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Reactivity study of 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoromethyl-3,6-dioxanon-1-ene in nucleophilic reactions: fluorination properties of secondary amine adducts

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Dedicated to Professor Lev M. Yagupolskii on the occasion of his 80th birthday.

Abstract

A series of nucleophiles was reacted with 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoromethyl-3,6-dioxanon-1-ene (**1**) as a representative of perfluoro(alkyl vinyl ethers). All reactions were completely regioselective with the nucleophilic attack at the terminal carbon atom. Reactions of hydroxy compounds, thiols and sec-amines afforded addition products, but butyllithium, tributylphosphane or complex hydrides caused displacement of vinylic fluorine: butyllithium afforded *cis*-derivative, while reactions with hydrides and the phosphane led to mixtures of *cis*- and *trans*-derivatives. Diethylamine and piperidine adducts displayed the property to substitute hydroxyl for fluorine in hexadecan-1-ol. Molecular properties of hexafluoropropene and perfluoro(methyl vinyl ether) were calculated by ab initio method at the MP2/6-311G(d,p) level of theory and their impact on relative reactivity was estimated.

Keywords: Perfluoro vinyl ether; 1,1,2,4,4,5,7,7,8,8,9,9,9-Tridecafluoro-5-trifluoromethyl-3,6-dioxanon-1-ene; Nucleophilic addition; Fluorination agent; Vinylic fluorine displacement; Ab initio calculation; Molecular properties; LUMO energy; Electrostatic potential-derived charge; Merz–Kollman–Singh scheme

1. Introduction

Nucleophilic reactions of terminal perfluoroolefins have been the subject of a broad academic research for tens of years [1–7]. On the other hand, the reports on the chemistry of perfluorinated vinyl ethers including olefins bearing perfluorinated polyether part have appeared relatively recently. Recent studies of radical additions to perfluoro vinyl ethers showed their high reactivity toward nucleophilic radicals [8–10]. The reactions were applied in a convenient synthesis of fluoroalkylated diols and the corresponding bis-methacrylates as special crosslinking agents [10]. Original papers on the reactivity of perfluoro vinyl ethers in nucleophilic reactions started to appear in the sixties of the last century: short communication on the reactions of perfluoro(methyl vinyl ether) with methanol or diethylamine [11] or with azide ion in trapping the intermediate carbanion [12]; reaction of perfluoro(propyl vinyl ether) with phenyllithium [13] and nucleophilic addition of pyridin-3-ol [14] and phenols [15] to perfluorinated vinyl ethers. Nucleophilic addition of alkanol to (trifluorovinyl)oxy group of a bifunctional monomer was also employed in the synthesis of polyether polymers [16]. Recently, we published [17] preliminary results on reactions of a variety of nucleophiles with 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoromethyl-3,6-dioxanon-1-ene (**1**) and found fluorinating properties of secondary amine adducts. Later on, papers on additions of alcohols [18] and secondary or tertiary amines [19] to olefin **1** were published in the Russion journal. The papers [18,19] were combined and published subsequently as a new publication [20] in this journal. At present time, the synthesis of sugar derivatives of the olefin **1** (Scheme 1), which display very good hemocompatibility and co-emulsifying properties when mixed with perfluorocarbon—Pluronic F-68 emulsion, has been reported [21].

In this work, we would like to report our completed results that were preliminary reported as original in [17]: we carried out reactions of olefin **1** with a range of nucleophilic

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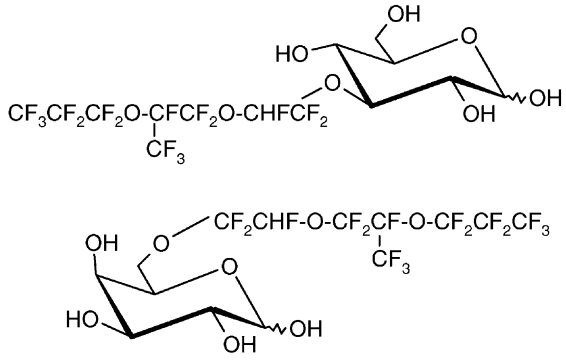


Scheme 1. D-Glucose and D-galactose hemocompatible derivatives of perfluorolefin **1**.

reagents under comparable conditions to get an overview on the reactivity abilities of the olefin **1**. In the case that in the meantime some compounds have been reported [20], we present novel procedures. We also present quantum chemical calculations of perfluoro(methyl vinyl ether) and hexafluoropropene as model compounds to compare the impact of substitution of fluoroalkene by perfluoroalkyl or perfluoroalkoxy group on its reactivity.

2. Results and discussion

2.1. General observation in the reaction of *1* with nucleophiles

The experiments were carried under nitrogen. All the reactions took place with the complete regioselectivity and exclusive nucleophilic attack at the terminal CF_2-group in olefin **1**. No by-products were formed in the reactions as verified by checking the reaction mixtures by ^{19}F NMR or following the reactions by ^{19}F NMR. An overview of the addition reactions is given in Table 1 together with the structures of the products **2**–**12**. In the additions, the second stereogenic center is formed at original vinyl ether carbon (the C-2). Thus, mixtures of diastereoisomers were formed in approximate ratio 1:1 as verified in some cases by ^{19}F NMR.

2.2. Electronic structure of perfluoro(methyl vinyl ether) and perfluoropropene

Fluoroalkenes react with nucleophilic reagents by either addition or addition–elimination mechanism depending on basicity of reagent and molecular properties of fluoroalkene. The attack proceeds with high regioselectivity on the terminal difluoromethylene group due to its higher positive charge and stabilization of intermediate carbanion by negative hyperconjugation [22]. To compare an impact of substitution of fluoroalkene by perfluoroalkyl or perfluoroalkoxy group, we calculated related molecular properties, i.e. Mullikan [23] and Lowdin [24] charges at both vinylic carbons, and orbital energies, of two corresponding model compounds, hexafluoropropene and perfluoro(methyl vinyl ether) at their equilibrium geometries. Moreover, as both above-mentioned charges assignments are somewhat arbitrary, we calculated charges fit to the electrostatic potential at points selected according to the Merz–Singh–Kollman scheme [25], which should better correspond to reality. For both fluoroalkenes, electrostatic potentials calculated at total electron density of 0.001 surface (darker areas indicate places of higher positive electrostatic potential) are depicted in Fig. 1 together with values of all three calculated charges.

Calculations confirmed that both Mullikan and Lowdin charges are not satisfactory for the description of electronic properties of fluoroalkenes, as seen from high differences between them. Higher positive charge calculated by MSK scheme on difluoromethylene group for hexafluoropropene reflects higher electron-acceptor power of trifluoromethyl group compared with trifluoromethoxy group.

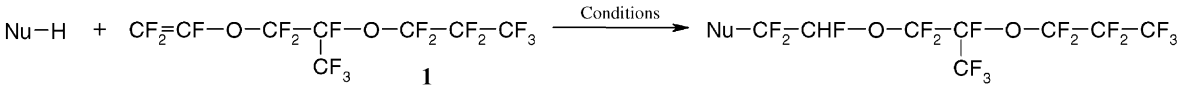
As the attack of the nucleophilic reagents to fluoroalkenes should be provided by a flow of electrons from HOMO orbital of the nucleophile to π^* antibonding orbital (LUMO) of the fluoroalkenes, we also calculated π^* orbital energies for both model fluoroalkenes, which are depicted together with the corresponding orbitals in Fig. 2.

Lower energy of π^* antibonding orbital of hexafluoropropene compared with perfluoro(methyl vinyl ether) again implies higher reactivity of perfluoroalkenes compared with perfluoro(alkyl vinyl ethers) towards nucleophilic reagents. The shape of π^* orbital of hexafluoropropene is distorted by electron-acceptor trifluoromethyl group, whereas oxygen atom in perfluoro(methyl vinyl ether) separates efficiently this influence at the corresponding π^* orbital.

