Brief Communications

α-Polyfluoroalkylbenzyl dichlorophosphates as alkylating agents in alkylation of aromatic compounds

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On heating, α-polyfluoroalkylbenzyl dichlorophosphates alkylate mesitylene, durene, and naphthalene to give the corresponding aromatic compounds containing the α-polyfluoroalkylbenzyl fragment as a substituent.

Key words: α-polyfluoroalkylbenzyl dichlorophosphates, aromatic compounds, alkylation.

We have previously established that α-polyfluoroalkylbenzyl dichlorophosphates can act as *O*-alkylating agents relative to primary,[1] secondary,[1,2] and tertiary[1] fluoroalkanols as well as polyfluorinated phenols.[3] These reactions result in the formation of the corresponding α-polyfluoroalkylbenzyl esters

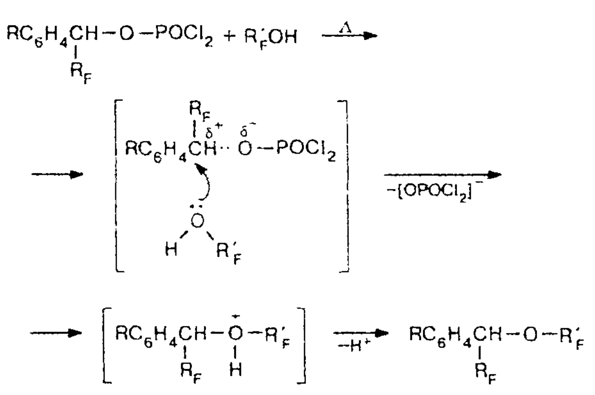
$$RC_6H_4CHR_FOPOCl_2 + R'_FOH \xrightarrow{\Delta} RC_6H_4CHR_FOR'_F$$

R = H, *p*-Me; R_F is polyfluoroalkyl; R'_F is polyfluoroalkyl or polyfluoroaryl

It has been assumed that alkylation occurs according to Scheme 1 including the thermal heterolysis of the C—OP bond of benzyl dichlorophosphate.[4]

If this heterolysis takes place, under certain conditions α-polyfluoroalkylbenzyl dichlorophosphates should manifest the alkylating effect relative to aromatic compounds as well.

Scheme 1



To check this assumption, we studied the reactions of α-trifluoromethylbenzyl dichlorophosphate (**1**) and α-heptafluoropropylbenzyl dichlorophosphate (**2**) with durene, mesitylene, and naphthalene. It has been established that heating of compounds **1** and **2** with durene at 160 and 190 °C results in the formation of 3-(α-poly-

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[†] Deceased.

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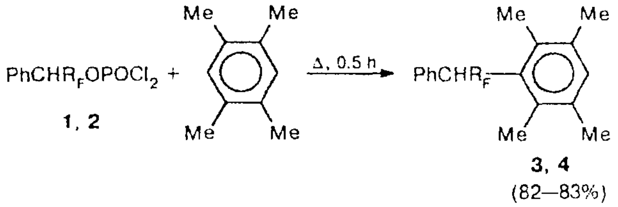
fluoroalkylbenzyl)-1,2,4,5-tetramethylbenzenes (**3** and **4**, respectively) in high yields (Scheme 2).

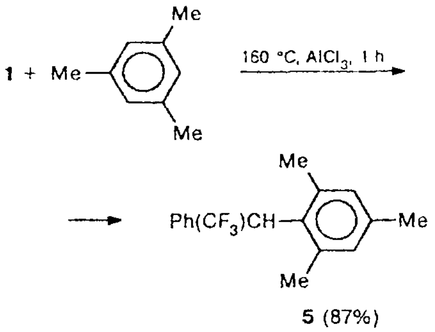
Scheme 2



R$_F$ = CF$_3$ (**1**, **3**), *n*-C$_3$F$_7$ (**2**, **4**)

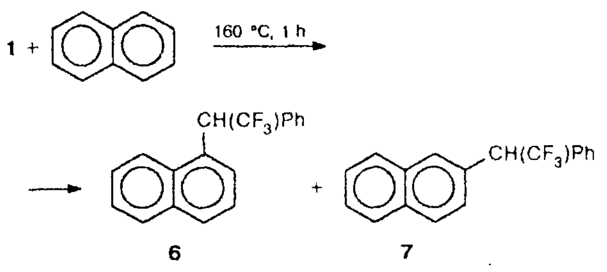
Catalytic quantities of Lewis acid (anhydrous $AlCl_3$) are needed to perform the reaction of mesitylene with dichlorophosphate **1** resulting in the formation of 2-(α-trifluoromethylbenzyl)-1,3,5-trimethylbenzene (**5**) (Scheme 3).

