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Short Communication

Reactions of sodium perfluorotertiary alkoxides with reactive halides

GEORGE J. MOORE, CHARLES F. SMITH and CHRIST TAMBORSKI
Air Force Materials Laboratory, Wright Patterson Air Force Base, Ohio 45433 (U.S.A.)
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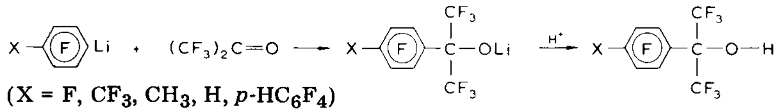
In an earlier account [1], a convenient general procedure for the synthesis of polyfluoroarylalkyl tertiary mono- and di-alcohols was reported.

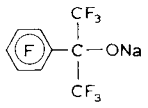


(X = F, CF_3, CH_3, H, p-HC_6F_4)

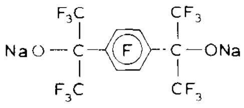
When X = H or p-HC_6F_4, a dilithio reagent can be formed which on further reaction with hexafluoroacetone yields the corresponding perfluoroarylalkyl diols. We have now extended this study to include some reactions of a mono- and di-tertiary alcohol with reactive halides. These reactions were carried out to provide model compounds representing various alkyl and aryl esters, silicates and carbonates which could provide preliminary data for new polymer systems.

Reactions of partially fluorinated primary, secondary and tertiary alcohols have been reported [2]. Reactions of perfluoroalkyltertiary alcohols, however, have only recently been reported [4 - 7] as methods for the synthesis of these alcohols became available. We have found, as have other authors, that these perfluorotertiary alcohols are unreactive towards acyl halides and silicon halides. $(CF_3)_3COH$ has been reported [3] to react very slowly with CH_3COCl in the presence of $AlCl_3$ to yield the ester. However, in the presence of a base, 2-methylpyridine, the alcohol reacts with acetic anhydride and trifluoroacetic anhydride to yield the corresponding esters [5]. DePasquale [6] has recently indicated that $(CF_3)_3COH$ is completely converted to the ester on reaction with $C_7F_{15}COCl$ in the presence of $(C_2H_5)_3N$.

Lithium [4, 8, 9], sodium [6, 8, 10] and potassium [8] salts of perfluoroalkyltertiary alcohols have been reported. Similarly, the sodium salts (I) and (II) can be prepared and isolated.



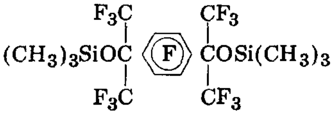
(I)



(II)

TABLE 1

Reactions of (I) and (II) with various substrates

Reaction	Product[a]	Yield (%)	M.p./°C	B.p./°C (mn
2(I) + ClCOCl	$(R_fO)_2CO$ (III)(nc)	55	63 - 65	
(I) + C_6F_5COCl	$R_fOOCC_6F_5$ (IV)(nc)	84	62 - 63.5	
2(I) + $ClOC(CF_2)_3COCl$	$R_fOOC(CF_2)_3COOR_f$ (V)(nc)	53	55 - 57	
4(I) + $SiCl_4$	$(R_fO)_3SiCl$ (VI)(nc)	32	97 - 98	
3(I) + CH_3SiCl_3	$(R_fO)_3SiCH_3$ (VII)(nc)	61	126 - 128	
2(I) + $(CH_3)_2SiCl_2$	$(R_fO)_2Si(CH_3)_2$ (VIII)(nc)	62		112 - 115(0
(I) + $(CH_3)_3SiCl$	$R_fOSi(CH_3)_3$ (IX)(nc)	48		48(7)[c]
(II) + $2(CH_3)_3SiCl$	 (X)(nc)	43	69 - 71	

[a] $R_f = C_6F_5C(CF_3)_2$.
[b] $n_D^{23} = 1.4012$.
[c] $n_D^{23} = 1.3919$.

