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^{17}O-NMR STUDY OF POLYFLUORINATED ALCOHOLS AND ETHERS

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SUMMARY

$\delta^{17}O$ values are reported for 16 polyfluorinated alcohols and ethers. The ^{17}O-nuclear shielding increases with fluorine substituents in γ-position and it decreases (much more than expected by comparison with $\delta^{13}C$-values) with fluorine substituents in β-position. The π-interactions between oxygen and a vinyl or a phenyl group (α,β -unsaturation) are greatly reduced if a CHF_2CF_2 group is attached to the oxygen. Conclusions from $\delta^{17}O$-data are supported by ^{13}C-, ^{11}B- and ^{29}Si-chemical shifts.

INTRODUCTION

The dramatic improvements in NMR instrumentation during the last decade have stimulated the study of such nucleides which are of fundamental importance in chemistry but which have unfavourable

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nuclear magnetic properties. A typical example for this is the ^{17}O-nucleus (natural abundance: 0.037% and I = 5/2), and it is only in the last 5-6 years, ca. 20 years after the pioneering work by Christ et al. [1], that a steadily growing number of ^{17}O-NMR studies (natural abundance or of labelled compounds) shows the potential of this method (for reviews see ref. [2-5]). As a consequence of the vast amount of different types of oxygen compounds available much of the activity in ^{17}O-NMR work still concentrates on the collection and classification of ^{17}O-NMR parameters (in particular ^{17}O-chemical shifts, $\delta^{17}O$) in order to establish empirical trends and to test theoretical models. From the information already available [2-5] it is evident that $\delta^{17}O$ values are very sensitive to changes in the electronic structure. Is was shown in case of alcohols [6] and dialkyl ethers [7], that there are linear correlations between $\delta^{17}O$- and $\delta^{13}C$-values of corresponding hydrocarbons (ROH/RCH_3 [6], ROR'/RCH_2R' [7]), indicating a similar dependance on structural effects for both nuclei. Furthermore, π-interactions are reflected by the $\delta^{17}O$-values, first suggested in ref. [1] and, later, corroborated in various ^{17}O-NMR studies [2-5],e.g.of boron-oxygen compounds [8,9], of carboxonium ions [10] and of ethers (α,β -unsaturated and aromatic) [11].

Our current interest in NMR spectroscopic properties of polyfluorinated organic compounds [12] prompted us to use ^{17}O-NMR as a probe for studying the influence of the polyfluorinated alkyl chain in alcohols and ethers. So far, compounds of this type have received only scant attention. To our knowledge, the $\delta^{17}O$-values of only three compounds have been reported. These are shifted

CF_3CH_2-O-H

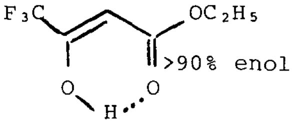
$\delta^{17}O$: -23.6 [6]

$\Delta^{17}O$: -29.5

$CHF_2CHFCH_2-O-CH=CH_2$

$\delta^{17}O$: +56 [11]

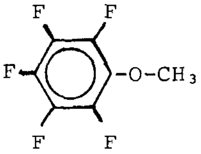
$\Delta^{17}O$: -28



$\delta^{17}O(a)$: +96.0[13]

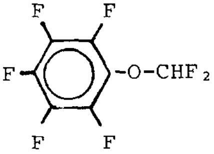
$\Delta^{17}O$: -28.0

considerably to low frequency with respect to the $\delta^{17}O$-values of their hydrocarbon analogues ($\Delta^{17}O$). A systematic ^{17}O-NMR study has been carried out for polyfluoroaromatic oxygen derivates [14]. It is shown that there is a shielding influence of the C_6F_5-group, but deshielding is observed if the α-carbon is substituted with fluorine:



$\delta^{17}O$: +8.0 [14]

$\Delta^{17}O$: -37.0



$\delta^{17}O$: +76.5 [14]

$\Delta^{17}O$: +31.5 (anisole),

+68.5 ($C_6F_5OCH_3$)

We have measured the ^{17}O-chemical shifts of 16 polyfluorinated alcohols (**1**) and ethers (**2**,**3**) in order to represent the surrounding of the oxygen atoms corresponding to the structures of type **A**, **B**, **C**. In addition, we looked at the mutual influence of α,β-unsaturatio and of the CHF_2CF_2-group on the ^{17}O-chemical shift (compounds **2d**,**e**,**f**).

