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Synthesis of 2-perfluoroalkyl-substituted acetals from the one-pot reaction of perfluoroalkyl iodides with vinyl ether and alcoholates

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Abstract

Treatment of perfluoroalkyl iodides, R_fI ($R_f=C_4F_9$, ClC_4F_8), with alcoholates and vinyl ethyl ether gave 2-perfluoroalkyl acetals via perfluoroalkyl radical intermediates. Both R_f and $R_fCH_2\dot{C}HOEt$ radicals were detected by ESR spectroscopy. A single-electron-transfer mechanism is proposed for this reaction.

Keywords: Synthesis; 2-Perfluoroalkyl-substituted acetals; Free radical; EPR spectroscopy; NMR spectroscopy; IR spectroscopy; Mass spectrometry

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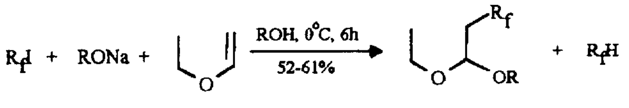
1. Introduction

Perfluoroalkyl iodides, R_fI, are highly reactive compounds and synthetic intermediates of great importance in organofluorine chemistry [1]. Their chemical properties and transformations have been studied extensively. They add readily to unsaturated compounds such as alkenes [2], alkyls [3] and conjugated dienes [4]. Tarrant and Stump [5] first reported the addition of fluoroalkane or haloalkane to vinyl ether under ultraviolet irradiation. Pazenik et al. [6] found that treatment of perfluoroalkyl iodides with alkyl vinyl ether initiated by $Pd(PPh_3)_4$ gave the 1:1 adduct. Recently, a similar result was reported and sodium dithionite was used to initiate the addition reaction of R_fI with vinyl ether [7].

In this paper we describe a convenient synthesis of 2-perfluoroalkyl acetal from the one-pot reaction of perfluoroalkyl iodides with vinyl ether in the presence of alcoholates.

2. Results and discussion

Treatment of perfluoroalkyliodides, R_fI, with equimolar amounts of alcoholate solution followed by ethyl vinyl ether at 0 °C gave the title products, 2-perfluoroalkyl acetals (**4**), in moderate yield and the ω-hydrogen perfluoroalkanes, R_fH (**5**), as byproducts.



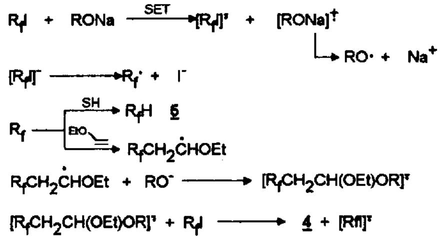
1 2 3 4 5

($R_f=C_4F_9$, R = Me, **4a**; $R_f=C_4F_9$, R = Et, **4b**; $R_f=ClC_4F_8$, R = Me, **4c**; $R_f=ClC_4F_8$, R = Et, **4d**; $R_f=ClC_4F_8$, R = Me, **4e**)

It is well known that perfluoroalkyl iodides are good electron acceptors [1]. A single-electron-transfer mechanism is proposed for this reaction; a rationalized reaction process is shown in Scheme 1.

Both radicals $R_f\cdot$ and $R_fCH_2\dot{C}HOEt$ are captured by ^tBuNO and can be detected. The ESR spectra of $R_fN(\dot{O})Bu^t$, $R_fCH_2CH(OEt)N(\dot{O})Bu^t$ and the EPR parameters of the spin adducts are shown in Fig. 1 [8,9].

Due to the electron-donor properties of the EtO group in the vinyl ether, the electrophilic $R_f\cdot$ radical only adds to the β-position forming the product **4**; at higher reaction temperatures (40 °C), the yield of **4** was less than 10%. In this case a ionic reaction, i.e. RO^- attack on the positively charger iodide atom appears more favored.



Scheme 1.

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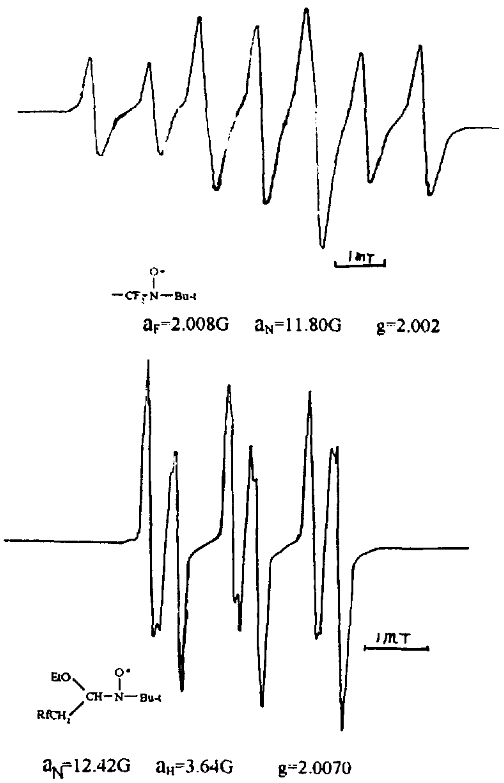
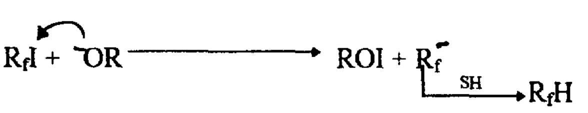
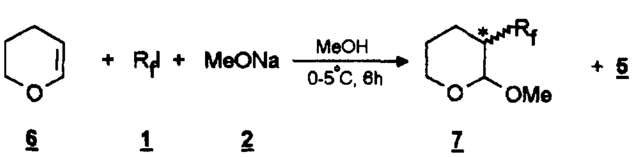