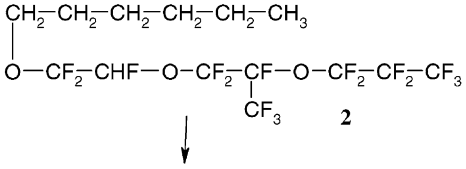
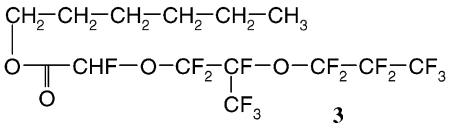
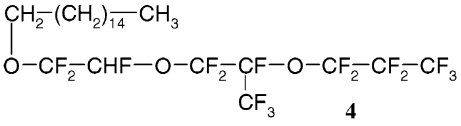
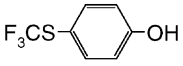
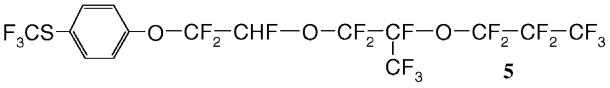
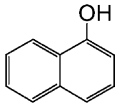
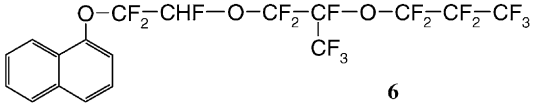
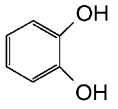
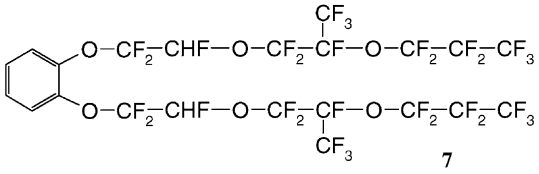
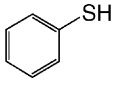
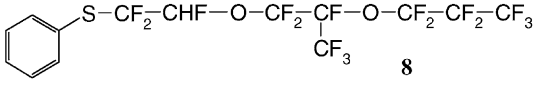
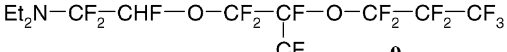
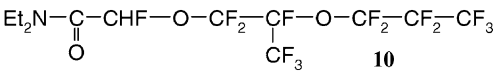
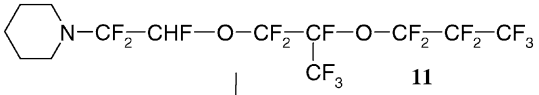
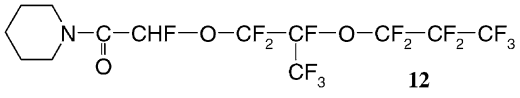
2.3. Additions of O- and S-nucleophiles to olefin *1*

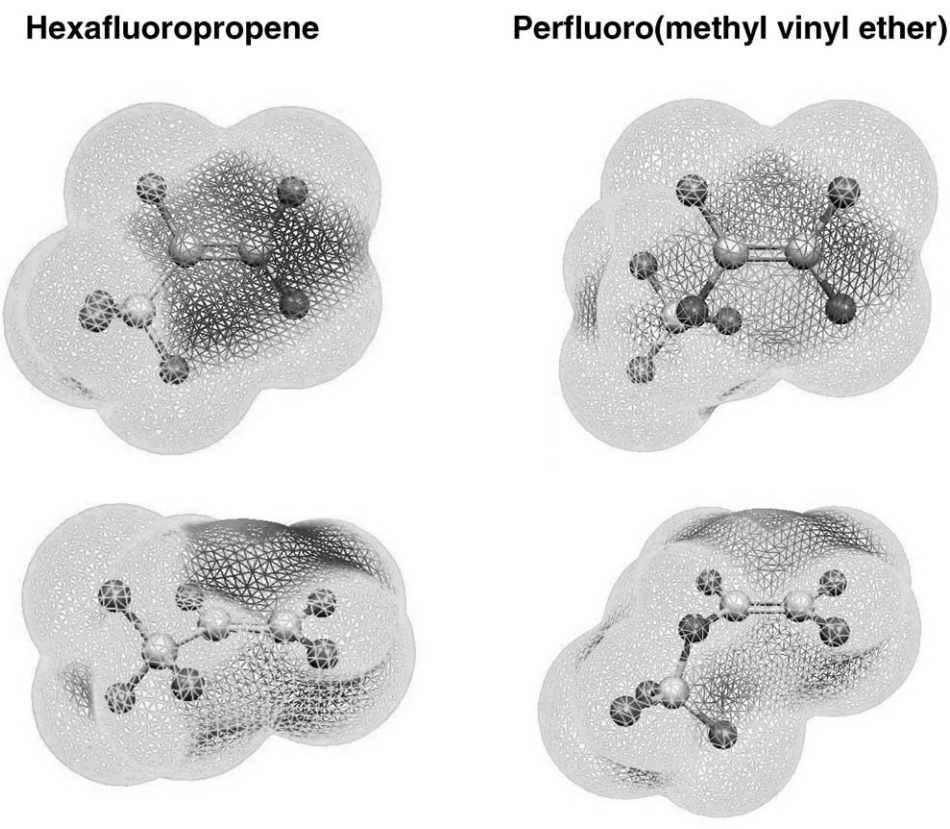
The reactions of hydroxy compounds were characterized by the fact that no unsaturated products were formed by replacement of vinylic fluorine in **1** or by a subsequent elimination of hydrogen fluoride from the primary addition products (check by ^{19}F NMR). This observation correlates with the calculated molecular properties (see Section 2.2 and Fig. 1). The reaction conditions for hydroxy compounds were optimized on the addition of 1-naphthol (Table 2). Sodium or lithium 1-naphthoxides were used as catalysts, but the best isolated yield was obtained with equimolar amount of the lithium salt in tetrahydrofuran (Table 2). This methodology was applied to other hydroxy compounds, viz. hexan-1-ol, hexadecan-1-ol, 4-(trifluoromethylsulfanyl)phenol, while disodium salt of benzene-1,2-diol was reacted in *N*,*N*-dimethylformamide (Table 2). Addition product of hexan-1-ol to olefin **1**, the product **2**, appeared to be unstable on heating during distillation or column chromatography on silica gel and underwent hydrolysis of the α-bonds C–F in grouping $–CH_2–O–CF_2–$ to afford the corresponding ester **3** bearing grouping $–CH_2–O–CO–$. Such hydrolysis is reported in literature by means of strong mineral acids [26] or on heating with silica gel [26]. On the other hand,

Table 1
Results of addition reactions of some nucleophiles Nu–H to perfluoro vinyl ether **1**



1

Nucleophilic reagent	Conditions	Product(s)	Yield (%)
$CH_3(CH_2)_4CH_2$–OH	BuLi, THF, −75 °C to RT; 5 days at RT	 **2**	38
	Distillation	 **3**	9
$CH_3(CH_2)_{14}CH_2$–OH	BuLi, THF, −75 °C to RT; 5 days at RT	 **4**	41
	BuLi, THF, −75 °C to RT; 5 days at RT	 **5**	30
	Na, THF, RT; 5 days at RT	 **6**	5
	Na, THF, DMF, RT; 5 days at RT	 **7**	25
	BuLi, THF, −75 °C to RT; 5 days at RT		54–61
	Na, DMF, 0 °C to RT; over night		41
	BuLi, THF, −75 °C to RT; 5 days at RT	 **8**	55
	Na, THF, 0 °C to RT; 5 days at RT		52
	THF, RT; 3 days at RT	 **9**	10
Et_2NH	3 days at RT		27
	Column chromatography	 **10**	
	5 days at RT	 **11**	79
	Column chromatography	 **12**	



Charges:	C^2	C^1	C^2	C^1
Mullikan	-0.08	0.46	0.20	0.45
Lowdin	-0.13	-0.04	-0.12	-0.06
Merz-Singh-Kollman	-0.19	0.59	0.15	0.46

Fig. 1. Electrostatic potential fitted to total electron density surface and Mullikan, Lowdin and Merz–Singh–Kollman charges at vinylic carbons for hexafluoropropene and perfluoro(methyl vinyl ether).

