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Synthesis of 2-(perfluoroalkyl)ethyl potassium sulfates based on perfluorinated Grignard reagents

Jana Paterová [a], Martin Skalický [a], Markéta Rybáčková [a], Magdalena Kvíčalová [b], Josef Cvačka [c], Jaroslav Kvíčala [a,*]

[a] Department of Organic Chemistry, Institute of Chemical Technology in Prague, Technická 5, 166 28 Prague 6, Czech Republic
[b] Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, v.v.i., Husinec-Řež 1001, 250 68 Řež, Czech Republic
[c] Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, v.v.i., Flemingovo nám. 2, 166 10 Prague 6, Czech Republic

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ABSTRACT

The first example of nucleophilic substitution with perfluoroalkyl Grignard reagents on the sp^3 carbon centre is described. Thus, a series of organometals R_F-MgBr, prepared from perfluorinated alkyl iodides R_F-I with $R_F = C_4F_9$, C_6F_{13}, C_8F_{17}, $C_{10}F_{21}$ and $C_{12}F_{25}$, reacted with 1,3,2-dioxathiolane-2,2-dioxide to afford the corresponding 2-(perfluoroalkyl)ethyl magnesium sulfates, which were isolated after metathesis to the corresponding potassium salts. In the model reaction, perfluorohexylmagnesium iodide was reacted with methyl triflate yielding polyfluorinated alkane. The attempts to extend the reaction to 1,3,2-dioxathiane-2,2-dioxide were unsuccessful due to its inferior reactivity and only reduced polyfluoroalkane and the product of coupling were detected in the reaction mixture. Polyfluorinated sulfates are easily hydrolyzed with hydrochloric or triflic acid to the corresponding alcohols, which is an alternative to standard transformation of perfluoroalkyl iodides to 2-(perfluoroalkyl)ethanols. Quantum-chemical calculations of the PES of the reaction with both sulfur-containing heterocycles found that the failure of the reaction with 1,3,2-dioxathiane-2,2-dioxide is caused by higher activation energy of the process.

1. Introduction

Perfluoroalkyl iodides belong to the most significant industrial sources of highly fluorinated compounds [1]. In contrast to their non-fluorinated analogues, their main transformation pathway is based on radical addition to unsaturated compounds [1,2]. Standard synthetic approaches employing organometallic chemistry are severely limited due to a low thermal stability of perfluorinated organometallic compounds [3–7]. Perfluorinated Grignard reagents hence cannot be synthesized by standard methodology and halogen–metal exchange reactions of perfluoroalkyl halides with alkylmagnesium bromides are generally preferred [3,7]. Known reactions of perfluorinated Grignard reagents are limited to addition reactions to unsaturated sp^2 carbon of aldehydes, ketones, esters or α,β-unsaturated oxo compounds [3–9]. Nucleophilic substitution on silicon sp^3 centre leading to perfluoroalkylated silanes are also feasible [3]. As a remarkable exception representing the only example known of nucleophilic substitution on carbon sp^3 centre, a series of perfluoroalkylated amines has been synthesized from aminals based on 1*H*-benztriazole [10].

Polyfluoroalkylated sulfates based on commercially available [11] alcohols bearing perfluorinated chain and ethylene spacer were synthesized from the fluoroalcohols and chlorosulfonic acid [12,13] and were studied as surfactants [12,13] or intermediates for anisotropic molecular magnetic materials [14]. However, neither full experimental nor analytical data have been reported for them.

We wish to present here the results of the research initiated by our recent aim to find appropriate polyfluorinated counteranions for fluorous imidazolium salts [15–17] together with the efforts to reveal the scope and limitations of the applications of perfluorinated Grignard reagents in nucleophilic substitution reactions.

2. Results and discussion

2.1. Model reaction with methyl triflate

In the search for an appropriate model substrate for nucleophilic substitution, our natural choice was methyl triflate due to minimal steric hindrance and high reactivity. Perfluorinated Grignard reagent **2b** was formed from the corresponding alkyl iodide **1b** according to our previous experience [7–9] at low

* Corresponding author. Tel.: +420 220444242; fax: +420 220444288.
E-mail address: kvicalaj@vscht.cz (J. Kvíčala).

