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Radical additions to fluoroolefins. Photochemical fluoroalkylation of alkanols and alkane diols with perfluoro vinyl ethers; photo-supported O-alkylation of butane-1,4-diol with hexafluoropropene

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Abstract

Butane-1,4-diol was fluoroalkylated by its photoaddition reactions with hexafluoropropene and perfluoro (propyl vinyl) ether under atmospheric pressure, by which monofluoroalkylated and bis-fluoroalkylated products were obtained. 1,3-Diols were completely unreactive under the conditions. 2,2,2-Trifluoroethanol, tert.butyl alcohol and methyl tert.butyl ether appeared to be inert solvents for the additions while acetonitrile quenched the reactions. The reactivity of perfluoro vinyl ethers was studied (tested) in their photoaddition reactions with alkanols that were less regioselective (up to 7% rel.of regioisomer) in comparison with hexafluoropropene. Surprisingly, photo-supported base-induced nucleophilic mono- and bis-addition of butane-1,4-diol onto hexafluoropropene was observed in acetonitrile.

Keywords: Radical addition; Regioselectivity; Perfluoroolefins; Perfluoro vinyl ethers; Hexafluoropropyl ethers; Photoaddition; Fluoroalkylation; Fluoroalkyl diols; Bis-(Fluoroalkyl) diols; Solvents for radical additions; Diastereoisomers

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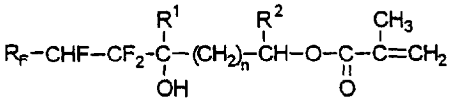
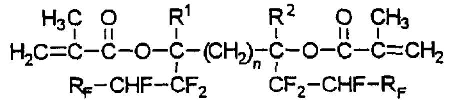
1. Introduction

Fluoroalkyl methacrylates are widely used as monomers for special polymers in technical and biomedical applications. Materials for medical applications prepared from these monomers, e.g. for contact and intraocular lenses, display enhanced oxygen transport, but they lack wettability when compared with classical hydrophillic polymers (e.g. poly(HEMA), poly(DEGMA) etc.) [1,2]. Hydrophillic properties of the materials can be improved by the introduction of hydroxylic groups into the ester groups of the monomers. An example of such a methacrylate monomer can be expressed by structure **1** (Scheme 1) which is in fact the monoester of a fluoroalkyl diol. In the literature, there is described a selective monoacylation of fluoroalkyl diols [3] with methacryloyl chloride that gives a good possibility for the synthesis of mono-methacrylates of the type **1** from fluorine-containing diols. Bis-methacrylates of diols are frequently used as cross-linking agents in the preparation of hydrophillic materials. Bis-methacrylates of fluoroalkyl diols, as represented by the structure **2**, in the form of cross-linking agents can also bring new interesting properties in polymer materials. Therefore, syntheses of fluorine-containing fluoroalkyl diols can be an important step in the preparation of some kinds of polymer materials.



$R_F{-}CHF{-}CF_2{-}\underset{OH}{\overset{R^1}{C}}{-}(CH_2)_n{-}\overset{R^2}{CH}{-}O{-}\underset{O}{\overset{\|}{C}}{-}\overset{CH_3}{C}{=}CH_2$

1



$H_2C{=}\overset{H_3C}{C}{-}\overset{O}{\overset{\|}{C}}{-}O{-}\underset{R_F-CHF-CF_2}{\overset{R^1}{C}}{-}(CH_2)_n{-}\underset{CF_2-CHF-R_F}{\overset{R^2}{C}}{-}O{-}\overset{O}{\overset{\|}{C}}{-}\overset{CH_3}{C}{=}CH_2$

2

R^1, R^2 = H, alkyl
R_F = perfluoroalkyl, perfluoroalkoxyl,
perfluoro(oxaalkyl, polyoxaalkyl)

Scheme 1. General structures of potential methacrylate monomers.