Fig. 1. The EPR spectra of $C_4F_9N(\dot{O})Bu^t$ and $C_4F_9CH_2CH(OEt)N(\dot{O})Bu^t$.



As expected, the electron scavenger *p*-dinitrobenzene significantly suppressed this reaction (see Table 1).

Similarly treatment of 2,4-dihydropyran with **1** and alcoholate gave 2-methoxyl-3-perfluoroalkyl pyrans:



The stereo conformation of product **7** is unsolved. It was noted that the fluorine chemical shifts of the two fluorine atoms bonded to the unsymmetric C-3 carbon atom were different, occurring at 35.3 and 40.5 ppm, respectively. The 2-perfluoroalkyl acetals **4** were readily hydrolyzed, giving the corresponding 2-perfluoroalkylaldehydes. Their chemical reactions are under investigation.

3. Experimental details

Boiling points are uncorrected. Solvents were purified and dried before use. ^1H NMR (60 MHz) and ^{19}F NMR (54.6 MHz) spectra were recorded on a Varian-360L instrument with TMS and TFA ($\delta_{CFCl_3} = \delta_{TFA} + 76.6$, and with upfield positive) as an internal and external standard, respectively. Elemental analysis were performed at this Institute. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Lower resolution mass spectra were obtained on a Finnigan GC–MS 4021 instrument.

All EPR spectra were measured on a Varian E-112 spectrometer with X-band, field modulation 100 kHz radiation, 0.25 s response time and 10 mT sweep width. The magnetic field was determined by a ^1H NMR field meter and the microwave frequency by a frequency meter for super-high frequency.

3.1. Preparation of 2-perfluoroalkyl acetals 4 and 2-methoxyl-3-perfluoroalkyl tetrahydropyrans 7: general procedure

Perfluorobutyl iodide (**1a**, 1.73 g, 5 mmol) was added to a 10 ml flask containing a solution of MeONa in MeOH (0.5 mol, 10 ml) at 0 °C. After stirring for 0.5 h, ethyl vinyl ether (0.8 g, 11 mmol) was added dropwise. Stirring of the reaction mixture was continued for another 6 h and then ice-water (10 ml) was added. The oil layer was separated and the aqueous layer extracted with ether (10 ml×3). The organic layer was combined, dried over Na_2SO_4 and distilled to give $C_4F_9CH_2CH(OMe)OEt$ (**4a**).

Table 1
Reaction of **1** with **3** or **6**

Entry No.	Reactants			Products	Yield (%)	B.p. (°C/Torr)
	1	2	3 or 6			
1	C_4F_9I	MeONa	**3**	**4a**	58	62–65/15
2	C_4F_9I	EtONa	**3**	**4b**	55	68–70/15
3	ClC_4F_8I	MeONa	**3**	**4c**	61	65–66/15
4	ClC_4F_8I	EtONa	**3**	**4d**	57	78–80/15
5[a]	ClC_4F_8I	MeONa	**3**	**4e**	8	–
6[b]	C_4F_9I	MeONa	**3**	**4a**	<5	–
7	C_4F_9I	MeONa	**6**	**7a**	55	83–85/15
8	ClC_4F_8I	MeONa	**6**	**7b**	60	87–89/15

[a] Reaction temperature 40–45 °C; main product ClC_4F_8H.

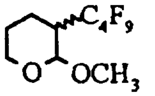
[b] Dinitrobenzene (10% mol) added.

$C_4F_9CH_2CH(OMe)OEt$ (**4a**): IR (KBr, ν, cm^{-1}): 2995, 2934, 1400 (Me, Et); 1194, 1139 (C–F); 1068 (C–O). ^1H NMR ($CDCl_3$) δ: 4.86 (t, CH, $^3J_{HH}=5$ Hz); 3.63 (m, OCH_2); 3.37 (s, OCH_3); 2.47 (t–d, CH_2CF_2 $^3J_{HH}=5$ Hz, $^3J_{HF}=18$ Hz); 1.25 (t, CH_3, $^3J_{HH}=5$ Hz) ppm. ^{19}F NMR δ: 5,3 (s, CF_3); 37.6 (m, CF_2CH_2); 48.3 (m, CF_2); 50.0 (m, CF_2) ppm. MS (m/z, %): 323 (M^+H, 6.53); 322 (M^+, 4.21); 69 (CF_3^+, 100.0). Analysis: Calc. for $C_9H_{11}F_9O_2$: C, 33.54; Hm, 3.42%. Found: C, 33.63; H, 3.70%.