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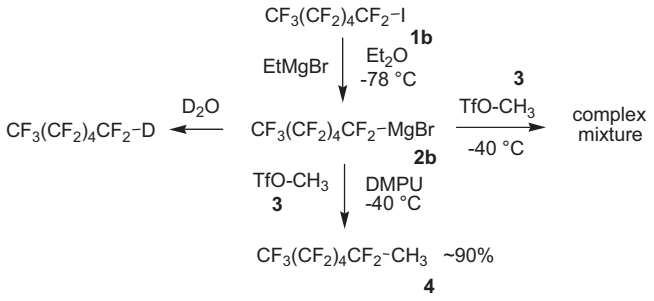
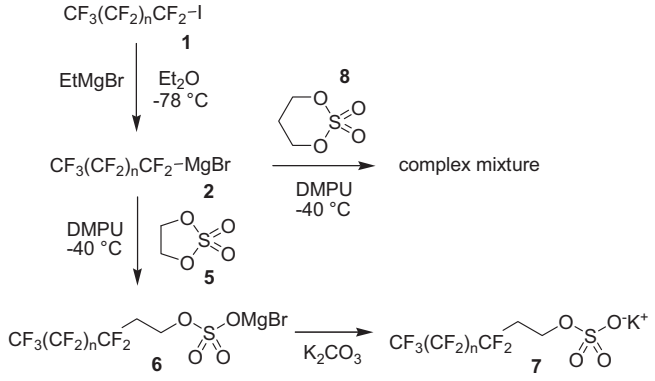


Scheme 1.

temperature using diethyl ether as a solvent. Although the Grignard reagent has been formed almost quantitatively, as was confirmed by quenching the sample of the reaction mixture at low temperature with D_2O and the analysis of the crude reaction mixture by ^{19}F NMR spectroscopy, no product was observed in the crude reaction mixture after 3 h reaction at −40 °C. Prolonged reaction time, as well as enhancing the reaction temperature resulted only in the decomposition of the reagent. We assumed that the Grignard reagent existed in the form of a highly polar covalent structure or a tight ion pair, which was the main limitation of the reaction [18]. Indeed, after addition of DMPU (1,3-dimethyltetrahydropyrimidine-2(1*H*)-one), a highly polar aprotic solvent which transforms efficiently tight ion pairs into solvent-separated ion pairs [19], the reaction proceeded smoothly and more than 90% yield of the product, 1*H*,1*H*,1*H*-perfluoroheptane (**4**), was obtained together with some 1*H*-perfluorohexane and unreacted starting iodide **1b** according to the analysis by ^{19}F NMR spectroscopy (Scheme 1). Unfortunately, we were not able to isolate pure product **4** due to a close boiling point to that of the solvent used, diethyl ether. Attempted fractional distillation yielded as the most enriched fraction a mixture containing 45% of product **4**, corresponding to ca. 15% isolated yield.

2.2. Reactions with cyclic sulfates

The problems with the isolation of polyfluorinated alkane **4** resulted in the search for highly reactive electrophiles which could afford easily isolable products. We first excluded epoxides as we were afraid of subsequent reactions of intermediary alkoxides formed. However, 1,3,2-dioxathiolane-2,2-dioxide (**5**) was recently employed as an excellent electrophile for nucleophilic trifluoromethylations [20] and difluoromethylations [21] and hence became our reagent of choice.



n = 2 (**1a**,**2a**,**6a**,**7a**), 4 (**1b**,**2b**,**6b**,**7b**), 6 (**1c**,**2c**,**6c**,**7c**), 8 (**1d**,**2d**,**6d**,**7d**), 10 (**1e**,**2e**,**6e**,**7e**)

Scheme 2.

Table 1
Results of preparation of polyfluorinated potassium sulfates **7**.

Entry	Product	NMR yield[a] (%)	Prep. yield (%)
1	$C_4F_9C_2H_4$–OSO_3^- K^+ (**7a**)	90	50
2	$C_6F_{13}C_2H_4$–OSO_3^- K^+ (**7b**)	82	55
3	$C_8F_{17}C_2H_4$–OSO_3^- K^+ (**7c**)	75	53
4	$C_{10}F_{21}C_2H_4$–OSO_3^- K^+ (**7d**)	67	53
5	$C_{12}F_{25}C_2H_4$–OSO_3^- K^+ (**7e**)	64	50

[a] Based on ^1H and ^{19}F NMR spectra of crude reaction mixtures.

Similar to the case of methyl triflate, no reactions of intermediary perfluorinated Grignard reagents **2** were observed in diethyl ether. However, addition of DPMU resulted in a clean reaction at −40 °C yielding the corresponding polyfluoroalkylated magnesium sulfates **6** in good to moderate yields according to the analysis of the crude reaction mixture by ^{19}F NMR spectroscopy (Scheme 2 and Table 1).

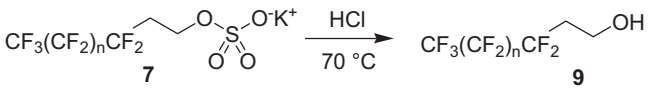
With the increasing length of the perfluorinated chain from C_4F_9 (**2a**) to $C_{12}F_{25}$ (**2e**) the reactivity of the Grignard reagents decreased, which resulted in lower yields.