Fluorine-containing diols bearing fluoroalkyls or a perfluorinated segment in the molecule can be prepared by several methods: reduction of carboxylic acid esters with complex hydrides are long known [4,5]; perfluoroalkyls can be introduced into molecules of non-fluorinated carboxylic acid derivatives as shown by fluoroalkylation of non-fluorinated esters [6,7], acid anhydrides and unsaturated acids [5]; the diols were also prepared by hydrolysis of fluoroalkyl

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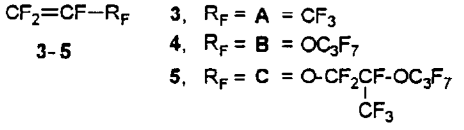
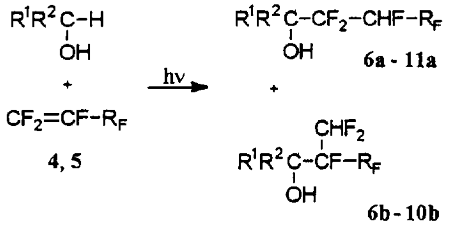


Scheme 2. Fluoroolefins used.



6, $R^1 = R^2 = H, R_F = B$
7, $R^1 = H, R^2 = CH_3, R_F = B$
8, $R^1 = R^2 = CH_3, R_F = B$
9, $R^1 = R^2 = H, R_F = C$
10, $R^1 = H, R^2 = CH_3, R_F = C$
11, $R^1 = R^2 = CH_3, R_F = C$

Scheme 3.

epoxides [8–12] and by the oxidation of fluoroalkylethenes [13,14]. In the patent literature, there is also mentioned the synthesis of a fluoroalkylated 1,2-diol by the reaction of hexafluoropropene with ethane-1,2-diol [15].

2. Results and discussion

In this article we studied the possibility of a direct fluoroalkylation under radical conditions of several alkane diols with perfluorolefins to obtain in one step fluoroalkylated diols from industrially produced perfluoroolefins, among which hexafluoropropene (**3**) and perfluoro vinyl ethers **4** and **5** were chosen for the reactions. Fluoroalkylation of alkanols with perfluoroalk-1-enes are known to proceed easily under different kinds of radical initiations [16–21]. Contrary to this known reaction, radical additions of alkanols to perfluoro(alkyl vinyl ethers), e.g. **4**, **5** (Scheme 2) have not yet been reported in the literature. The first reported photo-induced radical additions to these substrates have received preliminary report [22] and the additions of oxolane have been published in our preceding article [23].

2.1. *Testing of the reactivity of perfluoro(alkyl vinyl ethers) in photo-addition of alkanols*

Before the beginning of the experiments with alkane diols, we tested the reactivity of perfluoro(alkyl vinyl ethers) **4**, **5** to their photo-induced radical reaction with some alkanols without any sensitiser. In such circumstances, soft radical species are generated from the olefins by the photochemical excitation (see also Ref. [23]). In our experience [22,23], these species, contrary to initiation with thermal initiators, better reflect the reactivity of the olefins in free-radical chain reactions by their ability to abstract hydrogen from adding molecules. The reactions carried out are depicted in Scheme 3 which shows that two regioisomeric adducts were formed, Kharash major adducts **6a-11a** and anti-Kharash regioisomers **6b-10b** (vide infra).

Reaction conditions and summary yields of products **6-11** are given in Table 1. It shows that the conversion of olefins are mostly high under the reaction conditions and that relatively high concentrations of olefins can be used in the reaction mixtures. No byproducts formed in photoreactions were observed; thus, preparative yields reflect the efficacy of the separation of the products from unreacted educts (by fraction distillation).

Regioselectivity of the additions of alkanols, considered as the relative percent ratio of both regioisomers, depends on the alkanol structure and the fluoroolefin-chain length (Table 2). In the reaction of least bulky methanol, the highest relative amounts of minor regioisomers **6b** and **9b**, respectively, were formed while most bulky 2-propanol reacted with the formation of the lowest relative amount of the regioisomer **8b** (in the addition of 2-propanol to the longer-chain perfluoroolefin **5**, the relative amount of **11b** had to be below the value of 0.5% because its signals could not be detected in the

Table 1
Photo-addition[a] reactions of alkanols with perfluoro vinyl ethers 4, 5 (Scheme 3)