Unlike the perfluoroprimary metal alkoxides R_fOM, these tertiary alkoxide salts are thermally stable, the melting point of (I) being 139 - 141 °C while (II) does not melt or decompose up to 360 °C. These sodium alkoxides react at a more favorable rate than the free alcohols and provide a convenient method for the synthesis of many classes of compounds. Products resulting from the reactions of these salts with various acyl chlorides, chlorosilanes and phosgene are listed in Table 1. In the reaction between $C_6F_5(CF_3)_2CONa$ and $SiCl_4$ (4:1 mole ratio), only the trisubstituted product, $[C_6F_5(CF_3)_2CO]_3$-SiCl, was obtained, presumably because of steric hindrance involving the bulky arylalkoxy groups on the silicon atom.

It was also of interest to determine the relative stabilities of these highly fluorinated and sterically hindered model compounds to mildly acidic (0.05 *N* HCl) and basic (0.05 *N* NaOH) hydrolysis conditions*. Ether solutions of these compounds were exposed to aqueous acidic and basic conditions for 24 h and the percentage of starting material remaining unhydrolyzed was determined by VPC analysis. The carbonate (III) and the aryl ester (IV) were completely stable under these selected conditions while the silicates and alkyl diester were unstable. The relative order of stability was established as (III) ≅ (IV) > (IX) > (VIII) > (V).

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* No attempt was made to determine the absolute rates of hydrolysis. The crude data obtained serve only as a guide.

Experimental

Preparation of sodium salts

(a) $C_6F_5C(CF_3)_2CONa$ *(I):* Sodium (6.9 g, 0.30 mol) was added to anhydrous methanol (700 cm^3) at 0 °C. The alcohol, $C_6F_5(CF_3)_2COH$ (100 g, 0.30 mol), dissolved in 50 cm^3 of anhydrous methanol, was added slowly (2 h) to the stirred solution. After additional stirring for 1 h, the excess solvent was removed under vacuum. Benzene (300 cm^3) was added to the viscous residue, the mixture agitated and the solvent removed under vacuum. This process was repeated until a white solid remained on vacuum distillation of the solvent. The white salt was then dried in a vacuum oven at 90 °C for 24 h. The yield of (I) was 104.7 g (98%), m.p. 139 - 141 °C.

Alternatively, (I) may be prepared by adding the alcohol (0.08 mol) dissolved in anhydrous tetrahydrofuran (40 cm^3) to a stirred mixture of sodium hydride (0.08 mol) in tetrahydrofuran (100 cm^3). The reaction mixture was subsequently heated to reflux for 30 min and cooled to room temperature. The solution can be used for subsequent reactions without isolating the free sodium salt.

(b) p-$NaOC(CF_3)_2C_6F_4C(CF_3)_2ONa$ *(II):* The disodium salt (II) may be prepared in a similar manner to that described in (a) above. The crude viscous residue, resulting from the vacuum distillation of the excess methanol, was dissolved in hot benzene/methanol (2:1) mixture. On cooling, a white precipitate formed which was filtered and washed (3×) with hexane. On concentrating the filtrate, additional salt was obtained. The combined salts were dried in a vacuum oven at 90 °C for 24 h. The disodium salt (II) did not melt when heated to 360 °C.

General reactions of (I) and (II)

The compounds listed in Table 1 were prepared in a similar manner to that described in the following examples. Analyses are shown in Table II.

Bis(perfluoro-α,α-dimethylbenzyloxy)dimethylsilane (VIII): A solution of dichlorodimethylsilane (3.9 g, 0.03 mol) dissolved in tetrahydrofuran (50 cm^3) was added slowly to a stirred solution of $C_6F_5(CF_3)_2CONa$ (21.4 g, 0.06 mol) in tetrahydrofuran (150 cm^3). Reaction commenced immediately as evidenced by salt formation. The reaction mixture was refluxed for an additional 2 h and then cooled to room temperature. The NaCl precipitate was filtered off and the filtrate concentrated to a viscous liquid which was fractionally distilled to yield (VIII) (13.5 g, 62% yield) as a colorless liquid, b.p. 112 - 115 °C/0.04 mmHg, n_D^{23} 1.4012.