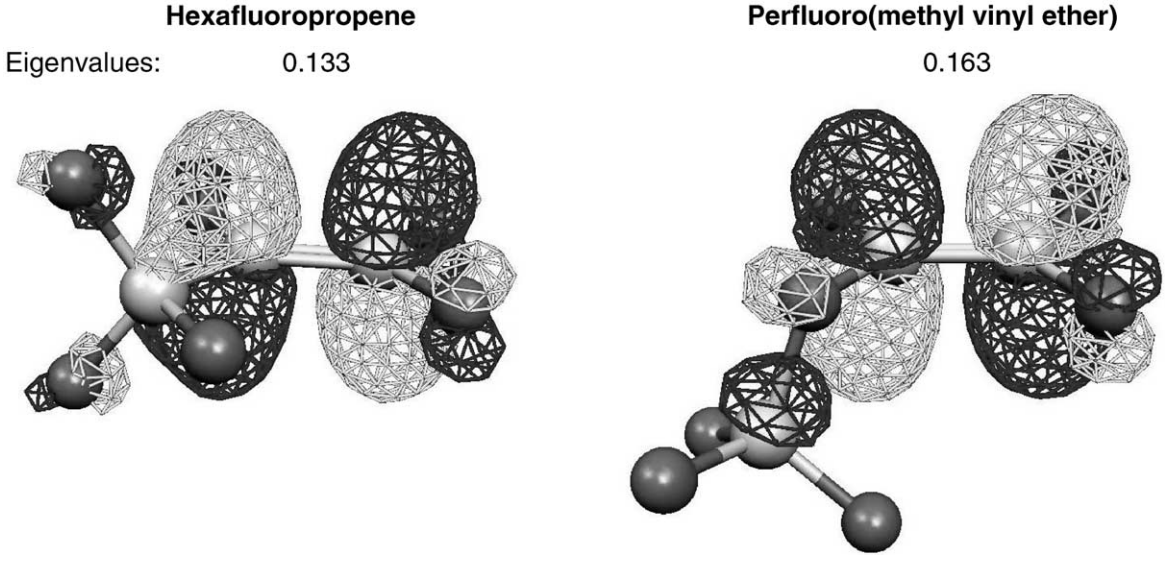


Fig. 2. π^* LUMO orbitals and their eigenvalues for hexafluoropropene and perfluoro(methyl vinyl ether).

Table 2
Yields of the addition of 1-naphthol to perfluoro vinyl ether **1**

Molar ratio (R-OH:**1**:alkoxide)	Alkoxide	Solvent	Yield (%)
1:1:0.2	Na[a]	THF	5
1:1:0.2	Na	THF/DMF	25
1:1.07:0.2	Li[b]	THF	54
1:1.07:0.3	Li	THF	55
1:0.95:1	Li	THF	61

[a] Generated by Na.
[b] Generated by butyllithium.

the product of the nucleophilic addition of hexadecan-1-ol to **1**, the ether **4**, appeared to be stable on column chromatography.

Phenolic compounds, 4-(trifluoromethylsulfanyl)phenol or 1-naphthol afforded the corresponding addition products **5** or **6** that were stable on column chromatography. Disodium salt of benzene-1,2-diol in *N*,*N*-dimethylformamide afforded the bis-addition product **7**, which is a sharp contrast to the reaction of benzene-1,2-diol with perfluoro(2-methylprop-1-ene) where 2-[1,1,1,3,3,3-hexafluoropropane-2,2-diyl]-1,3-benzo[*b*]dioxole was formed [27].

The reaction of perfluoro vinyl ether **1** with *S*-nucleophiles have not been reported so far. Therefore, we carried out an examination of reaction conditions using benzenethiol. The results are given in Table 3. Benzenethiol afforded small amount of the addition product **8** (10% yield) even at the absence of a catalyst. The highest yields were obtained with lithium thiolate (Table 3) and the sulfide **8** was stable on aluminum oxide chromatography.

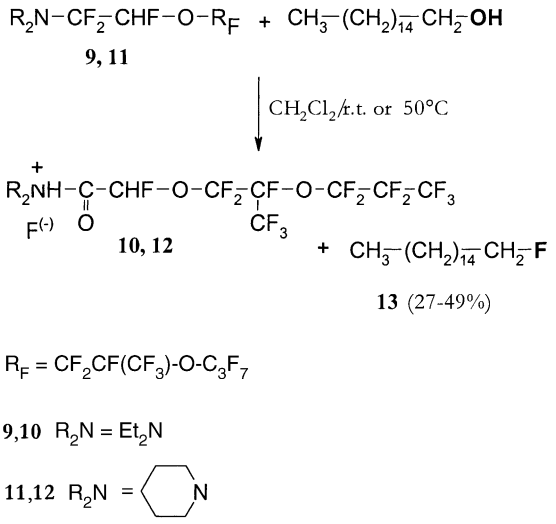
2.4. Additions of N-nucleophiles to olefin *1*, fluorination properties of the adducts

One of the aims of our first report [17] on the reaction of olefin **1** with secondary amines had been to verify, whether the adducts display fluorination ability similar to that of Yarovenko–Raksha [28] or Ishikawa reagents [29,30] or dimethylamine adduct to tetrafluoroethene [31]. In the meantime, two papers have appeared [19,20] where the reactions were carried out [19,20] in tetrahydrofuran and crude products were hydrolyzed in water to give the corresponding amines. The products were not tested for fluorination properties. We carried out the additions of diethylamine and piperidine to olefin **1** without a solvent with respect to a further use of the reaction mixture as a reagent. The addition products **9** and **11** were characterized by their ^{19}F NMR spectra (Table 1) and displayed high sensitivity to moisture. On column chromatography, the adducts **9** and **11** were completely hydrolyzed to the corresponding amides **10** and **12** (Table 1).

Table 3
Yields of the addition of benzenethiol to perfluoro vinyl ether **1**

Thiolate	Molar ratio (PhSH:**1**:thiolate)	Yield (%)
–	1:1:0	10
Na	1:0.94:0.46[a]	45
Na	1:1.05:1.27	52
Li	1:1.10:0.97[b]	55
Li	1:1.07:0.57	55

[a] Generated by Na.
[b] Generated by butyllithium.



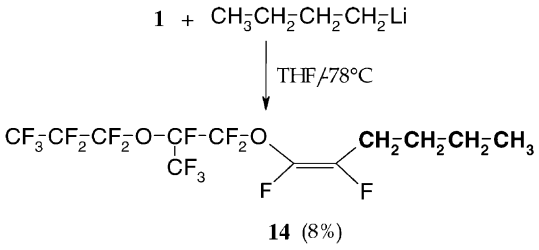
Scheme 2. Fluorination properties of amine adducts **9** and **11**.

Fluorination properties of the amine adducts **9** and **11** were verified in the following arrangement (Scheme 2): a solution of hexadecan-1-ol in dichloromethane was added to the reaction mixture containing crude amine adduct. The reaction with the adduct **9** was carried by refluxing the mixture to afford 1-fluorohexane in 49% isolated yield. When the fluorination of hexadecan-1-ol with the amine adduct **11** was performed at RT, the isolated yield was only 29%. The second products of fluorinations, the corresponding amides **10** and **12** were characterized as quarternary ammonium fluorides (Scheme 2).