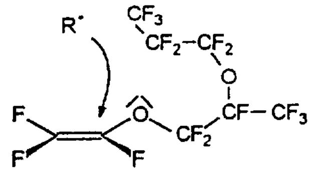
Fluoroolefin			Alkanol [b]			Conversion time of olefin		Products			
R_F	(g)	(mmol)	R^1, R^2	(g)	(mol)	(h)	(%)		(g)	(%) [c,d]	B.p. (°C mm^{-1} Hg)
4	5.32	20	D	6.41	0.20	1	76	**6**	3.02	50.8	135–136
4	4.00	150	E	6.91	0.15	1	71	**7**	2.01	42.9	138–140
4	2.66	10	F	6.01	0.10	0.35	80	**8**	1.92	58.9	139–141
5	2.52	5.8	D	8.1	0.254	5	87	**9**	1.93	72	37–38/50
5	0.601	1.4	E	9.1	0.198	5	77	**10**	0.405	61	61–62/50
5	2.77	6.4	F	12.1	0.20	5	92	**11**	2.26	78	73–75/50

[a] Initiation by UV light.
[b] D, $R^1 = R^2 = H$; E, $R^1 = H, R^2 = CH_3$; F, $R^1 = R^2 = CH_3$.
[c] Preparative yield calculated on the starting olefin.
[d] GC purity 97–99% (as the sum of both regioisomers).

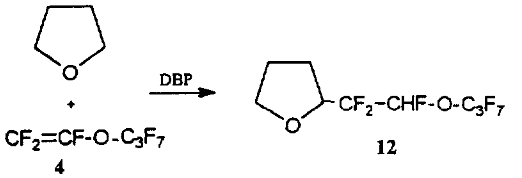
Table 2
Regioselectivity of the addition of alkanols to perfluoro vinyl ethers 4 and 5 (Scheme 3)

Olefin	Alkanol	Minor adduct "b"	
			% rel.
4	CH_3OH	**6b**	7
4	CH_3CH_2OH	**7b**	4
4	$(CH_3)_2CHOH$	**8b**	1
5	CH_3OH	**9b**	5
5	CH_3CH_2OH	**10b**	<0.5 [a]
5	$(CH_3)_2CHOH$	**11b**	0

[a] Non-confirmed estimation.



Scheme 4.



Scheme 5.

^{19}F NMR spectra). Thus, it seems to be evident that the regioselectivity is substantially influenced by a bulk effect of the hydroxyalkyl radical that attacks the double bond.

The chain length of perfluoro(oxaalkyl vinyl ethers) has also influence on the regioselectivity of the addition (Table 2): in the reaction of a longer-chain fluoroolefin **5** smaller amounts of regiomers are formed; this selectivity factor was found for all the alkanols used. An analogous effect was observed in the radical additions of oxolane [23] to three perfluoro-(oxaalkyl vinyl ethers) with different chain lengths. These observations can be explained by a conformational 'tail effect' of the fluorocarbon chain as depicted in Scheme 4: conformational movements of the perfluoro-(polyether) chain tend to form a coiled conformation in solution in which both steric hindrance and electronic repulsion between the adding radical and non-bonded electron pairs can arise causing the formation of the anti-Kharash regioisomer in lesser amount.

2.2. *Testing of inertness of solvents for radical reactions*

The addition reactions with viscous diols require a solvent especially when a gaseous fluorolefin is introduced at low temperatures under photochemical conditions. In our preliminary experiment [22], we tried methanol as a relatively unreactive alkanol [1,21]. However, owing to the low reactivity of the alkane diol used, the product of methanol addition dominated. Therefore we tested the inertness of a series of solvents under the conditions of a radical reaction. The addition of oxolane to perfluoro ether **4** [23] with dibenzoyl peroxide initiation was chosen (because the peroxide is a stronger initiator than a photochemical initiation) as a standard reaction (Scheme 5). The results of the reactions are summarised in Table 3.