$-CF_2-CF_2-O'$

A

$-CF_2-CF_2-CH_2-O'$

B

$-CF_2-CF_2-CH_2-CH_2-O'$

C

RESULTS AND DISCUSSION

^{17}O-chemical shifts, $\delta\,^{17}$O, of compounds 1 - 3 are given in Table 1, together with the line widths, $\Delta\nu_{1/2}$, and the shift differences, Δ^{17}O, with respect to the corresponding hydrocarbon analogues. The influence on the shielding of neighboured nucleides exerted by the CHF_2CF_2- or the C_6F_{13}- and C_7F_{15}-group is very similar as evidenced by $\delta\,^{13}$C-data previously obtained [12,15,16] and those given in Table 2, and also by $\delta\,^{17}$O data (see entries in Table 1 for compounds 1ab, 3ac). Therefore, fluorine atoms or other substituents in δ-position or further removed from the nucle in question (^{13}C or ^{17}O) will have only a very small or negligible influence on its shielding. This is apparent from Δ^{13}C data [12, 15,16] and from small Δ^{17}O values (1c, 2b (OCH_3), 3def). That means, in structures of type C we will observe $\delta\,^{17}$O values very close to the hydrocarbon analogue.

An inspection of Table 1 shows immediately that structures of type A and B are readily distinguished. In case of the latter (B) there is always an increase in shielding. For the alcohols 1ab the increase in shielding is larger than for the silanes 3ac. However, part of the increased shielding for 1ab must be attributed to the reduced tendency of hydrogen bonding in the polyfluorinated alcohols. For type A (compounds 2) a decrease in shielding of the ^{17}O-nucleus is observed, its magnitude depends on the nature of the other substituent.

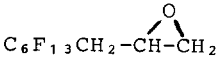
The $\Delta^{17}O$-values for compounds 2abc are fairly constant (58 ± 2 ppm), indicating that the reduced shielding of oxygen is caused solely by the CHF_2CF_2-group. This situation changes for compounds 2de with $\Delta^{17}O$-values $\sim$ 20 ppm. Clearly, this is the result of changes in π-interaction between the oxygen lone electron pair and the vinylic or the aromatic π-system. If the CHF_2CF_2-group is replaced by an ethyl group π-interactions are virtually undisturbed as was shown qualitatively by ^{17}O-NMR [11] and by many other physical methods (see references cited in [11]).

The smaller $\Delta^{17}O$-values suggest that the π-contributions which deshield the ^{17}O-nucleus by ca. 55 - 75 ppm in the hydrocarbon analogues are reduced in 2de. Therefore, the $CHCF_2CF_2$-group reduces the availability of the oxygen lone electron pairs for these π-interactions. This argument is supported by the $\delta^{13}C$-data for 2de (Table 2) which reflect a reduced π-electron charge density at the terminal vinylic carbon (2e) and at the para-carbon (2d).

The comparison with $\delta^{13}C$-values of polyfluorinated alkanes [12, 15,16] shows that the shielding of the ^{17}O-nucleus is much more sensitive to the fluorine substitution at the α- or β-carbon atom. A crude estimate from $\Delta^{13}C$-values [12,15,16] gives $\sim +3 \pm 1$ ppm per fluorine atom at the α-carbon (i.e. in β-position) and $\sim -3.5 \pm 1$ per fluorine atom at the β-carbon (i.e. in γ-position for $^{13}CH_2$-groups in polyfluorinated alkanes. A similarly crude estimate from $\Delta^{17}O$-values for comparable compounds in this study shows that a fluorine at the α-carbon (i.e. in β-position) produces a deshielding effect of $\sim + 36 \pm 5$ ppm ('β-effect'), whereas a fluorine at the β-carbon (i.e. in γ-position) causes shielding of the ^{17}O-nucleus by -10 ± 3 ppm (the wellknown 'γ-effect' [17]).

TABLE 1

^{17}O Chemical shifts [a] ($\delta^{17}O$) and line widths ($\Delta\nu_{1/2}$ [b], Hz) of polyfluorinated alcohols and ethers in comparison to their hydrocarbon analogues ($\Delta^{17}O$)