We first attempted to isolate polyfluorinated magnesium sulfates **6** by simple evaporation of solvents, but were unable to remove high-boiling DMPU completely. Extractive work-up was also unsuccessful. We finally found that metathesis to potassium cation using excess of K_2CO_3 gave polyfluorinated potassium sulfates **7** with limited solubility in water. We were thus able to obtain pure crystalline products as white crystals in good to moderate yield (Scheme 2 and Table 1). With the increasing length of the fluorinated chain the solubility in water markedly diminished and hence the yields of the work-up improved, which resulted in an overall yield of the two-step synthesis in the range of 50–55% (Table 1).

Encouraged by the successful opening of cyclic sulfate **5** with perfluorinated Grignard reagents **2**, we attempted to perform this reaction with analogous six-membered cyclic sulfate **8**. However, all efforts to synthesize the corresponding (perfluoroalkyl)propyl sulfates failed and the only products obtained were starting perfluoroalkyl iodides **1**, the corresponding 1*H*-perfluoroalkanes, products of dimerization of iodides **1** and other minor unidentified products. This stemmed our aim in the theoretical study of the system (vide infra).

2.3. Hydrolysis of fluorosulfates 7 to fluoroalcohols 9

1*H*,1*H*,2*H*,2*H*-Perfluoroalcohols **9** with even number of carbon atoms are extensively used fluorinated building blocks. With the exception of the largest member of the series, tetradecanol **9e**, they are commercially available from most of the major suppliers of fluorochemicals. They are synthesized by radical addition of perfluoroalkyl iodides on ethene followed by hydrolysis with aqueous amides or oleum [21]. In the laboratory, the use of oleum or separation of high-boiling organic amides from the products can be inconvenient. We were hence interested whether sulfates **7** can be employed for their synthesis. We indeed found that acidic hydrolysis using aqueous hydrochloric acid at 70 °C for 24 h or trifluoromethanesulfonic acid at room temperature for 0.5 h furnished the target fluoroalcohols **9** with good to excellent yields (Scheme 3 and Table 2). Moreover, the whole transformation from



n = 2 (**7a**,**9a**), 4 **7b**,**9b**), 6 (**7c**,**9c**), 8 (**7d**,**9d**), 10 (**7e**,**9e**)

Scheme 3.

Table 2
Results of preparation of fluoroalcohols **9**.

Entry	Product	Yield from **7**[a] (%)	Yield from **1**[b] (%)
1[c]	$C_4F_9C_2H_4OH$ (**7a**)	87	–
2[c]	$C_6F_{13}C_2H_4OH$ (**7b**)	90	53
2[d]	$C_6F_{13}C_2H_4OH$ (**7b**)	96	-
3[c]	$C_8F_{17}C_2H_4OH$ (**7c**)	83	56
4[c]	$C_{10}F_{21}C_2H_4OH$ (**7d**)	89	54
5[c]	$C_{12}F_{25}C_2H_4OH$ (**7e**)	89	53

[a] Hydrolysis of fluorosulfates **7**.
[b] One pot procedure from iodides **1**.
[c] HCl, 70 °C, 24 h.
[d] TfOH, r.t., 0.5 h.

perfluoroalkyl iodides **1** via perfluorinated Grignard reagents **2** and fluoroalkyl sulfates **7** could be accomplished with advantage as a one-pot synthesis (Table 2) and represents thus a convenient alternative to the formerly published approaches [22].

2.4. Quantum chemistry calculations of opening of dioxathiolane 5 or dioxathiane 8 with pentafluoroethyl anion

The striking differences in the reactivity of perfluoroalkylmagnesium bromides **2** with dioxathiolane **5** or dioxathiane **8** initiated our aim in the simulation of both reactions. Due to the feasibility of the calculations we employed a simplified approach using a naked pentafluoroethyl anion as the model nucleophile. Study of the PES of both nucleophilic substitutions revealed the structures of transition states, as well as the corresponding conformational minima of educts and products. IRC calculations confirmed the connections of the respective saddle points. Both reactions are highly exothermic with early transitions states, however, the activation energy of the reaction with dioxathiane **8** is twice as high as that with dioxathiolane **5** (Fig. 1). This together with the low stability of the corresponding perfluorinated Grignard reagents probably causes the failure of the former reaction.

The higher reactivity of dioxathiolane **5** compared to dioxathiane **8** can be explained by a higher positive electrostatic potential on the sp^3 reaction centre caused by the amplification of an electron-withdrawing power of the sulfonyloxy group by the CH_2OSO_2 group connected from the other side of the ring. In contrast to that, dioxathiane **8** contains another CH_2 group between the reaction centre and the CH_2OSO_2 group with no amplification. Deeper blue colour of the more positive electrostatic potential mapped on the isodensity surface at the reaction centre of dioxathiolane **5** illustrates this well (Fig. 2).