The negative result of the reaction in acetonitrile is rather surprising because this solvent is widely used in photochemistry as an inert solvent for different radical-like photoreactions [24]. Interesting is the complete inertness of 2,2,2,-trifluoroethanol because this fluoroalkanol has been successfully added to hexafluoropropene under thermal initiation [19]. The values of the conversions of olefin **4** in different solvents (Table 3) show that the reaction rate is not influenced practically by the solvents.

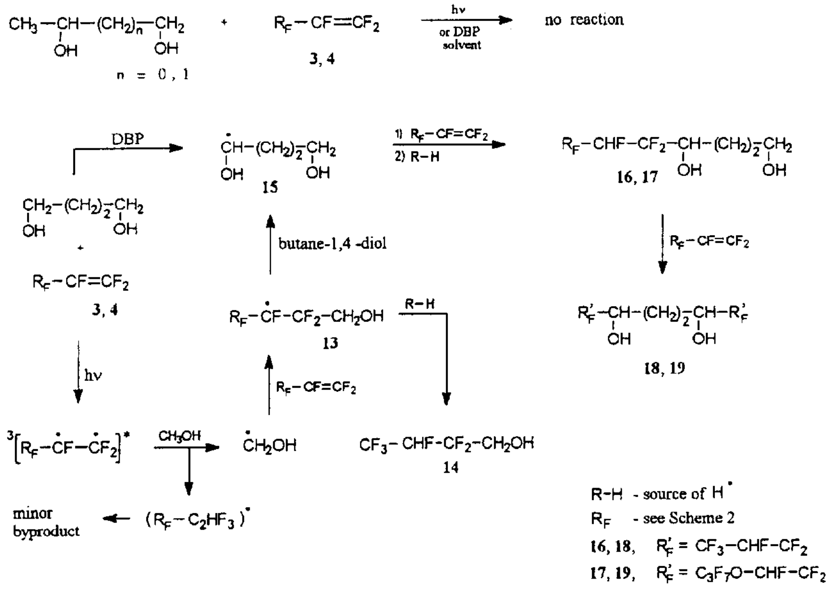
2.3. *Fluoroalkylations of alkane diols*

Radical reactions of perfluorolefins with alkane diols, to our knowledge, have not been reported in the literature (with the exception of the reference to fluoroalkylation of ethane-1,2-diol with hexafluoropropene in a patent [15]); additionally, there is described a photochemical chlorotrifluoroethylation of several alkane diols [25], but the reactions led

Table 3
Radical addition[a] of oxolane to perfluoro vinyl ether 4 in different solvents (Scheme 5)

Solvent	Fluoroolefin 4	Oxolane	Temperature [d]	Time	Olefin 4 conversion [e]	
	(g) [b]	(g) [c]	(g) [b]	(°C)	(h)	(%)
CH_3CN	2.05	2.66	3.60	35	3	0
$(CH_3)_3COH$	3.70	2.66	3.60	35–67	3	75
CF_3CH_2OH	5.00	2.66	3.60	35–65	3	78
$(CH_3)_3COCH_3$	4.41	2.66	3.60	35–53	3	80

[a] Dibenzoyl peroxide as initiator (0.24 g, 1 mmol).
[b] 50 mmol.
[c] 10 mmol.
[d] Reaction temperature in refluxing mixture.
[e] Calculated from ^{19}F NMR spectra.



Scheme 6.

to mixtures of products together with byproducts formed from the sensitiser used.

We used different initiation systems in our photoreactions than in [25] to avoid the formation of difficult to separate byproducts from the sensitiser: methanol was used as a reactive solvent which is known to add photochemically onto fluorolefins without any initiator [19,21]. It has been supposed that in the case of the low reactivity of diols, the adduct **13** formed from methanol (for the initiation mechanism see Ref. [23]) will be able to abstract hydrogen from a diol to form 'byproduct **14**' and diol-radical **15**; this radical was supposed to react by radical addition to form monofluoroalkylated diols **16**, **17** (Scheme 6).