Nr.	Compound	$\delta^{17}O$	$\Delta\nu_{1/2}$	Solvent/°C	$\Delta^{17}O$
1a	$HCF_2CF_2CH_2$-OH	-26.8 -27.6	410 170	$CDCl_3$/28 $CDCl_3$/55	 -27.0[c]
1b	$C_7F_{15}CH_2$-OH	-28.0	>700	$CDCl_3$/60	-27.0[c]
1c	$C_6F_{13}CH_2CH_2$-OH	-7.0	630	$CDCl_3$/30	-6.0[c]
2a	HCF_2CF_2-O-CH_3	+34.0	100	C_6D_6/28	+56.5[d]
2b	$HCF_2CF_2\text{-}\overset{(a)}{O}\text{-}CH_2CH_2\text{-}\overset{(b)}{O}\text{-}CH_3$	+55.0 (a) -28.3 (b)	200 165	$CDCl_3$/50	+60.0[e] (a) -1.3[e] (b)
2c	HCF_2CF_2-O-$CH_2CH{=}CH_2$	+60.0	155	$CDCl_3$/50	+58.5[f]
2d	HCF_2CF_2-O-C_6H_5	+101.0	390	C_6D_6/30	+23.0[f]
2e	HCF_2CF_2-O-$CH{=}CH_2$	+107.0	120	C_6D_6/30	+19.0[f]
2f	HCF_2CF_2-O-$CH{=}C{=}CH_2$	+152.5	250	C_6D_6/28	--
2g	C_3F_7-O-$CF{=}CF_2$	+95.0	175	$CDCl_3$/30	+11.0[f]
3a	$HCF_2CF_2CH_2$-O-$Si(CH_3)_3$	-13.8	110	$CDCl_3$/28	-18.0[g]
3b	$HCF_2CF_2CH_2$-O-BC_8H_{14} [i]	+92.0	480	$CDCl_3$/30	-26[g]
3c	$C_7F_{15}CH_2$-O-$Si(CH_3)_3$	-17.0	700	$CDCl_3$/30	-20.0[g]
3d		-20.0	440	$CDCl_3$/30	±0[h]
3e	$C_6F_{13}CH_2CH_2$-O-$Si(CH_3)_3$	+6.0	700	$CDCl_3$/30	±0[g]
3f	$C_6F_{13}CH_2CH_2$-O-BC_8H_{14} [i]	+116.0	>800	$CDCl_3$/30	±0[g]

Footnotes to Table 1

[a] A positive sign denotes a high frequency shift with respect to the ^{17}O-resonance of external H_2O; the accuracy of the $\delta^{17}O$-values depends on the line widths:
$\Delta\nu_{1/2} < 200$ Hz, ± 0.5 ppm; < 400 Hz, ± 1.5 ppm; < 600 Hz, ± 3 ppm; > 600 Hz ± 5 ppm.

[b] Approximate error: $\Delta\nu_{1/2} < 200$ Hz, ± 20 Hz; < 400 Hz, ± 40 Hz; < 600 Hz, ± 70 Hz; > 600 Hz, ± 100 Hz.

[c] Ref. [6].

[d] Ref. [7a].

[e] This work; $CH_3O\text{-}CH_2CH_2\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}CH_3$ in C_6D_6/28°C;
$\delta^{17}O$: -5.0 ($CH_2\text{-}O\text{-}CH_2$), $\Delta\nu_{1/2} = 185$ Hz; -27.0 ($CH_3\text{-}O\text{-}CH_2$), $\Delta\nu_{1/2} = 105$ Hz.

[f] Ref. [11].

[g] B.Wrackmeyer, unpublished ^{17}O-NMR measurements.

[h] $\delta^{17}O$ of 1,2-butylenoxide: -18.0 [7b].

[i] BC_8H_{14} = 9-borabicyclo[3.3.1]nonyl.

If the changes in the magnetic shielding for both nuclei (^{13}C, ^{17}O) can be accounted for by Pople's approximation of the local paramagnetic screening constants (eqn. (1)) [18], the ratio of the radial expansion terms for oxygen and carbon $\langle r_{2p}^{-3}\rangle_{^{17}O}$ to $\langle r_{2p}^{-3}\rangle_{^{13}C}$ (theoretically 2.74, experimentally 2.96 [7a], 3.83 [6, 7b]) should explain the main part of the different sensitivity.

$$\sigma_p^{AA} = \frac{\mu_o \cdot \mu_B}{2\pi} \cdot \Delta E^{-1} \cdot \langle r_{2p}^{-3}\rangle \cdot \left(Q_{AA} + \sum_{A \neq B} Q_{AB}\right) \qquad (1)$$

μ_o = permeability of free space, μ_B = Bohr magneton

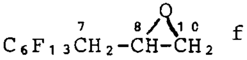
ΔE = average excitation energy

r_{2p} = radius of the valence p electrons, $\sum Q$ represents the imbalance of electronic charge.