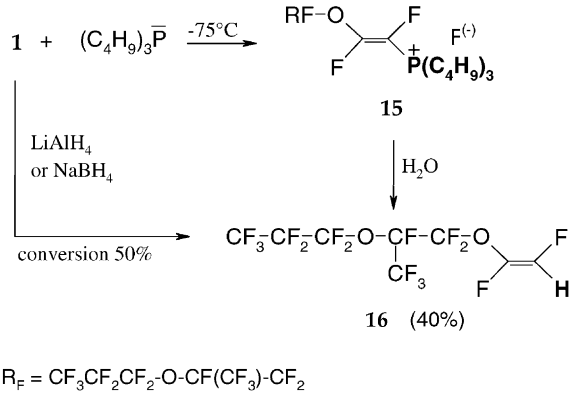
2.5. Replacement of vinylic fluorine: reactions of butyllithium, hydride ion and phosphane nucleophiles with olefin *1*

The previous reaction between perfluoro(propyl vinyl ether) and phenyllithium [13] at RT yielded mono-, di- or trisubstituted products in dependence on the stoichiometry of the reactants. In the 1:1 stoichiometry [13], (*Z*)-substitution product was obtained in a relative yield of 92%. In our reaction of olefin **1** with butyllithium (Scheme 3), only the product **15**, formed by the substitution of terminal fluorine, having (*Z*)-configuration was obtained in low yield at −78 °C. Thus, the reaction appeared to be completely regio- and stereoselective. At higher temperatures, a rich mixture of compounds was obtained.

Tributylphosphane was found [32,33] to displace fluorine at the terminal carbon of the double bond in perfluoroolefins to form the corresponding phosphonium fluorides, which by



Scheme 3. Reaction of alkene **1** with butyllithium.



Scheme 4. Reduction of perfluorvinyl ether **1**.

hydrolysis afforded 1*H*-derivatives of the starting perfluoroolefins with (*E*)-configuration. The reactions of phosphanes with perfluoro vinyl ethers have not been reported in the literature. The reaction of perfluoro vinyl ether **1** with tributylphosphane (Scheme 4) we carried out at −78 °C; the hydrolysis of the reaction mixture at −78 °C afforded the (*E*)-1*H*-perfluoro(5-methyl-3,6-dioxanon-1-ene) (**16**) as the exclusive product, no isomers were observed in NMR spectra. The intermediate phosphonium salt **15** was not analyzed.

There is a number of papers reporting the reactions of perfluoroolefins with complex hydrides, e.g. lithium aluminum hydride or sodium borohydride [34,35]. The reactions of (per)fluoroalk-1-enes afforded mixtures of regioisomers and configurational isomers. We have not found any report on the reactions of perfluoro vinyl ethers in the literature. We carried the reactions of fluoroolefin **1** with complex hydrides at −78 °C (Scheme 4) and obtained the product **16** as a mixture of (*E*)–(*Z*) configurational isomers in a 1:1 ratio. The results under various conditions are summarized in Table 3. We have not found any product of a two-fold reduction of the starting compound **1** even after 6 h reduction (check by ^{19}F NMR). Both complex hydrides used gave approximately the same yields of the product **16** (Table 3).

3. Conclusions

All the reactions of perfluoro vinyl ether **1** with nucleophiles carried out were completely regioselective with nucleophilic attack at the terminal carbon. Alcohols, phenols, benzenethiol or secondary amines used added to **1** as protonic acids to afford saturated products even when alkali salts of hydroxy compounds or benzenethiol were used. Butyllithium, tributylphosphane or complex hydrides reacted by replacement of vinylic fluorine: butyllithium afforded (*Z*)-substituted product (**14**) and tributylphosphane gave after hydrolysis (*E*)-hydrogenated product **16** exclusively, while complex hydrides reacted with the formation of a 1:1 (*E*)–(*Z*) mixture of **16**. Diethylamine and piperidine adducts (**9** and **11**) possessing very reactive α-bonds C–F were found to substitute hydroxyl for fluorine in hexadecan-1-ol. Quantum chemical calculations of perfluoro(methyl vinyl ether) and hexafluoropropene as model compounds to compare the impact of substitution of fluorine by perfluoroalkyl or perfluoroalkoxy group on the reactivity of fluoroalkene revealed a better reactivity for hexafluoropropene toward nucleophilic attack than for perfluoro vinyl ether **1**.

4. Experimental

4.1. General experimental procedures

The temperature data were not corrected. Column chromatography: CC1 ($d = 2.0$ cm); CC2 ($d = 3.0$ cm); CC3 ($d = 5.0$ cm). GC analyses were performed on a Chrom 5 (Laboratorní přístroje, Prague; FID, 350 cm × 0.3 cm packed column, silicone elastomer E-301 on Chromaton N-AW-DMCS (Lachema, Brno), nitrogen) and a Chrom 3 (Laboratorní přístroje, Prague; FID, 350 cm × 0.5 cm packed column, silicone elastomer E-301 on Chromaton N-AW-DMCS (Lachema, Brno), nitrogen) instruments. NMR spectra were recorded on a Bruker 400 AM (FT, ^{19}F at 376.5 MHz, ^{1}H at 400.1 MHz, ^{13}C at 100.6 MHz), Varian Gemini 300 HC (FT, ^{1}H at 300 MHz) and a Bruker WP 80 SY (FT, ^{19}F at 75.4 MHz) instruments: TMS and $CFCl_3$ as the internal standards, chemical shifts in ppm (s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet), coupling constants *J* in Hz, solvent $CDCl_3$. MS spectra were scanned on a Hewlett-Packard MSD 5971A instrument (1989, EI 70 eV).

Ab initio calculations were performed using the PC GAMESS version [36] of the GAMESS (US) QC package [37]. The energy minima were determined by complete optimization of the geometrical parameters by gradient methods using 6–311G(d,p) basis set with d polarization functions on C, O, F, and p polarization function on H at the MP2 levels of theory. Vibrational frequencies were calculated for both structures to characterize them as minima. Calculated charges at carbon atoms were based on Mulliken [23] and Lowdin [24] population analyses. Electrostatic potential-derived charges were calculated according to the Merz–Kollman–Singh scheme [25] using Gaussian 98W program suite [38]. Visualization were performed with MOLEKEL molecular graphics package [39].

Chemical used were as follows: 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoro-methyl-3,6-dioxanon-1-ene (**1**) was

prepared according to the literature [8,40]; 1-naphth-ol, benzene-1,2-diol, hexan-1-ol and hexadecan-1-ol (Lachema); 4-(trifluoromethylsulfanyl)phenol (Baeyer), benzenethiol (Aldrich); chloroform, heptane, acetone, petroleum ether (bp 40–65 °C), tetrahydrofuran were dried and purified according to standard laboratory procedures; diethylamine and piperidine were distilled before use. Butyllithium solution (hexane, 2.4 or 1.8N; Aldrich), lithium aluminum hydride (Merck), sodium borohydride (Lachema, Brno), silica gel (60–100 μm, Merck), tributylphosphane 85% (Aldrich).

4.2. Addition of alcohols to 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoromethyl-3,6-dioxanon-1-ene (*1*) (products *2–7*)

4.2.1. General procedure

The reactions were carried out in a sealed (with septum) round-bottomed flask (magnetic spinbar) under inert atmosphere. To a solution of alcohol in dry tetrahydrofuran (3 ml) cooled to −70 °C (dry-ice–ethanol bath), a solution of butyllithium in hexane was added while stirring. After 10 min reaction, the mixture was rapidly withdrawn with a pre-cooled syringe, and added to cooled (−70 °C) solution of perfluoro vinyl ether in tetrahydrofuran (1 ml). The reaction mixture was stirred for 1 h at −70 °C, then allowed to warm to RT and continued until no apparent change occurred (check by TLC). The reaction was quenched by the addition of trifluoroacetic acid, volatile components were removed on rotary evaporator and the residue was chromatographed or distilled to get a product.