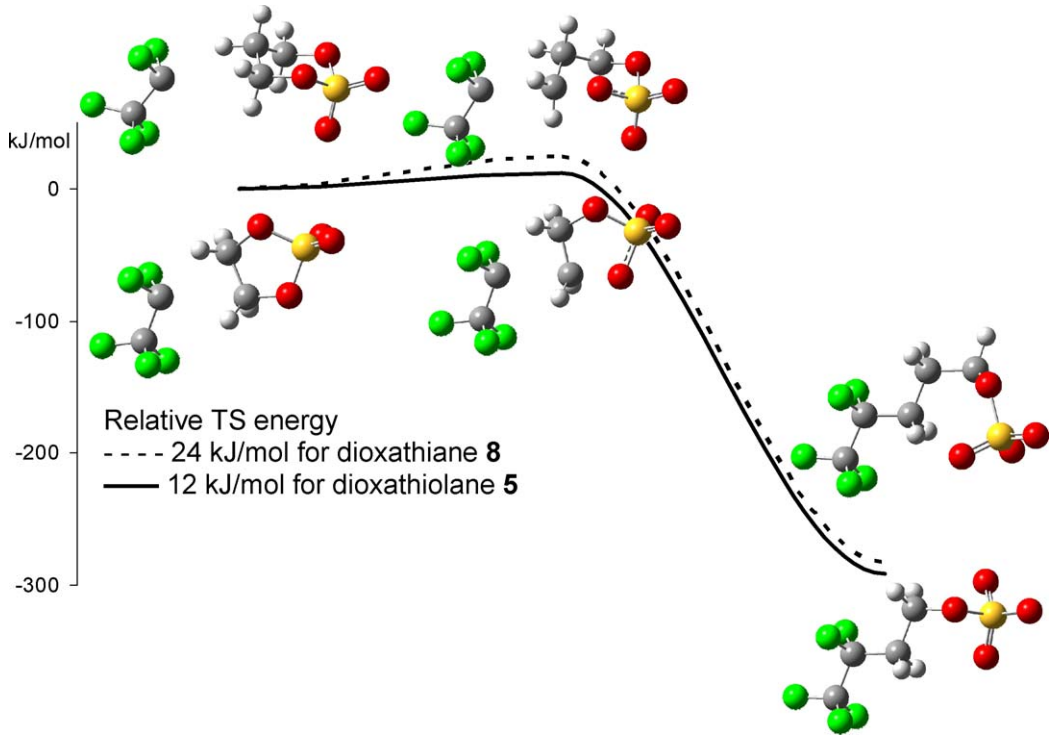


Fig. 1. Comparison of PES of reaction of $C_2F_5^-$ with dioxathiolane **5** or dioxathiane **8**.

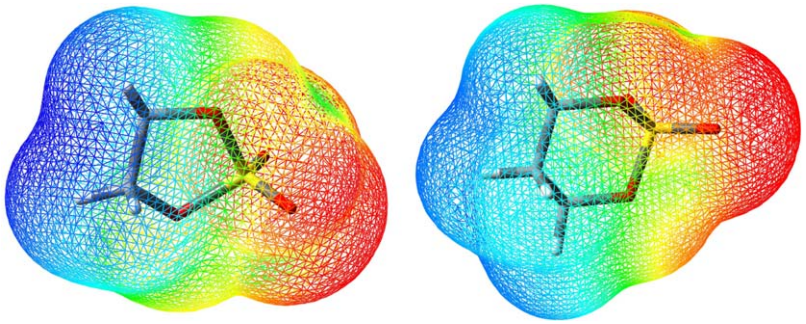


Fig. 2. Comparison of mapped electrostatic potential for dioxathiolane **5** (left) and dioxathiane **8** (right)

2.5. Computational details

DFT calculations were performed using Gaussian 03W program suite using PBE1PBE (i.e. PBE0) functional together with Pople 6-311+G(d) basis set [23]. IRC calculations were accomplished at the same level of theory with Firefly QC package [24], which is partially based on the GAMESS (US) source code [25]. Vibrational frequencies were calculated for all species to characterize them as minima or transition states. Transition state geometries were found starting from the corresponding minima on the potential energy surfaces and estimated transition states using Schlegel's QST2 or QST3 method [26]. In all cases, the connections of the corresponding transition states and minima were verified by IRC calculations of the simulated reaction pathways. Electrostatic potentials were calculated according to the Merz–Singh–Kollman scheme [27]. Visualizations of the molecules were performed with the GaussView program [28].

3. Conclusions

Perfluorinated Grignard reagents **2**, prepared by the halogen–metal exchange from perfluoroalkyl iodides **1** and ethylmagnesium bromide, were successfully reacted at low temperatures with methyl triflate (**3**) or 1,3,2-dioxathiolane-2,2-dioxide (**5**) to give polyfluoroalkane **4** and magnesium salts of polyfluoroalkyl sulfates **6**, respectively. Pure potassium salts **7** could be easily obtained from them by the metathesis with K_2CO_3. These reactions belong to the first published nucleophilic substitutions with perfluorinated Grignard reagents on carbon sp^3 centres. Attempted analogous reaction with 1,3,2-dioxathiane-2,2-dioxide (**8**) failed. Acidic hydrolysis of sulfates **7** gave polyfluorinated alcohols **9** in good yields. Quantum-chemical calculations implied that simulated reactions are driven kinetically in both cases and the higher activation energy of the latter reaction is probably responsible for the failure.