Scheme 3



α-Polyfluoroalkylbenzyl dichlorophosphates can also alkylate polycyclic aromatic compounds. For example, heating of dichlorophosphate **1** and naphthalene at 160 °C in the absence of a catalyst (Scheme 4) gives (in 85% yield) a mixture of 1- and 2-(α-trifluoromethylbenzyl)naphthalenes (**6** and **7**) in the ~3 : 2 ratio (according to the ^{19}F NMR spectrum). Compound **6** was isolated in the individual state from this mixture using fractional crystallization from hexane followed by sublimation *in vacuo*.

Scheme 4



The observed capability of α-polyfluoroalkylbenzyl dichlorophosphates to alkylate aromatic compounds and the fact that these reactions are catalyzed by Lewis acids support our assumption of the heterolytic character of the cleavage of the C—OP bond in the monoesters of phosphoric acid dichlorides considered.

The reactions of *C*-alkylation of aromatic compounds by α-polyfluoroalkylbenzyl dichlorophosphates occur in high yields, are virtually not accompanied by the formation of any by-products, and can serve as a convenient method for the synthesis of aromatic systems containing α-polyfluoroalkylbenzyl fragments as substituents.

The structures of the (α-polyfluoroalkylbenzyl)benzenes and -naphthalenes obtained were confirmed by the data of NMR (^1H, ^{19}F) (Table 1) and IR spectroscopy and GLC-MS. The ^1H NMR spectra of substituted durenes **3** and **4** exhibit magnetic nonequivalence of all four methyl groups, and the ^1H NMR spectrum of substituted mesitylene **5** indicates that both methyl groups in positions 1 and 3 and protons in positions 4 and 6 of the same aromatic ring are magnetically nonequivalent. It is most likely that in both cases the magnetic nonequivalence observed is related to difficult rotation of fragments of the molecule around the C—C bond between the substituted aromatic ring and benzyl group. This assumption is supported by the fact that when the temperature is changed, in the spectrum of compound **5** the behavior of the signals belonging to the 1-Me and 3-Me groups corresponds to the situation typical of exchange processes: at ~45 °C these signals coalesce, and at 100 °C already one sufficiently narrow ($\nu_{1/2} \approx$ 3 Hz) singlet is observed.

The mass spectra of all compounds obtained contain an intense peak of the molecular ion, and $[M-R_F]^+$ is the main fragmentation ion.

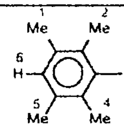
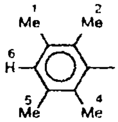
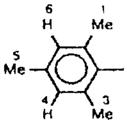
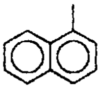
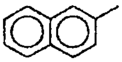
The position of the α-trifluoromethylbenzyl fragment in the naphthalene ring of compound **6** was determined on the basis of the IR spectrum in the region of out-of-plane deformation vibrations of C—H (700—900 cm^{-1}). The presence of the absorption band at 805 cm^{-1} in this spectral region indicates the substitution to position 1.[5] At the same time, a band at 820 cm^{-1} corresponding to the 2-substituted product appears additionally in the IR spectrum of a mixture of compounds **6** and **7**.

Experimental

^1H and ^{19}F NMR spectra were recorded on a Bruker WP-200SY instrument relative to HMDS (internal standard) and CF_3COOH (external standard), respectively. GLC analyses were carried out on a Varian instrument with an SE-54 15-m capillary column using an AT-800 ion trap (Finnigan MAT) and helium as the carrier gas; samples were introduced directly in the column, and the temperature of the column was varied from 50 to 180 °C with the rate of 4 °C min^{-1} and then to 285 °C with the rate of 10 °C min^{-1}. IR spectra were recorded on a UR-20 instrument.