4.2.2. Addition of 1-hexanol: 1,1,2,4,4,5,7,7,8,8,9,9,9-Tridecafluoro-5-trifluoromethyl-3,6,10-trioxahexadecane (*2*) and hexyl 2,4,4,5,7,7,8,8,9,9,9-undecafluoro-5-trifluoromethyl-3,6-dioxanonanoate (*3*)

A mixture of hexan-1-ol (0.67 g, 6.56 mmol), perfluoro vinyl ether **1** (3.25 g, 7.53 mmol), and butyllithium(3.28 mmol, 2.47 M in *n*-hexane) was stirred for 5 days. Tetrahydrofuran was removed by distillation. Fractional distillation of the residue afforded two fractions: first, bp 111–113 °C/120 mmHg (0.915 g, 63% of **2**, 6% of **3**, check by GC); second, bp 113 °C/120 mmHg (0.981 g, 76% of **2**, 10% of **3**). Samples for analyses were purified by preparative GC, yields: **2**, 1.32 g (38%); **3**, 0.34 g (9%).

2: ^{1}H NMR (300.07 MHz, $CDCl_3$): δ 0.88 (t, 3H, CH_3, $^3J_{HH} = 6.5$ Hz); 1.30 (m, 6H, CH_2); 1.64 (p, 2H, CH_2, $^3J_{HH} = 7.1$ Hz); 3.95 (t, 2H, CH_2, $^3J_{HH} = 6.5$ Hz); 5.83 (d, 1H, CHF, $^2J_{HF} = 53.3$ Hz) ppm. For ^{19}F NMR spectra (376.6 MHz, $CDCl_3$) see Table 4. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 22.9; 25.7; 29.4; 31.8; 65.3 (CH_2); 13.9 (CH_3); 98.8 (m, CHF, $^1J_{CF} = 244.1$ Hz, $^2J_{CF} = 43.3$ Hz) ppm. Anal. calcd. for $C_{14}H_{14}F_{16}O_3$: C, 31.5; H, 2.6. Found: C, 30.5; H, 2.8%.

3: ^{1}H NMR (300.07 MHz, $CDCl_3$): δ 0.88 (t, 3H, CH_3, $^3J_{HH} = 6.6$ Hz); 1.31 (m, 6H, CH_2); 1.68 (p, 2H, CH_2, $^3J_{HH} = 7.1$ Hz); 4.54 (t, 2H, CH_2, $^3J_{HH} = 6.6$ Hz); 6.07 (d, 1H, CHF, $^2J_{HF} = 54.9$ Hz) ppm. For ^{19}F NMR spectra (75.4 MHz, $CDCl_3$) see Table 4. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 23.1; 25.9; 28.9; 31.9; 68.1 (CH_2); 14.5 (CH_3); 162.4 (d, CO, $^2J_{CF} = 30.2$ Hz) ppm. IR (cm^{-1}): 2933, 2861, 1775, 1249, 1309, 1159, 1051. Anal. calcd. for $C_{14}H_{14}F_{14}O_4$: C, 32.8; H, 2.7. Found: C, 33.0; H, 2.9%.

4.2.3. Addition of hexadecan-1-ol: 1,1,1,2,2,3,3,5,6,6,8,9,9-Tridekafluoro-5-trifluoromethyl-4,7,10-trioxahexacosane (*4*)

A mixture of hexadecan-1-ol (0.44 g, 1.83 mmol), perfluoro vinyl ether **1** (0.83 g, 1.92 mmol), butylithium (1.8 mmol, 1.8 M in *n*-hexane) was stirred for 5 days. Column chromatography CC1 (Al_2O_3, 35 g, heptane-acetone 4:1, check by TLC). Yield of **4**: 0.50 g (41%).

^{1}H NMR (300.07 MHz, $CDCl_3$): δ 0.88 (t, 3H, CH_3, $^3J_{HH} = 6.9$ Hz); 1.26 (s, 26H, CH_2); 1.64 (t, 2H, CH_2, $^3J_{HH} = 6.6$ Hz); 3.95 (t, 2H, CH_2); 5.83 (dt, 1H, CHF, $^2J_{HF} = 53.8$ Hz, $^3J_{HF} = 2.9$ Hz) ppm. For ^{19}F NMR spectra (75.4 MHz, $CDCl_3$) see Table 4. Anal. calcd. for $C_{24}H_{34}F_{16}O_3$: C, 42.7; H, 5.1; F, 45.1. Found: C, 42.3; H, 4.7; F, 45.1%.

4.2.4. Addition of 4-(trifluoromethylsulfanyl)phenol: 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoromethyl-1-[4-(trifluoromethylsulfanyl)-1-phenyloxy]-3,6-dioxanonane (*5*)

A mixture of 4-(trifluoromethylsulfanyl)phenol (0.23 g, 1.14 mmol), perfluoro vinyl ether **1** (0.64 g, 1.47 mmol), butyllithium (1.12 mmol, 1.8 M in *n*-hexane) was stirred for 5 days. Column chromatography CC1 (Al_2O_3, 10 g, heptane–acetone 4:1, check by TLC). Yield of **5**: 0.21 g 30%.

^{1}H NMR (300.07 MHz, $CDCl_3$): δ 7.24 (d, 2H, CH, $^3J_{HH} = 8.2$ Hz); 7.69 (dt, 2H, CH, $^4J_{HF} = 2.2$ Hz); 6.07 (dt, 1H, CHF, $^2J_{HF} = 53.2$ Hz, $^3J_{HF} = 2.7$ Hz) ppm. ^{19}F NMR (75.4 MHz, $CDCl_3$): δ −43.4 (s, 1F, CF_3S). For the main part of the ^{19}F NMR spectra (75.4 MHz, $CDCl_3$) see Table 4. MS ($M_r = 626$), *m/z* (% relative intensity): EI: 538/2 ($M_r - CF_3$–F), 507/2, 438/2, 338/8, 372/7, 335/10, 290/6, 275/20, 243/10, 193/20, 177/40, 169/50, 108/25, 69/100, 50/15.

4.2.5. Addition of 1-naphthol: 1-(2,2,3,5,5,6,8,8,9,9,10,10,10-tridecafluoro-5-trifluoromethyl-1,4,7-trioxadecyl)naphthalene (*6*)

Procedure A: The reactions were carried out in a sealed (with septum) round-bottomed flask (magnetic spinbar) under inert atmosphere. To a solution of 1-naphthol (0.20 g, 1.38 mmol) in dry tetrahydrofuran (2 ml) and *N*,*N*-dimethylformamide, pieces of sodium (0.01 g, 0.26 mmol) were added while stirring. Then, perfluoro vinyl ether **1** (0.81 g, 1.41 mmol) was added dropwise to the mixture at RT. After 5-day reaction, solvents were removed in vacuum by rotary evaporator. The residue was then chromatographed. Column chromatography CC1 (Al_2O_3, 10 g, heptane–acetone 4:1, check) to afford product **6**,