4. Experimental

4.1. General remarks

Temperature data were uncorrected. NMR spectra were recorded with a Varian MercuryPlus spectrometer, ^{1}H NMR spectra at 299.97 MHz and ^{13}C NMR spectra at 75.43 MHz using residual deuterated solvent signals as the internal standards, ^{19}F NMR spectra at 282.22 MHz using CCl_3F as the internal standard. Chemical shifts are given in ppm, coupling constants in Hz. Mass spectra (ESI, APCI) were measured with a LCQ Fleet (Finnigan) instrument, HRMS spectra (ESI, APCI, FAB) with a LTQ Orbitrap XL (Thermo Fisher Scientific) or ZAB-EQ (VG Analytical) instruments.

All reactions except hydrolytic reactions were performed in dry inert atmosphere in an oven-dried apparatuses. 1,1,1,2,2,3,3,4,4-Nonafluoro-4-iodobutane (**1a**, perfluorobutyl iodide), 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoro-6-iodohexane (**1b**, perfluorohexyl iodide), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-8-iodooctane (**1c**, perfluorooctyl iodide), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heneicosafluoro-10-iododecane (**1d**, perfluorodecyl iodide) and 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-pentacosafluoro-12-iododododecane (**1e**, perfluorododecyl iodide) were kindly gifted by Atochem. Methyl triflate (**3**), 1,3,2-dioxathiolane-2,2-dioxide (**5**), 1,3,2-dioxathiane-2,2-dioxide (**8**), ethylmagnesium bromide (3 M solution in diethyl ether) and 1,3-dimethyltetrahydropyrimidine-2(1*H*)-one (DMPU) were purchased from Sigma–Aldrich. Acetonitrile was distilled over P_2O_5 and stored over molecular sieves, DMPU was dried over molecular sieves, diethyl ether and THF were distilled over sodium benzophenone ketyl.

4.2. Attempted preparation of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluoroheptane ((4), 1H,1H,1H-perfluoroheptane)

A flask was charged with perfluorohexyl iodide (**1b**, 3.92 g, 8.80 mmol) and diethyl ether (140 ml), the solution was cooled to −78 °C by a solid CO_2/ethanol bath and ethylmagnesium bromide (3 M solution in diethyl ether, 3.52 ml, 10.6 mmol) was dropwise added to it. The mixture was stirred for 30 min, during which time the temperature was allowed to rise to −40 °C, and then recooled to −78 °C. DMPU (2.08 ml, 17.2 mmol) and methyl triflate (**3**, 1.44 g, 8.80 mmol) were dropwise added. The mixture was then allowed to warm to −40 °C, stirred at −40 °C for 3 h, allowed to warm to r.t. and quenched with water (10 ml). The organic phase was separated and extracted with water (2 × 10 ml). Combined aqueous parts were extracted with diethyl ether (10 ml), both organic parts were combined and dried with anhydrous $MgSO_4$. Estimated yield of the reaction based on ^{1}H NMR analysis of the crude reaction mixture was ∼90%. Attempted fractional distillation afforded 1.02 g of fraction containing 45% of product **4**, 3% of 1,1,1,2,2,3,3,4,4,5,5,6,6-tridecafluorohexane (1*H*-perfluorohexane) formed by reduction of perfluoroalkyl iodide **1b** and 52% of diethyl ether, estimated yield (^{1}H NMR) 15%. ^{1}H NMR (299.97 MHz, $CDCl_3$) δ 1.84 (t, 3H, H-7, $^3J_{HF}$ = 7.2 Hz). ^{19}F NMR (282.23 MHz, $CDCl_3$) δ −81.3 (m, 3F, F-1); −106.9 (m, 2F); −122.5 (m, 2F); −123.4 (m, 2F); −124.5 (m, 2F); −126.6 (m, 2F).