Bis(perfluoro-α,α-dimethylbenzyl)carbonate (III): $C_6F_5(CF_3)_2COH$ (40.1 g, 0.12 mol) in tetrahydrofuran (100 cm^3) was added slowly to a stirred mixture of sodium hydride (6.0 g, 0.12 mol) in tetrahydrofuran (100 cm^3). The reaction mixture was refluxed for 30 min and cooled to 0 °C.

TABLE 2

Analyses of compounds

Compound	Mass spectral data	Combustion data (calc./found)				NMR data	
		C	H	F	Cl	^{19}F spectra	^{1}H spectra
(III)	M (694)	32.87 32.98	—	60.21 60.02	—	72(m, 12F, CF_3); 137(m, 4F, *o*-F); 160(m, 4F, *m*-F); 147(m, 2F, *p*-F)	
(IV)	M (528)	36.39 36.38	—	57.55 57.52	—	72(m, 6F, CF_3); 136(m, 4F, *o*-F); 160(m, 4F, *m*-F); 145(tt, 1F, *p*-F); 148(tt, 1F, *p*-F)	
(V)	M (872)	31.67 31.61	—	61.00 61.17		72(t, 12F, CF_3); 137(m, 4F, *o*-F); 159(m, 4F, *m*-F); 147(m, 2F, *p*-F); 117(m, 4F, $CF_2C{=}O$); 123(m, 2F, CF_2)	
(VI)	M (1062)	30.51 30.52	—	—	3.34 3.32	74(t, 18F, CF_3); 133(m, 6F, *o*-F); 160(m, 6F, *m*-F); 148(m, 3F, *p*-F)	
(VII)	M (1042)	32.26 32.23	0.29 0.36	60.15 59.73	—	75(t, 18F, CF_3); 134(m, 6F, *o*-F); 161(m, 6F, *m*-F); 149(tt, 3F, *p*-F)	0.52(s, CH_3)
(VIII)	M (724)	33.17 33.18	0.84 0.99	57.70 56.04	—	75(t, 12F, CF_3); 134(m, 4F, *o*-F); 161(m, 4F, *m*-F); 149(tt, 2F, *p*-F)	0.38(s, CH_3)
(IX)	M − CH_3 (391)	35.48 35.58	2.23 2.23	51.44 51.95	—	75(t, 6F, CF_3); 134(m, 2F, *o*-F); 161(m, 2F, *m*-F); 150(tt, 1F, *p*-F)	0.23(s, CH_3)
(X)	M − CH_3 (611)	34.51 34.50	2.89 3.04	48.52 48.89	—	75(t, 12F, CF_3); 133(m, 4F, *o*-F)	0.23(s, CH_3)

[a] NMR spectra were recorded on a Varian A56/60 spectrometer in CCl_4 solution. Chemical shifts are expressed in ppm using tetramethylsilane (TMS) as an internal standard for ^{1}H and fluorotrichloromethane ($CFCl_3$) as an internal standard for ^{19}F spectra.

Phosgene (5.9 g, 0.06 mol) was slowly bubbled into the tetrahydrofuran solution, and the reaction mixture was stirred for 18 h. The solids were removed by filtration, washed with diethyl ether and the combined tetrahydrofuran/diethyl ether filtrate was concentrated to a viscous liquid. Fractional distillation yielded a liquid, b.p. 110 - 150 °C/0.05 mmHg, which when chromatographed on an alumina column and eluted with petroleum ether (b.p. 35 - 60 °C) yielded (III) as a white solid (19.5 g, 55% yield) m.p. 63 - 65°C

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