Table 4
^{19}F NMR spectra of compounds **2–12**, **14** and **16**

h g f d c b a
CF_3—CF_2—CF_2—O—CF(e CF_3)—CF_2—O—CHF—CF_2—

	a CF_2	b CHF	c CF_2	d CF	e CF_3	f CF_2	g CF_2	h CF_3
2	F_A −90.5, F_B −90.9, $^2J_{FF}$ = 146.1	$ds_{1,2}$ −145.1, $ds_{3,4}$ −145.2, $^3J_{FF}$ = 7.4	$ds_{1,2}$ F_A −84.2, F_B −86.4, $^2J_{FF}$ = 141.1, $ds_{3,4}$ F_A −84.5, F_B −86.8, $^2J_{FF}$ = 140.4	−145.4 t, $^3J_{FdFf}$ = 20.3	−80.6 m	F_A −82.3, F_B −82.7, $^2J_{FF}$ = 142.3	−130.1 s	−81.9 s
3		$ds_{1,2}$ −135.9, $ds_{3,4}$ −136.0, $^3J_{FF}$ = 7.3	−84.6 to −85.5 m	−145.2 t, $^3J_{FdFf}$ = 19.9	−80.5 m	−82.1 m	−130.0 s	−81.8 s
4	−90.1 m	−145.2 m	$ds_{1,2}$ −84.5, $ds_{3,4}$ −85.5 m	−145.2 m	−80.6 m	−81.9 m	−130.1 s	−81.7 s
5	−87.1 m	−145.5 m	−84.2 to (−86.0) m	−145.1 m	−80.5 m	−82.1 m	−130.1 s	−81.8 s
6	F_A −85.7, F_B −87.0, $^2J_{FF}$ = 146.1	$ds_{1,2}$ −144.0, $ds_{3,4}$ −144.6, $^3J_{FF}$ = 8.3	$ds_{1,2}$ F_A −83.9, F_B −85.7, $^2J_{FF}$ = 144.2, J_{FF} = 5.6, $ds_{3,4}$ F_A −84.1, F_B −86.0, $^2J_{FF}$ = 141.5	−145.4 t, $^3J_{FdFf}$ = 21.0	−80.4 m	F_A −81.9, F_B −82.3, $^2J_{FF}$ = 145.3	−130.0 s	−82.9 s
7	89.8 m	−144.8 m	−82.5 to (−90.0)	−145.4 t, $^3J_{FdFf}$ = 18.6	−80.7 m	−82.5 to (−90.0) m	−130.2 s	−81.9 s
8	−90.5 m	−140.2 m	−84.2 to (−85.7) m	−145.4 m	−80.5 m	−81.9 m	−130.0 s	−81.8 s
9	−84.7 m	−144.9 m	−85.7 to (−86.7) m	−145.4 t, $^3J_{FdFf}$ = 18.6	−80.5 m	−81.5 to (−82.3) m	−130.2 s	−81.9 s
10	−87.1 m	−145.5 m	−84.2 to (86.0) m	−145.1 m	−80.5 m	−82.1 m	−130.1 s	−81.8 s
11		$ds_{1,2}$ −128.9, $ds_{3,4}$ −129.1, $^2J_{FF}$ = 55.8	$ds_{1,2}$ F_A −84.5, F_B −85.9, $^2J_{FF}$ = 142.7, $ds_{3,4}$ F_A −84.4, F_B −85.9, $^2J_{FF}$ = 141.9	−145.4 m	−80.4 s	F_A −81.8, F_B −82.3, $^2J_{FF}$ = 144.9	−130.0 s	−81.7 s
12		$ds_{1,2}$ −129.0, $ds_{3,4}$ −129.1, $^4J_{FF}$ = 11.9	$ds_{1,2}$ F_A −84.6, F_B −85.9, $^2J_{FF}$ = 140.7, $ds_{3,4}$ F_A −84.6, F_B −86.1, $^2J_{FF}$ = 143.7	−145.1 t, $^3J_{FdFf}$ = 19.9	−80.5 m	F_A −81.8, F_B −82.5, $^2J_{FF}$ = 144.7	−130.2 s	−81.9 s
	CF=	=CF–						
14	−149.9 m	109.4 m, $^3J_{FF}$ = 23.6	85.2 m	−145.3 m	−82.4 m	−81.8 s	−129.4 s	−81.8 s
16	−145.5 m	−135.3 d, $^3J_{FF}$ = 49.9	−84.2 to −86.1 m	−145.5 m	−80.3 m	−82.0 m	−130.0 s	−81.8 s

yield 0.19 g (25%). For another reaction conditions see Table 4.

Procedure B: A mixture of 1-naphthol (0.10 g, 0.71 mmol), butylithium (0.72 mmol, 2.47 M in *n*-hexane), alkene **1** (0.39 g, 0.67 mmol, molar ratio 1-naphthole: alkene **1**: BuLi 1:0.95:1.01) was stirred for 5 days. Column chromatography CC1 (Al_2O_3, 10 g, heptane–acetone 4:1, check by TLC). Yield of **6**: 0.238 g (61%). For another reaction conditions see Table 2.

^{1}H NMR (300.07 MHz, $CDCl_3$): δ 7.35–7.54 (m, 4H, CH); 8.07 (dd, 1H, CH, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 1.5 Hz); 7.82 (dd, 1H, CH); 7.71 (dd, 1H, CH); 6.21 (dt, 1H, CHF, $^2J_{HF}$ = 53.4 Hz, $^3J_{HF}$ = 2.5 Hz) ppm. For ^{19}F NMR spectra (376.6 MHz, $CDCl_3$) see Table 4. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 145.6 (C); 128.4 (C); 135.7 (C); 118.1 (CH); 125.9 (CH); 122.3 (CH); 128.5 (CH); 127.5 (CH); 127.6 (CH); 118.2 (CH); 99.2 (ttd, CHF, $^1J_{CF}$ = 245.0 Hz, $^2J_{CF}$ = 41.8 Hz, J_{CF} = 4.8 Hz); 103.6 (sextet d, CF, $^1J_{CF}$ = 269.4 Hz; $^2J_{CF}$ = 37.9 Hz); 107.5 (sextet t, CF_2, $^1J_{CF}$ = 268.9 Hz, $^2J_{CF}$ = 39.0 Hz); 116.4 (dtt, CF_2, $^1J_{CF}$ = 288.6 Hz, $^2J_{CF}$ = 29.0 Hz, J_{CF} = 4.3 Hz); 117.4 (dt, CF_2, $^1J_{CF}$ = 297.5 Hz, $^2J_{CF}$ = 29.3 Hz); 118.1 (dt, CF_2, $^1J_{CF}$ = 286.0 Hz, $^2J_{CF}$ = 28.7 Hz); 118.0 (tq, CF_3, $^1J_{CF}$ = 287.1 Hz, $^2J_{CF}$ = 32.8 Hz); 118.6 (dq, CF_3, $^1J_{CF}$ = 223.8 Hz, $^2J_{CF}$ = 31.0 Hz) ppm. Anal. calcd. for $C_{18}H_8F_{16}O_3$: C, 37.5; H, 1.4; F, 52.7. Found: C, 37.8; H, 1.5; F, 52.6%.

4.2.6. Addition of benzene-1,2-diol: 1,2-bis-(1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoromethyl-3,6-dioxanonan-1-yloxy)-benzene (7)

Sodium (5.4 mg, 2.35 mmol) was added to a solution of benzene-1,2-diol (0.13 g, 1.18 mmol) in dry dimethylformamide (2 ml) in round-bottomed flask (magnetic spinbar), The reaction mixture was stirred overnight. To the solution of alkoxide, perfluoro vinyl ether **1** (0.728 g, 1.68 mmol,

143 mol%) was added under ice-cooling the reaction flask and the mixture was stirred overnight at RT. The mixture was poured into water (5 ml) and extracted with diethyl ether (3 × 5 ml). Combined ethereal extracts were dried over $MgSO_4$ and volatile components were removed in vacuum (rotary evaporator). The residue–crude product was purified by column chromatography (CC1, Al_2O_3, 15 g, petroleum ether–aceton 4:1, check by TLC) to afford product **7**, yield 0.34 g (41%).

^{1}H NMR (300.07 MHz, $CDCl_3$): δ 7.28–7.40 (m, 4H, CH); 6.05 (d, 2H, CHF, $^2J_{HF}$ = 53.8 Hz) ppm. For ^{19}F NMR spectra (75.4 MHz, $CDCl_3$) see Table 4. Anal. calcd. for $C_{22}H_6F_{32}O_6$: C, 27.1; H, 0.6; F, 62.4. Found: C, 27.4; H, 0.8; F, 62.5%.

4.3. Addition of benzenethiol: 1-phenylsulfanyl-1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoromethyl-3,6-dioxanonane (8)

Procedure A: A mixture of perfluoro vinyl ether **1** (0.35 g, 0.82 mmol) and benzenethiol (0.09 g, 0.83 mmol) in dry tetrahydrofurane (3 ml) was stirred for 3 days at RT. The solvent was then removed in vacuum (rotary evaporator) and the crude product was purified by column chromatography (CC1, Al_2O_3, 10 g, petroleum ether–acetone 4:1, check by TLC) to afford pure **8**, yield 0.04 g (10%).