1,2,4,5-Tetramethyl-3-(α-trifluoromethylbenzyl)benzene (3). A mixture of compound **1** (2.7 g, 9.2 mmol) and durene (2.4 g,

Table 1. Parameters of ^{1}H and ^{19}F spectra of (α-polyfluoroalkylbenzyl)benzenes and -naphthalenes $PhCH[(CF_2)_nCF_3]Ar$ (**3**—**7**)

Compound	*n*	Ar	δ ^{1}H (*J*/Hz)^a									δ ^{19}F (*J*/Hz),^{a} CF$_3$
									H arom.			
			CH	Me(1) (s)	Me(2) (s)	Me(3) (s)	Me(4) (s)	Me(5) (s)	H(4) (s)	H(6)	Ph (m)	
3	0		5.45 (q, J_{H-F} = 10.6)	2.05	1.70	—	2.31	2.26	—	6.86 (s)	6.99—7.22	16.40 (d,^{b} J_{H-F} = 10.6)
4	2		5.55 (dd, $^3J_{H-F}$ = 16.1, $^3J_{H-F}$ = 20.2)	2.10	1.84	—	2.31	2.28	—	6.88 (s)	7.04—7.24	−2.00 (t, $^4J_{F-F}$ = 12.0)
5	0		5.27 (q, J_{H-F} =10.6)	1.77	—	2.40	—	2.18	6.82	6.68 (s)	7.03—7.22	15.56 (d,^{b} J_{H-F} = 10.7)
6	0		5.42 (q, J_{H-F} = 9.6)	—	—	—	—	—	—	6.96—7.88 (m)	—	13.37 (d,^{b} J_{H-F} = 9.6)
7^c	0		4.69 (q, J_{H-F} = 9.8)	—	—	—	—	—	—	7.00—7.91 (m)	—	12.54 (d,^{b} J_{H-F} = 9.8)

^{a} In CCl_4.
^{b} When the spin-spin coupling of ^{19}F nuclei with protons is suppressed, doublets are transformed into singlets.
^{c} In a mixture with compound **6**.

17.9 mmol) was heated at 160 °C for 0.5 h until HCl ceased to be released and extracted with ether (10 mL). The extract was chromatographed on Al_2O_3 (5 g) using ether as the eluent. The solvent was removed, and the excess of durene was distilled off *in vacuo*. Compound **3** was obtained in 82% yield (2.2 g), m.p. 91.0—92.5 °C (hexane). Found (%): C, 74.0; H, 6.4; F, 19.4. $C_{18}H_{19}F_3$. Calculated (%): C, 74.0; H, 6.6; F, 19.5. MS, *m/z* (I_{rel} (%)): $[M]^+$ 292 (100), $[M-CF_3]^+$ 223 (25).

3-(α-Heptafluoropropylbenzyl)-1,2,4,5-tetramethylbenzene (4). A mixture of compound **2** (1.2 g, 3 mmol) and durene (0.8 g, 6 mmol) was heated at 190 °C for 0.5 h until HCl ceased to be released and extracted with ether (5 mL). The extract was chromatographed on Al_2O_3 (3 g) using ether as the eluent. The solvent was removed, and the excess of durene was distilled *in vacuo*. Compound **4** (1.0 g, 83%) was obtained, m.p. 60—61 °C (after sublimation *in vacuo*). Found (%): C, 61.5; H, 5.0; F, 33.7. $C_{20}H_{19}F_7$. Calculated (%): C, 61.2; H, 4.9; F, 33.9. MS, *m/z* (I_{rel} (%)): $[M]^+$ 392 (88), $[M-C_3F_7]^+$ 223 (72).

1,3,5-Trimethyl-2-(α-trifluoromethylbenzyl)benzene (5). A mixture of compound **1** (10.0 g, 34 mmol), mesitylene (10.0 g, 83 mmol), and anhydrous $AlCl_3$ (0.1 g, 0.75 mmol) was heated at 160 °C for 1 h until HCl ceased to be released. The excess of mesitylene was distilled off *in vacuo*, and the residue was extracted with ether (20 mL). The extract was chromatographed on Al_2O_3 (15 g) using ether as the eluent. The solvent was removed, and the residue was fractionated *in vacuo* to obtain compound **5** (8.2 g, 87%), b.p. 98.5—99.5 °C (0.5 Torr), n_D^{20} 1.5820, d_4^{20} 1.1540. Found (%): C, 73.4; H, 6.2; F, 20.4. $C_{17}H_{17}F_3$. Calculated (%): C, 73.4; H, 6.2; F, 20.5. MS, *m/z* (I_{rel} (%)): $[M]^+$ 278 (100), $[M-CF_3]^+$ 209 (92).