TABLE 2

Relevant ^{13}C chemical shifts [a] ($\delta^{13}C$) of polyfluorinated alcohols and ethers in comparison to their hydrocarbon analogues [$\Delta^{13}C$ given in square brackets]

Nr	Compound	$\delta^{13}C$						Solvent
1a	$H\overset{1}{C}F_2\overset{2}{C}F_2\overset{3}{C}H_2{-}OH$	109.9(1) [83]	115.5(2) [103.7]	59.7(3) [-5.2]				$CDCl_3$
1b	$C_7F_{15}\overset{8}{C}H_2{-}OH$	60.9(8) [-1.3]						$CDCl_3$/ 60°C
1c	$C_6F_{13}\overset{7}{C}H_2\overset{8}{C}H_2{-}OH^b$	35.4(7) [22]	55.7(8) [-6.5]					C_6D_6
2a	$H\overset{1}{C}F_2\overset{2}{C}F_2{-}O{-}\overset{4}{C}H_3{}^b$	109.8(1) [92.8]	119.4(2) [53.2]	51.3(4) [-6.6]				C_6D_6
2b	$H\overset{1}{C}F_2\overset{2}{C}F_2{-}O{-}\overset{4}{C}H_2{-}\overset{5}{C}H_2{-}O{-}\overset{7}{C}H_3$	107.9(1) [91.5]	117.4(2) [50.5]	63.5(4) [-7.1]	69.9(5) [-2.1]	58.1(6) [-0.8]		C_6D_6
2c	$H\overset{1}{C}F_2\overset{2}{C}F_2{-}O{-}\overset{4}{C}H_2\overset{5}{C}H{=}\overset{6}{C}H_2{}^b$	109.4(1) [94.6]	118.9(2) [53.0]	66.2(4) [-5.4]	132.7(5) [-2.7]	119.3(6) [2.9]		C_6D_6
2d	$H\overset{1}{C}F_2\overset{2}{C}F_2{-}O{-}\overset{i,o,m,p}{C_6H_5}$	108.3(1) [93.6]	117.1(2) [52.5]	149.3(i) [-9.6]	121.8(o) [7.8]	129.8(m) [1.1]	126.7(p) [5.6]	C_6D_6
2e	$H\overset{1}{C}F_2\overset{2}{C}F_2{-}O{-}\overset{4}{C}H{=}\overset{5}{C}H_2{}^b$	109.2(1) [94.5]	117.8 [53.2]	140.9(4) [-11.6]	101.1(5) [14.9]			C_6D_6

2f	$H\overset{1}{C}F_2\overset{2}{C}F_2-O-\overset{4}{C}H=\overset{5}{C}=\overset{6}{C}H_2$	108.1(1)	117.1(2)	110.7(4)	202.4(5)	89.8(6)		C_6D_6
		[93.4]	[52.5]	[-11.0]	[0.1]	[0.2]		
3a	$H\overset{1}{C}F_2\overset{2}{C}F_2\overset{3}{C}H_2-O-Si(\overset{6}{C}H_3)_3$ [c]	109.4(1)	115.5(2)	60.8(3)	-1.4(6)			$CDCl_3$
3b	$H\overset{1}{C}F_2\overset{2}{C}F_2\overset{3}{C}H_2-O-B\overset{6,7,8}{C_8}H_{14}$ [d] [i]	109.5(1)	115.0(2)	63.0(3)	24.3(6)	33.1(7)	23.0(8)	$CDCl_3$
3c	$C_7F_{15}\overset{8}{C}H_2-O-Si(\overset{12}{C}H_3)_3$ [e]	61.1(8)	-1.5(12)					$CDCl_3$
3d	 $C_6F_{13}\overset{7}{C}H_2-\overset{8}{C}H-\overset{10}{C}H_2$ [f]	35.5(7)	44.6(8)	45.1(10)				C_6D_6
3e	$C_6F_{13}\overset{7}{C}H_2\overset{8}{C}H_2-O-Si(\overset{11}{C}H_3)_3$ [g]	34.6(7)	55.0(8)	-1.4(11)				$CDCl_3$
3f	$C_6F_{13}\overset{7}{C}H_2\overset{8}{C}H_2-O-B\overset{11,12,13}{C_8}H_{14}$ [h] [i]	33.7(7)	58.0(8)	24.5(11)	33.3(12)	23.2(13)		$CDCl_3$

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a For the $\delta\,^{13}C$-values of C_6F_{13}-, C_7F_{15}-groups and coupling constants $J(^{19}F^{13}C)$ see Ref. 12 and Ref. cited therein.

b Data from Ref. 12.

c $\delta\,^{29}Si = 23.7$; $^1J(^{29}Si^{13}C) = 59.9$ Hz.

d $\delta\,^{11}B = +59.0$, $\Delta\nu\,1/2 = 250$ Hz.

e $\delta\,^{29}Si = +23.9$; $^1J(^{29}Si^{13}C) = 60.0$ Hz.