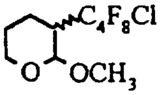
$C_4F_9CH_2CH(OEt)_2$ (**4b**): IR (KBr, ν, cm^{-1}): 2995, 2930, 1410 (Et); 1193, 1138 (C–F); 1065 (C–O) ppm. ^1H NMR ($CDCl_3$) δ: 4.83 (t, CH); 3.60 (m, OCH_2); 2.43 (t–d, CH_2CF_2); 1.18 (t, CH_3) ppm. ^{19}F NMR δ: 4.8 (s, CF_3); 37.2 (m, CF_2CH_2); 47.6 (m, CF_2); 49.8 (m, CF_2) ppm. MS (m/z, %): 327 (M^+H, 3.46); 219 ($C_4F_9^+$, 100.0). Analysis: Calc. for $C_{10}H_{13}F_9O_2$: C, 36.89; H, 3.99%. Found: C, 36.97; H, 4.12%.

$ClC_4F_8CH_2CH(OMe)OEt$ (**4c**): IR (KBr, ν, cm^{-1}): 2997, 2935, 1408 (Me, Et); 1197, 1140 (C–F); 1063 (C–O). ^1H NMR ($CDCl_3$) δ: 4.76 (t, CH); 3.53 (m, OCH_2); 3.37 (m, OCH_3); 2.36 (t–d, CH_2CF_2); 1.13 (t, CH_3) ppm. ^{19}F NMR δ: -8.0 (s, $ClCF_2$); 38.3 (m, CF_2CH_2); 44.0 (m, CF_2); 47.3 (m, CF_2) ppm. MS (m/z, %): 341/339 (M^+H, 2.3/6.5); 201 ($HC_4F_8^+$, 100.0). Analysis: Calc. for $C_9H_{11}ClF_8O_2$: C, 31.81; H, 3.24%. Found: C, 31.54; H, 3.71%.

$ClC_4F_8CH_2CH(OEt)_2$ (**4d**): IR (KBr, ν, cm^{-1}): 2998, 2934, 1408 (Et); 1200, 1137 (C–F); 1067 (C–O). ^1H NMR ($CDCl_3$) δ: 4.80 (t, CH); 3.63 (m, OCH_2); 2.70 (t–d, CH_2CF_2); 1.20 (t, CH_3) ppm. ^{19}F NMR δ: -8.5 (s, $ClCF_2$); 37.6 (m, CF_2CH_2); 43.6 (m, CF_2); 46.5 (m, CF_2) ppm. Analysis: Calc. for $C_{10}H_{13}ClF_8O_2$: C, 33.95; H, 3.68%. Found: C, 33.70; H, 4.01%.



(**7a**): IR (KBr, ν, cm^{-1}): 2996, 2930, 2880, 1410 (CH_3, CH_2); 1200–1100 (C–F); 1060, 1045 (C–O). ^1H NMR ($CDCl_3$) δ: 4.86 (s, OCHO); 4.05 (broad, CHC_4F_9); 3.70 (m, OCH_2); 3.43 (s, OCH_3); 2.15–1.40 (m, CH_2CH_2) ppm. ^{19}F NMR δ: 4.7 (s, CF_3); 35.3 (m, 1F, CF_2CH); 40.5 (m, 1F, CF_2CH); 46.3 (m, CF_2); 49.5 (m, CF_2) ppm. Analysis: Calc. for $C_{10}H_{11}F_9O_2$: C, 35.93; H, 3.29%. Found: C, 35.76; H, 3.51%.



(**7b**): IR (KBr, ν, cm^{-1}): 2995, 2934, 2896, 1425 (CH_3, CH_2); 1205–1100 (C–F); 1058, 1040 (C–O). ^1H NMR ($CDCl_3$) δ: 4.75 (s, OCHO); 4.00 (broad, CHC_4F_8Cl); 3.67 (m, OCH_2); 3.40 (s, OCH_3); 2.10–1.40 (m, CH_2CH_2) ppm. ^{19}F NMR δ: -8.0 (s, $ClCF_2$); 37.7 (m, CF_2CH); 44.3 (m, CF_2); 48.0 (m, CF_2) ppm. MS (m/z, %): 353/351 (M^+H, 2.13/6.30); 137/135 ($ClCF_2CF_2^+$, 32.5/100.0). Analysis: Calc. for $C_{10}H_{11}ClF_8O_2$: C, 34.24; H, 3.14%. Found: C, 34.46; H, 3.51%.

Acknowledgements

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