4.3. Potassium 2-(perfluoroalkyl)ethyl sulfates 7. General procedure

A flask was charged with perfluoroalkyl iodide **1** (0.5–1.1 mmol) and diethyl ether (20 ml), the solution was cooled to −78 °C by a solid CO_2/ethanol bath and ethylmagnesium bromide (3 M solution in diethyl ether, ca. 1.25 mmol/mmol of iodide **1**) was dropwise added to it. The mixture was stirred for 30 min, during which time the temperature was allowed to rise to −40 °C, and then recooled to −78 °C. 1,3,2-Dioxathiolane-2,2-dioxide (**5**, 1.5 mmol/mmol of iodide **1**) and DMPU (1 ml) were dissolved in 1 ml of diethyl ether and the solution was dropwise added to the preformed fluoro Grignard reagent **2**. The mixture was allowed to warm to −40 °C and stirred at this temperature for a given time. The mixture was allowed to warm to 0 °C and water (5–10 ml) was added to it. From this mixture, diethyl ether was removed on a rotary vacuum evaporator (40 °C/1 h/1 kPa), K_2CO_3 (350 mg) was added and the mixture was stirred for 3 h to 50 °C, during which white solid was formed. After cooling to r.t., 1 ml of concentrated sulfuric acid was carefully added (foaming) and the mixture was left in refrigerator at ∼5 °C. After 1–7 days crystals of product **7** formed were separated by filtration, quickly washed with cold acetone (for **7a**) or cold water (for **7b–7e**) and dried by vacuum (20 °C/8 h/50 Pa).

4.4. Potassium 6,6,6,5,5,4,4,3,3-nonafluorohexyl sulfate (7a)

From 170 mg (0.50 mmol) of iodide **1a**, 0.22 ml (0.66 mmol) of EtMgBr solution and 100 mg (0.77 mmol) of cyclic sulfate **5**, 95 mg (50%) of sulfate **7a** was obtained after 5 h reaction (white needles, m.p. 188–196 °C). ^{1}H NMR (299.97 MHz, D_2O) δ 2.52 (tt, 2H, H-2, $^3J_{HF}$ = 18.5 Hz; $^3J_{HH}$ = 6.0 Hz); 4.20 (t, 2H, H-1, $^3J_{HH}$ = 6.1 Hz). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 33.9 (t, 1C, C-2; $^2J_{CF}$ = 21.0 Hz); 54.1 (t, 1C, C-1, $^3J_{CF}$ = 5.0 Hz); 100–126 m, 4C (C-3–C-6). ^{19}F NMR (282.23 MHz, D_2O) δ −81.6 (m, 3F, F-6); −114.2 (m, 2F); −125.4 (m, 2F); −126.6 (m, 2F). MS (ESI^-), *m*/*z* (%): 725 (100%) $[(C_4F_9C_2H_4OSO_3)_2\ K]^-$; 343 (19%) $[C_4F_9C_2H_4OSO_3]^-$. HRMS (ESI^-), *m*/*z* (%): calcd. for $C_6H_4F_9O_4S$ $[M]^-$, 342.96921; found 342.96927.

4.5. Potassium 8,8,8,7,7,6,6,5,5,4,4,3,3-tridecafluorooctyl sulfate (7b)

From 450 mg (1.01 mmol) of iodide **1b**, 0.44 ml (1.32 mmol) of EtMgBr solution and 200 mg (1.54 mmol) of cyclic sulfate **5**, 266 mg (55.2%) of sulfate **7b** was obtained after 6 h reaction (white crystals, m.p. 200–204 °C). ^{1}H NMR (299.97 MHz, acetone-d_6) δ 2.65 (tt, 2H, H-2, $^3J_{HF}$ = 18.5 Hz; $^3J_{HH}$ = 6.0 Hz); 4.25 (t, 2H, H-1, $^3J_{HH}$ = 6.0 Hz). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 33.9 (t, 1C, C-2; $^2J_{CF}$ = 21.0 Hz); 54.1 (t, 1C, C-1, $^3J_{CF}$ = 5.0 Hz); 100–126 m, 6C (C-3–C-8). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −81.4 (m, 3F, F-8); −113.7 (m, 2F); −122.2 (m, 2F); −123.2 (m, 2F); −123.9 (m, 2F); −126.5 (m, 2F). MS (ESI$^-$), *m*/*z* (%): 925 (64%) $[(C_6F_{13}C_2H_4OSO_3)_2\ K]^-$; 443 (100%) $[C_6F_{13}C_2H_4OSO_3]^-$. HRMS (ESI$^-$), *m*/*z* (%): calcd. for $C_8H_4F_{13}O_4S$ $[M]^-$, 442.96282; found 442.96247.