Procedure B: Sodium (0.6 g, 2.35 mmol) was added to a solution of benzenethiol (0.20 g, 1.81 mmol) in dry tetrahydrofurane (2 ml) in round-bottomed flask (magnetic spinbar). To the thiolate solution, perfluoro vinyl ether **1** (0.84 g, 1.95 mmol) was added under ice-cooling the reaction flask and the mixture was stirred for 5 days at RT. Tetrahydrofuran was removed in vacuum (rotary evaporator) and the residue was chromatografted (CC1, Al_2O_3, 30 g, petroleum ether–acetone 4:1, check by TLC) to obtain pure **8**, yield 0.65 g (52%). For another reaction conditions see Table 3.

Procedure C: A solution of buthyllithium (2.04 mmol, 2.47 M in *n*-hexane) was added to a solution of benzenethiol (0.23 g, 2.1 mmol) in dry tetrahydrofuran (2 ml) in a flask cooled to −70 °C under nitrogen atmosphere while stirring. After 10 min reaction, the mixture was rapidly withdrawn by a pre-cooled syringe and put in cooled (−70 °C) solution of perfluoro vinyl ether (1.0 g, 2.32 mmol) in tetrahydrofuran (1 ml). The reaction was stirred at −75 °C for 2 h and than at room temperature for 5 days. The mixture was quenched with trifluoroacetic acid and volatile components were removed in vacuum (rotary evaporator). The residue was purified by column chromatography (CC1, Al_2O_3, 30 g, petroleum ether–acetone 4:1) to afford product **8**, yield 0.45 g (55%). For another reaction conditions see Table 3.

^{1}H NMR (300.07 MHz, $CDCl_3$): δ 7.20–7.65 (m, 5H, CH); 5.92 (dt, 1H, CHF, $^2J_{HF}$ = 54.9 Hz, $^3J_{HF}$ = 3.9 Hz) ppm. For ^{19}F NMR spectra (75.4 MHz, $CDCl_3$) see Table 4. MS (M_r = 542) *m/z* (% relative intensity): EI: 542/20 (M^+), 473/2 ($M - CF_3$), 423/2, 357/2, 355/2, 304/3, 206/2, 191/4, 159/100, 119/5, 109/65, 77/32, 69/55.

4.4. Addition of amines to 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoromethyl-3,6-dioxanon-1-ene (1) (products 9–12)

4.4.1. General procedure

Perfluoro vinyl ether **1** was dropwise added to amine in a round-bottomed flask under cooling (ice bath). The mixture stirred at room temperature, a sample of reaction mixture was rapidly withdrawn by syringe, the ^{1}H NMR and ^{19}F NMR spectra were taken. Amine was removed under reduced pressure (rotary evaporator). The residue was purified by column chromatography.

4.4.2. Addition of diethyl amine: N,N-diethyl-1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-5-trifluoromethyl-3,6-dioxanonan-1-amine (9) and N,N-diethyl-2,4,4,5,7,7,8,8,9,9,9-undecafluoro-5-trifluoromethyl-3,6-dioxanonanamide (10)

A mixture of diethyl amine (0.38 g, 5.29 mmol), perfluoro vinyl ether **1** (1.69 g, 3.91 mmol) was stirred for 3 days. Amine **9** was identified in crude reaction mixture and spontaneously hydrolyzed to amide **10** on the air moisture. Column chromatography CC2 (SiO_2, 35 g, heptane–acetone 4:1, check by TLC). Yield of **10**: 1.02 g (54%) (literature [10]: yield 74%, bp 57–58 °C/0.2 mmHg).

9: ^{1}H NMR (300.07 MHz, $CDCl_3$): δ 1.08 (t, 6H, CH_3, $^3J_{HH}$ = 7.1 Hz); 2.9 (q, 4H, CH_2); $ds_{1,2}$ 5.96, $ds_{3,4}$ 6.02 (1H, CHF, $^2J_{HF}$ = 54.4 Hz, $^2J_{HF}$ = 53.3 Hz) ppm. For ^{19}F NMR spectra (75.4 MHz, $CDCl_3$) see Table 4.

10: ^{1}H NMR (300.07 MHz, $CDCl_3$): δ 1.18 (t, 6H, CH_3, $^3J_{HH}$ = 7.3 Hz); 3.35 (q, 4H, CH_2); 6.24 (d, 1H, CHF) ppm. For ^{19}F NMR spectra (470.5 MHz, $CDCl_3$) see Table 4. ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 12.1 (CH_3); 14.0 (CH_3); 40.8 (CH_2); 117.9 (tq, CF_3, $^1J_{CF}$ = 270.4 Hz, $^2J_{CF}$ = 27.6 Hz); 117.7 (dq, CF_3, $^1J_{CF}$ = 272.8 Hz, $^2J_{CF}$ = 31.3 Hz); 106.6 (qt, CF_2, $^1J_{CF}$ = 269.5 Hz, $^2J_{CF}$ = 37.9 Hz); 115.4 (tt, CF_2, $^1J_{CF}$ = 287.5 Hz, $^2J_{CF}$ = 29.9 Hz); 118.3 (dt, CF_2, $^1J_{CF}$ = 296.5 Hz, $^2J_{CF}$ = 28.9 Hz); 101.4 (dq, CF, $^1J_{CF}$ = 269.1 Hz, $^2J_{CF}$ = 38.3 Hz); 101.3 (d, CHF, $^1J_{CF}$ = 250.5 Hz); 160.5 (d, CO, $^2J_{CF}$ = 24.5 Hz) ppm. IR (cm^{-1}) 3025 (CH_3, CH_2); 1667 (C=O); 1245 (–O–); 1306, 1159 (CF). Anal. calcd. for $C_{12}H_{11}F_{14}NO_3$: C, 29.8; H, 2.3; F, 55.0. Found: C, 30.4; H, 2.5; F, 55.2%.

4.4.3. Addition of piperidine: 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-1-(piperidin-1-yl)-5-trifluoromethyl-3,6-dioxanonane (11) and 1-(2,4,4,5,7,7,8,8,9,9,9-undecafluoro-5-trifluoromethyl-3,6-dioxanonanoyl)piperidine (12)

A mixture of piperidine (1.64 g, 19.21 mmol), perfluoro vinyl ether **1** (2.95 g, 6.38 mmol) was stirred for 5 days. Amine 11 was identified in crude reaction mixture and spontaneously hydrolyzed to amide **12** on the air moisture. Column chromatography CC3 (SiO_2, 70 g, petroleum ether–acetone 6:1, check by TLC). Yield of **12**: 2.64 g (78%) (literature [10] yield 70%, bp 92–93 °C/0.4 mmHg).

11: ^{1}H NMR (300.07 MHz, $CDCl_3$): δ 1.55 (m, 6H, CH_2); 3.45 (m, 4H, CH_2); $ds_{1,2}$ 6.00, $ds_{3,4}$ 6.03 (1H, CHF, $^2J_{HF} = 53.8$ Hz, $^2J_{HF} = 52.9$ Hz, $^3J_{HH} = 3.2$ Hz, $^3J_{HH} = 2.4$ Hz) ppm. For ^{19}F NMR spectra (75.4 MHz, $CDCl_3$) see Table 4.

