental analysis data for (III), (VII), and (VIII) were in accord with the calculated values.

## CONCLUSIONS

α-Polyfluoroalkylbenzyl dichlorophosphates alkylate polyfluorinated phenols with the formation of the corresponding ethers.

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