4.6. Potassium 10,10,10,9,9,8,8,7,7,6,6,5,5,4,4,3,3-heptadecafluorodecyl sulfate (7c)

From 270 mg (0.50 mmol) of iodide **1c**, 0.22 ml (0.66 mmol) of EtMgBr solution and 100 mg (0.77 mmol) of cyclic sulfate **5**, 155 mg (53.3%) of sulfate **7c** was obtained after 6 h reaction (white crystals, m.p. 195–198 °C). ^{1}H NMR (299.97 MHz, acetone-d_6) δ 2.57 (tt, 2H, H-2, $^3J_{HF}$ = 18.5 Hz; $^3J_{HH}$ = 6.0 Hz); 4.22 (t, 2H, H-1, $^3J_{HH}$ = 6.0 Hz). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 34.0 (t, 1C, C-2; $^2J_{CF}$ = 21.0 Hz); 54.1 (t, 1C, C-1, $^3J_{CF}$ = 5.0 Hz); 100–126 m, 8C (C-3–C-10). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −81.3 (m, 3F, F-10); −113.9 (m, 2F); −122.2 (m, 2F); −122.4 (m, 4F); −123.3 (m, 2F); −124.0 (m, 2F); −126.8 (m, 2F). MS (ESI$^-$), *m*/*z* (%): 1125 (100%) $[(C_8F_{17}C_2H_4OSO_3)_2\ K]^-$; 543 (81%) $[C_8F_{17}C_2H_4OSO_3]^-$. HRMS (ESI$^-$), *m*/*z* (%): calcd. for $C_{10}H_4F_{17}O_4S$ $[M]^-$, 542.95643; found 542.95631.

4.7. Potassium 12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5,4,4,3,3-heneicosafluorododecyl sulfate (7d)

From 700 mg (1.08 mmol) of iodide **1d**, 0.44 ml (1.32 mmol) of EtMgBr solution and 200 mg (1.54 mmol) of cyclic sulfate **5**, 360 mg (52.8%) of sulfate **7d** was obtained after 7 h reaction (white crystals, sublimes 220–240 °C). ^{1}H NMR (299.97 MHz, acetone-d_6) δ 2.57 (tt, 2H, H-2, $^3J_{HF}$ = 18.5 Hz; $^3J_{HH}$ = 6.0 Hz); 4.22 (t, 2H, H-1, $^3J_{HH}$ = 6.0 Hz). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 34.0 (t, 1C, C-2; $^2J_{CF}$ = 21.0 Hz); 54.1 (t, 1C, C-1, $^3J_{CF}$ = 5.0 Hz); 100–126 m, 10C (C-3–C-12). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −81.3 (m, 3F, F-12); −113.9 (m, 2F); −122.2 (m, 2F); −122.4 (m, 4F); −123.3 (m, 2F); −124.0 (m, 2F); −126.8 (m, 2F). MS (ESI$^-$), *m*/*z* (%): 643 (100%) $[C_{10}F_{21}C_2H_4OSO_3]^-$. HRMS (ESI$^-$), *m*/*z* (%): calcd. for $C_{10}H_4F_{17}O_4S$ $[M]^-$, 642.95004; found 642.94968.

4.8. Potassium 14,14,14,13,13,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5,4,4,3,3-pentacosafluorotetradecyl sulfate (7e)

From 800 mg (1.08 mmol) of iodide **1e**, 0.44 ml (1.32 mmol) of EtMgBr solution and 200 mg (1.54 mmol) of cyclic sulfate **5**, 391 mg (50.0%) of sulfate **7e** was obtained after 7 h reaction (white crystals, sublimes 220–250 °C). ^{1}H NMR (299.97 MHz, acetone-d_6) δ 2.58 (tt, 2H, H-2, $^3J_{HF}$ = 18.5 Hz; $^3J_{HH}$ = 6.0 Hz); 4.20 (t, 2H, H-1, $^3J_{HH}$ = 6.0 Hz). ^{13}C NMR (75.44 MHz, acetone-d_6) δ 33.9 (t, 1C, C-2; $^2J_{CF}$ = 21.0 Hz); 54.0 (t, 1C, C-1, $^3J_{CF}$ = 5.0 Hz); 100–126 m, 12C (C-3–C-14). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −81.3 (m, 3F, F-14); −113.8 (m, 2F); −121.2 (m, 2F); −121.9 (m, 10F); −122.9 (m, 4F); −123.4 (m, 2F); −126.4 (m, 2F). MS (ESI$^-$), *m*/*z* (%): 743 (100%) $[C_{12}F_{25}C_2H_4OSO_3]^-$. HRMS (ESI$^-$), *m*/*z* (%): calcd. for $C_{14}H_4F_{25}O_4S$ $[M]^-$, 742.94366; found 742.94297.

4.9. Attempted preparation of potassium 7,7,7,6,6,5,5,4,4-nonafluoroheptyl sulfate

A flask was charged with iodide **1a** (340 mg, 1.00 mmol), diethyl ether (20 ml), the solution was cooled to −78 °C by a solid CO_2/ethanol bath and ethylmagnesium bromide (3 M solution in diethyl ether, 0.44 ml, 1.32 mmol) was dropwise added to it. The mixture was stirred for 30 min, during which time the temperature was allowed to rise to −40 °C, and then recooled to −78 °C. 1,3,2-Dioxathiane-2,2-dioxide (**8**, 230 mg, 1.54 mmol) and DMPU (1.5 ml) were dissolved in 1 ml of diethyl ether and the solution was dropwise added to the preformed fluoro Grignard reagent **2a**. The mixture was allowed to warm to −40 °C and stirred at this temperature for 6 h. The mixture was allowed to warm to 0 °C and water (5–10 ml) was added to it. According to ^{19}F NMR analysis the reaction mixture contained 8% of starting iodide **1a**, 73% of 1,1,1,2,2,3,3,4,4-nonafluorobutane and 19% of dimerization product, perfluorooctane with the NMR spectrum corresponding to the published data [29].