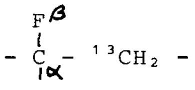
f G.Serratrice, M.-J.Stebe and J.-J.Delpuech, J. Fluorine Chem. 25 (1984) 275.

g $\delta\,^{29}Si = +19.4$; $^1J(^{29}Si^{13}C) = 58.9$ Hz.

h $\delta\,^{11}B = +57.8$; $\Delta\nu\,1/2 = 280$ Hz.

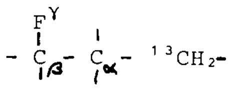
i BC_8H_{14} = 9-borabicyclo[3.3.1]nonyl

Apparently, the ratio of the 'γ -effects' for ^{17}O and ^{13}C are in the order of magnitude predicted by the ratio of the radial expansion terms. However, the 'β -effect' of fluorine is very



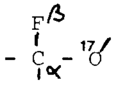
$-\overset{F^{\beta}}{\underset{\alpha}{C}}-{}^{13}CH_2-$

$\Delta^{13}C$ +3 ± 1



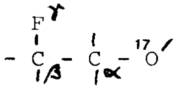
$-\overset{F^{\gamma}}{\underset{\beta}{C}}-\underset{\alpha}{C}-{}^{13}CH_2-$

$\Delta^{13}C$ -3.5 ± 1



$-\overset{F^{\beta}}{\underset{\alpha}{C}}-{}^{17}O/$

$\Delta^{17}O$ +36 ± 5



$-\overset{F^{\gamma}}{\underset{\beta}{C}}-\underset{\alpha}{C}-{}^{17}O/$

$\Delta^{17}O$ -10 ± 3

large in case of the ^{17}O-shielding. Although there is much conflicting evidence [17], the nature of the 'γ -effect' is believed to be more a 'through bond' than an 'through space' effect. In contrast, the ' β -effect' may be operative efficiently 'through bond" and, in special cases, even more efficiently 'through space'. The latter mechanism is expected to be more effective in the presence of polarizable lone pairs at the oxygen atom as compared with C-H σ -bonds. Therefore, it is likely that changes of the other relevant terms in Pople's approximation (Eq.(1)), ΔE, and the Q-terms should be taken into account for the discussion of the 'β -effects.' In particular, the ΔE approximation may not be valid at all in the case of ^{17}O-shielding with fluorine atoms in β-position.

Another description of the ' γ -' and the ' β -effect' invokes changes in orbital energies induced by the fluorine substituents. Thus, the low frequency shift of the ^{17}O- or ^{13}C-resonances (' γ -effect') may be the result of stabilization of n- or σ-orbitals (C-O, C-C, C-H) <u>vs.</u> σ^*-orbitals leaving the radial term almost unaffected. This will reduce paramagnetic circulations from the type $n \leftrightarrow \sigma^*$ or $\sigma \leftrightarrow \sigma^*$ and increase the magnetic shielding. Although, the analogous effect is expected in case of the 'β-effect' it may be more than offset by an increase in the radial term. Furthermore, the C-F σ-orbitals, the fluorine 'lone pairs' and the oxygen lone pairs will be comparable in energy. Thus, delocalization of fluorine and oxygen 'lone pair' electrons can be anticipated. Magnetic field induced circulations of these charges can also produce a marked deshielding of the ^{17}O-nucleus.