1-(α-Trifluoromethylbenzyl)naphthalene (6). A mixture of compound **1** (1.45 g, 5 mmol) and naphthalene (1.3 g, 10 mmol) was heated at 160 °C for 1 h until HCl ceased to be released and extracted with ether (10 mL). The extract was chromatographed on Al_2O_3 (3 g) using ether as the eluent. The solvent was removed, and the excess of naphthalene was removed by sublimation *in vacuo*. A mixture of products **6** and **7** (1.2 g, 85%) was obtained. Compound **6** (0.15 g) with m.p. 85—87 °C was isolated by fractional crystallization from hexane followed by sublimation *in vacuo*. Found (%): C, 75.6; H, 4.6; F, 19.6. $C_{18}H_{13}F_3$. Calculated (%): C, 75.5; H, 4.6; F, 19.9. MS, *m/z* (I_{rel} (%)): $[M]^+$ 286 (55), $[M-CF_3]^+$ 217 (92).

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The ESR study of the influence of fluorinated alcohols on spin-adducts of phosphoryl radicals with C_{60} and C_{70}: a change of magnetic resonance parameters and exclusive formation of monoadducts

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Complex formation of $^{\cdot}C_{60}P(O)(OPr^i)_2$ or three isomers of $^{\cdot}C_{70}P(O)(OPr^i)_2$ with fluorinated alcohols CF_3CH_2OH (**1**), $(CF_3)_3COH$ (**2**), and $(CF_3)_2CHOH$ (**3**) results in an increase in the hyperfine splitting constants with the ^{31}P nucleus by approximately 3—4 G. Only monoadducts are formed when alcohols **1**—**3** are added to toluene saturated solutions of $Hg[P(O)(OPr^i)_2]_2$ and C_{60} under photochemical conditions of multi-addition of phosphoryl radicals to C_{60}.

Key words: ESR, radical, phosphoryl; fullerene, complex formation; alcohols.

The capability of fullerenes to add easily free radicals is their characteristic feature caused by the great number of weakly conjugated double bonds in their molecules.[1—4] We have previously studied[5—7] the structure and reactivity of spin-adducts of mono- and polyaddition of dialkoxyphosphoryl radicals $^{\cdot}P(O)(OR)_2$ to fullerenes C_{60} and C_{70} and organic derivatives of C_{60}. It has been found that phosphorylfullerenyl radicals (PFR) co-exist in two conformation, the equilibrium between which depends on the temperature. Two isomers different in hyperfine coupling (HFC) constants (~4.0 G) are detected at low temperatures, whereas at high temperatures, the rotation rate increases, and an averaged picture is observed.[8] It could be assumed that the rate of mutual transitions between conformers depends on the temperature and the nature of a solvent. Therefore, in this work, we studied the effect of ethanol and fluorine-containing alcohols CF_3CH_2OH (**1**), $(CF_3)_3COH$ (**2**), and $(CF_3)_2CHOH$ (**3**) capable of interacting with the phosphoryl group[9] on the magnetic resonance parameters of phosphorylfullerenyl radicals.

Experimental

The solutions under study were irradiated with the focused light of a DRSh-1000 high-pressure mercury lamp (1 kW). ESR spectra were recorded on a Varian E-12A spectrometer. Samples were thermostatted using a Unipan electronic regulator.

Results and Discussion

Phosphorylfullerenyl radicals were generated according to the following scheme:

$$Hg[P(O)(OPr^i)_2]_2 \xrightarrow{h\nu} 2\ {}^{\cdot}P(O)(OPr^i)_2 + Hg,$$

$$C_{60} + {}^{\cdot}P(O)(OPr^i)_2 \longrightarrow \underset{\mathbf{4}}{{}^{\cdot}C_{60}P(O)(OPr^i)_2},$$

$$2\ \underset{\mathbf{4}}{{}^{\cdot}C_{60}P(O)(OPr^i)_2} \longrightarrow \underset{\mathbf{5}}{(OPr^i)_2(O)PC_{60}—C_{60}P(O)(OPr^i)_2}.$$

The influence of alcohols on the spectral parameters of PFR were studied by two methods. Alcohol **1** (5 vol.%)

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