4.10. Hydrolysis of sulfates 7 to alcohols 9 with hydrochloric acid. General procedure

Potassium fluoroalkyl sulfate **7** (ca. 40 μmol) was dissolved in water (5 ml), sufficient amount of 35% HCl was added until pH 0–1 was reached and the mixture was heated to 70 °C for 25 h. The reaction mixture was extracted with diethyl ether (2 × 5 ml), the organic parts were combined, dried with anhydrous $MgSO_4$ and diethyl ether was removed on a rotary vacuum evaporator (30 °C/1 h/1 kPa) to afford the target alcohol **9**.

4.11. Hydrolysis of sulfate 7a to 6,6,6,5,5,4,4,3,3-nonafluorohexan-1-ol (9a)

From 15 mg (39 μmol) of sulfate **7a**, 9.0 mg (87%) of fluoroalcohol **9a** (colourless liquid) was obtained with NMR spectra identical with the published data [22].

4.12. Hydrolysis of sulfate 7b to 8,8,8,7,7,6,6,5,5,4,4,3,3-tridecafluorooctan-1-ol (9b)

From 20 mg (41 μmol) of sulfate **7b**, 14 mg (90%) of fluoroalcohol **9b** (colourless liquid) was obtained with NMR spectra identical with the published data [22].

4.13. Hydrolysis of sulfate 7c to 10,10,10,9,9,8,8,7,7,6,6,5,5,4,4,3,3-heptadecafluorodecan-1-ol (9c)

From 25 mg (43 μmol) of sulfate **7c**, 17 mg (83%) of fluoroalcohol **9c** (white wax) was obtained with NMR spectra identical with the published data [22].

4.14. Hydrolysis of sulfate 7d to 12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5,4,4,3,3-heneicosafluorododecan-1-ol (9d)

From 30 mg (44 μmol) of sulfate **7d**, 22 mg (89%) of fluoroalcohol **9d** (white wax) [30] was obtained. ^{1}H NMR (299.97 MHz, acetone-d_6) δ 2.40 (tt, 2H, H-2, $^3J_{HF}$ = 19.0 Hz; $^3J_{HH}$ = 6.4 Hz); 3.82 (t, 2H, H-1, $^3J_{HH}$ = 6.4 Hz). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −81.3 (m, 3F, F-12); −114.0 (m, 2F); −122.0 (m, 8F); −123.0 (m, 4F); −124.0 (m, 2F); −126.5 (m, 2F).

4.15. Hydrolysis of sulfate 7e to 12,12,12,11,11,10,10,9,9,8,8,7,7,6,6,5,5,4,4,3,3-heneicosafluorododecan-1-ol (9e)

From 35 mg (45 μmol) of sulfate **7e**, 26 mg (89%) of fluoroalcohol **9e** (white wax) [31] was obtained. ^{1}H NMR (299.97 MHz,

acetone-d_6) δ 2.40 (tt, 2H, H-2, $^3J_{HF}$ = 19.0 Hz; $^3J_{HH}$ = 6.4 Hz); 3.81 (t, 2H, H-1, $^3J_{HH}$ = 6.4 Hz). ^{19}F NMR (282.23 MHz, acetone-d_6) δ −81.3 (m, 3F, F-12); −114.0 (m, 2F); −121.9 (m, 10F); −122.9 (m, 4F); −123.4 (m, 2F); −126.4 (m, 2F).

4.16. Hydrolysis of sulfate 7b to alcohol 9b with trifluoromethanesulfonic acid

Sulfate **7b** (15 mg, 39 μmol) was dissolved in water (5 ml) and ca. 20 M excess of trifluoromethanesulfonic acid (70 μl) was added. The mixture was stirred for 10 min at r.t. and extracted with diethyl ether (2 × 5 ml). Combined organic layers were evaporated on rotary vacuum evaporator (30 °C/1 h/1 kPa) to afford the target alcohol **9b** (10 mg, 96% yield).

4.17. Attempted reaction of sulfate 7b with sodium azide

Sulfate **7b** (240 mg, 500 μmol) was dissolved in acetonitrile (15 ml), followed by addition of sodium azide (200 mg, 3.00 mmol) and DMPU (3 ml). The mixture was refluxed for 5 days and monitored by ^{1}H and ^{19}F NMR spectroscopy. No change in the composition of the mixture was observed.

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