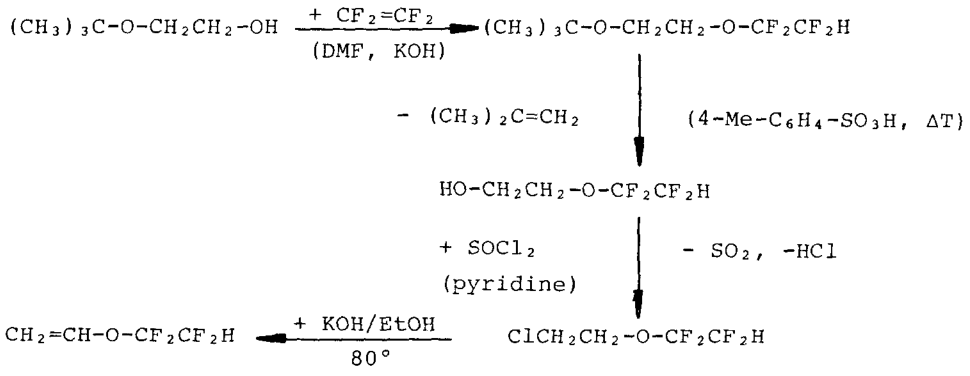
The δ^{29}Si-values (Table 2) (compare with a compilation in ref. [19]) of **3ace** indicate the electron withdrawing ability of the polyfluorinated alkyl chains. This is, as expected, greater in **3ac** than in **3e**.

Both, δ^{17}O- and δ^{11}B-values (Table 2) of **3bf** are indicative of BO(pp) π-interactions (compare data in ref. [9]). These interactions may be slightly stronger in **3f** than in **3b**, on the basis of the δ^{11}B-values. This is supported by the more negative Δ^{17}O-value for **3b** with respect to **3ac**. Since part of the high frequency shift of the ^{17}O-resonances in oxoboranes can be assigned to π-interactions, a significant increase in ^{17}O-shielding, as observed in **3b**, suggests reduced π-interactions.

This study has shown that multinuclear magnetic resonance provides interesting information which should be complementary for the various nuclei. Thus, changes in the electronic structure of the molecules are reflected by ^{11}B-, ^{13}C-, ^{17}O- and ^{29}Si-chemical shifts. The great sensitivity of the ^{17}O-nuclear shielding to the presence of fluorine atoms in β-position has been firmly established.

EXPERIMENTAL

All NMR spectra (64.2 MHz ^{11}B, 50.3 MHz ^{13}C, 27.1 MHz ^{17}O, 39.7 MHz ^{29}Si) were recorded with a BRUKER WP 200 NMR spectrometer. If not noted otherwise in the Tables, the measurements have been carried out at 27-28μC in 20mm (o.d.) tubes using concentrated solutions (~50-60% W/V) in C_6D_6 or $CDCl_3$. External references were $(C_2H_5)_2O\text{-}BF_3$ ($\delta^{11}B$), $(CH_3)_4Si$ ($\delta^{13}C$, $\delta^{13}C$ $(C_6D_6) = 128.0$, $\delta^{13}C$ $(CDCl_3) = 77.0$), H_2O ($\delta^{17}O$), and $(CH_3)_4Si$ ($\delta^{29}Si$). The ^{17}O-NMR spectra required between 10^4 to 10^5 scans (acquisition time ~0.02s, pulse angle ~70° = 35μs). A delay of 35μs between the end of the RF-pulse and the beginning of acquisition was introduced to obtain a straight base line. ^{29}Si-NMR spectra were obtained using the DEPT pulse sequence [20] with ^1H-decoupling. Most compounds have been prepared by standard procedures [21]. The silanes 3ace were obtained in quantitative yield by the reaction of the alcohols 1abc with hexamethyldisilazane. The boranes 3b, 3f are also formed quantitatively when the alcohols 1ac are reacted with 9-borabicyclo[3.3.1]nonane [22]. The vinyl ether 2e has been obtained by the following reaction sequence:



$$\begin{tikzcd}
(CH_3)_3C\text{-}O\text{-}CH_2CH_2\text{-}OH \arrow[r, "+\,CF_2{=}CF_2", "\text{(DMF, KOH)}"'] & (CH_3)_3C\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}CF_2CF_2H \arrow[d, "-\,(CH_3)_2C{=}CH_2"', "(4\text{-}Me\text{-}C_6H_4\text{-}SO_3H,\ \Delta T)"] \\
 & HO\text{-}CH_2CH_2\text{-}O\text{-}CF_2CF_2H \arrow[d, "+\,SOCl_2\ \text{(pyridine)}"', "-\,SO_2,\ -HCl"] \\
CH_2{=}CH\text{-}O\text{-}CF_2CF_2H & ClCH_2CH_2\text{-}O\text{-}CF_2CF_2H \arrow[l, "+\,KOH/EtOH"', "80^\circ"]
\end{tikzcd}$$

2e: bp. 37°C

The yield in the final dehydrochlorination step was only 55 % since Grob-fragmentation under formation of vinyl chloride occured as a side reaction.

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