12: ^{1}H NMR (300.07 MHz, $CDCl_3$): δ 1.55 (m, 6H, CH_2, $^3J_{HH} = 7.3$ Hz); 3.45 (m, 4H, CH_2); 6.23 (d, 1H, CHF, $^2J_{HF} = 56.0$ Hz) ppm. For ^{19}F NMR spectra (470.5 MHz, $CDCl_3$) see Table 4. ^{13}C NMR (125.75 MHz, $CDCl_3$): δ 24.7 (CH_2); 25.9 (CH_2); 44.5 (CH_2); 118.1 (tq, CF_3, $^1J_{CF} = 287.9$ Hz, $^2J_{CF} = 31.3$ Hz); 118.3 (dq, CF_3, $^1J_{CF} = 274.3$ Hz, $^2J_{CF} = 31.2$ Hz); 107.1 (qt, CF_2, $^1J_{CF} = 268.6$ Hz, $^2J_{CF} = 37.3$ Hz); 116.0 (dt, CF_2, $^1J_{CF} = 292.7$ Hz, $^2J_{CF} = 31.4$ Hz); 119.8 (dt, CF_2, $^1J_{CF} = 295.2$ Hz, $^2J_{CF} = 28.6$ Hz); 103.3 (dq, CF, $^1J_{CF} = 270.0$ Hz, $^2J_{CF} = 37.0$ Hz); 102.1 (d, CHF, $^1J_{CF} = 250.4$ Hz); 160.0 (d, CO, $^2J_{CF} = 24.5$ Hz) ppm. IR (cm^{-1}) 3020, 2928, 2882 (CH_2); 1685 (C=O); 1244 (–O–); 1305, 1158 (CF). Anal. calcd. for $C_{13}H_{11}F_{14}NO_3$: C, 31.5; H, 2.2; F, 53.7. Found: C, 31.9; H, 2.4; F, 51.2%.

*4.4.4. Fluorination properties of amine adducts **9** and **11**: 1-fluorohexadecane (**13**)*

*4.4.4.1. Fluorination with the adduct **9**.* Under nitrogen, perfluoro vinyl ether **1** (2.14 g, 4.96 mmol) was dropwise added through septum by syringe to diethylamine (0.430 g, 5.88 mmol) in a round-bottomed flask (10 ml) while cooling (ice bath) and stirring (magnetic spinbar) for 1 h. After that, the mixture was stirred for 24 h at RT, then the flask immersed in ice bath and a solution of hexadecan-1-ol (0.601 g, 2.48 mmol) in dichloromethane (7 ml) was added through septum. After 1 h, the mixture was slowly heated to 50 °C and gently refluxed for 12 h. Then, the mixture was washed in a dropping funnel with potassium solution (10%, 2 × 5 ml) and water (2 × 5 ml) and dried over $MgSO_4$. Volatile components were then removed on rotary evaporator (30 °C, ca. 30 mmHg) and the residue (0.924 g) was purified by chromatography (CC1, SiO_2, 30 g, petroleum ether) to afford product **13**, yield 0.293 g (48%) and amide **10** as an ammonium salt.

*4.4.4.2. Fluorination with the adduct **11**.* By the protocol according to Section 4.4.4.1, perfluoro vinyl ether **1** (2.32 g, 5.37 mmol), piperidine (0.50 g, 5.87 mmol) and hexadecan-1-ol (0.575 g, 2.37 mmol) were reacted and the end reaction mixture treated as above. After evaporation of volatile components, the residue (1.58 g) was chromatographed (CC2, SiO_2, 45 g, petroleum ether) to afford product **13**, yield 0.156 g (27%) and amide **12** as an ammonium salt.

13: ^{1}H NMR (300.07 MHz, $CDCl_3$): δ 0.88 (t, 3H, CH_3, $^3J_{HH} = 6.9$ Hz); 1.26 (s, 26H, CH_2); 1.69 (pd, 2H, CH_2, $^3J_{HH} = 6.4$ Hz, $^3J_{HF} = 24.7$ Hz); 4.44 (td, 2H, CH_2F, $^2J_{HF} = 47.2$ Hz) ppm. ^{19}F NMR (75.4 MHz, $CDCl_3$): δ −211.4 (tt) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 24.7 (CH_2); 25.1 (CH_2); 25.2 (CH_2); 29.3 (CH_2); 29.4 (CH_2); 29.5 (CH_2); 29.6 (CH_2); 30.3 (CH_2); 30.6 (CH_2); 31.9 (CH_2); 84.2 (t, CH_2F, $^1J_{CF} = 164.7$ Hz) ppm. Anal. calcd. for $C_{16}H_{33}F$: C, 78.6; H, 13.6; F, 7.9. Found: C, 78.9; H, 13.6; F, 8.2%.

*4.5. Reaction of fluoroolefin **1** with butyllithium: (Z)-5,6,8,8,9,11,11,12,12,13,13,13-dodecafluoro-9-trifluoromethyl-7,10-dioxatridec-5-ene (**14**)*

A solution of butyllithium (3.0 ml, 5.4 mmol, 1.8 M in *n*-hexane) was added dropwise to a solution of perfluoro vinyl ether **1** (2.25 g, 5.2 mmol) in dry diethyl ether (2.5 ml) in a round-bottomed flask under inert atmosphere while cooling (−70 °C) and stirring (magnetic spinbar). The mixture was stirred for 2 h at −70 °C, allowed to warm to RT, then quenched with trifluoroacetic acid and neutralized with a solution of potassium carbonate. Solvents were removed by distillation and subsequent distillation of the residue afforded not pure 14 (0.419 g, purity ca. 42%, calcd. from GC), bp 120–140 °C, calculated yield ca. 8%. Sample for analysis was purified by preparative GC.

^{1}H NMR (300.07 MHz, $CDCl_3$): δ 0.92 (t, 3H, CH_3, $^3J_{HH} = 7.4$ Hz); 2.22 (dtd, 2H, CH_2, $^3J_{HF} = 22.7$ Hz); 1.53 (p, 2H, CH_2, $^3J_{HH} = 7.4$ Hz); 1.35 (sextet, 2H, CH_2) ppm. For ^{19}F NMR spectra (75.4 MHz, $CDCl_3$) see Table 4. Anal. calcd. for $C_{12}H_9F_{15}O_2$: C, 30.6, H, 1.9, F, 60.6. Found: C, 30.9, H, 1.5, F, 60.3%.

*4.6. Reaction of fluoroolefin **1** with tributylphosphane: 1,2,4,4,5,7,7,8,8,9,9,9-dodecafluoro-5-trifluoromethyl-3,6-dioxanon-1-ene (**16**)*

Tributylphosphane (85%, 1.94 g, 8.15 mmol) was added dropwise through septum to a stirred solution of alkene **1** (3.74 g, 8.66 mmol) in dry diethyl ether (3 ml) at −75 °C under nitrogen. The mixture was stirred for 2 h at −75 °C, then water (0.5 ml) was added and the mixture dried over molecular sieves (A4). Distillation afforded not completely pure **15** (1.72 g, purity ca. 85%, GC, calculated yield ca. 41%), fraction 65–100 °C. Sample for analysis was purified by preparative GC.

^{1}H NMR (300.07 MHz, $CDCl_3$): δ 5.68 (dd, $^2J_{HF} = 57.7$ Hz, $^3J_{HF} = 4.4$ Hz). For ^{19}F NMR spectra (75.4 MHz, $CDCl_3$) see Table 4. MS ($M_r = 414$) *m/z* (% relative intensity): EI: 414/2 (M^+), 383/3, 335/7, 285/2, 169/75, 149/5, 119/15, 100/18, 83/100, 69/95, 51/15, 33/20.

*4.7. Reaction of fluoroolefin **1** with lithium aluminum hydride or sodium borohydride: product **16***

The suspension of a hydride in dry tetrahydrofurane in a round-bottomed flask under nitrogen was cooled to −75 °C. Perfluoro vinyl ether **1** was slowly added to the flask through septum while stirring. In intervals 1 and 6.5 h after the addition of the olefin **1**, a sample of reaction mixture was rapidly withdrawn by pre-cooled syringe, put in cooled water, organic layer separated and the ^{19}F NMR spectrum was taken. The contents of the starting alkene **1**

Table 5
Reduction of perfluoro vinyl ether **1** by complex hydrides

Hydride	Molar ratio (**1**: hydride)	Time (h)	Reaction mixture composition (% relative intensity[a])	
			1	16
$NaBH_4$	1:0.49	0.75	80	20
$LiAlH_4$	1:0.83	1	70	30
$NaBH_4$	1:0.49	6.5	50	50
$LiAlH_4$	1:0.73	6.5	50	50

[a] ^{19}F NMR.

and product **16** under various conditions are given in Table 5.

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