First we tried to react butane-1,3-diol or diethylene glycol with perfluoroolefins **3**, **4**, but no product was found in the reaction mixture (Scheme 6). In the case of propane-1,2-diol, only a very small amount of the product of the addition of methanol to hexafluoropropene (**14**, vide infra, Scheme 6) was found. Much more positive was the result of the reaction of hexafluoropropene with butane-1,4-diol in methanol: in the end-reaction mixture, hexafluorobutanol **14** was the major product (22% yield), while monofluoroalkyl diol **16** and bis-fluoroalkylated diol **18** were formed in smaller yields (10.4 and 6.4%, respectively). Thus, the result of the reaction was opposite to our expectation because an initiation reaction involving methanol predominated.

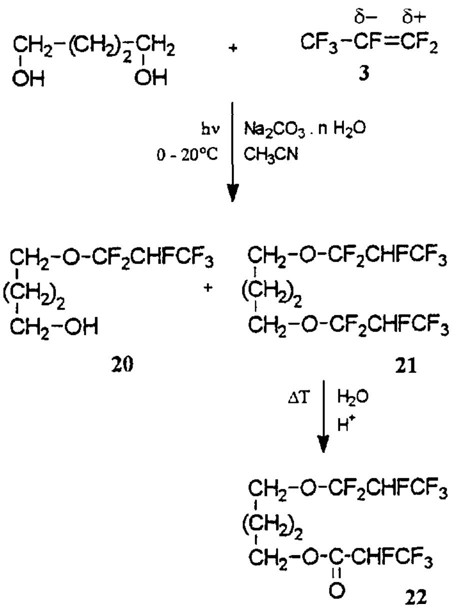
The reactions of vinyl ether **4** with butane-1,4-diol were carried out in completely inert solvents (vide supra), i.e. tert.butyl alcohol and 2,2,2,-trifluoroethanol. The relative yields of monofluoroalkylated diol **17** and bis-fluoroalkylated diol **19** were dramatically dependent on the kind of initiation: while in the photochemical reaction bis-fluoroalkylated diol **19** predominated (ratio 17:19 = 11:89), in the peroxide-initiated reaction, almost the opposite ratio of monofluoroalkylated diol **17** (ratio 17:19 = 74:26) was found. It is surprising that in the peroxide initiation the hydrogen abstraction from monofluoroalkylated diol by dibenzoyl peroxide fragments takes place less easily than in the case of usually softer photochemical initiation (an example is given in the preceding article [23]). The formation of bis-fluoroalkylated diols in the former article [25] was explained by intramolecular 1,5- and 1,6-transfer of hydrogen; however, in our case it would be the intramolecular 1,7-transfer of hydrogen and this was less probable.

2.4. Photo-supported nucleophilic addition of butane-1,4-diol to hexafluoropropene

Nucleophilic addition reactions of hydroxy compounds to fluoroolefins are well known [26–28]. They have been reviewed several times, e.g. [29–32] and in monographs in organofluorine chemistry. Among many additions of numerous hydroxy compounds to fluoroolefins, reactions of alkane diols are comparatively rare [27,33] with yields below 50% [33].

In an attempt to carry out photo-fluoroalkylation of butane-1,4-diol in acetonitrile in the presence of sodium carbonate, nucleophilic addition of the diol to hexafluoropropene took place (Scheme 7) instead of a radical addition. Sodium carbonate evidently acted as a basic catalyst for the generation of an alkoxide-type reagent (e.g. Ref. [27]). The reaction took place only if the mixture was irradiated. In the absence of irradiation or the base the reaction did not proceed. It is obvious that this reaction was promoted by UV light. Similar unexpected UV-light acceleration was observed in dehalogenations with lithium aluminium hydride [34,35].

In the nucleophilic addition reaction (Scheme 7) the conversion of hexafluoropropene was complete. The reaction mixture consisted of hexafluoropropyl ether **20** and prevailing bis-hexafluoropropyl ether **21**. We observed that a-fluorine bonds in bis-ether **21** are susceptible to nucleophilic attack in acidic media [36,37]; because of this reactivity, it



Scheme 7.

was possible to convert the bis-ether **21** to the corresponding propanoate **22** in the presence of acid.

3. Conclusions

Tests of the reactivity of perfluoro vinyl ethers in radical addition reactions with alkanols and oxolane showed that they display a similar reactivity to hexafluoropropene and the products can be obtained in good yields. Radical fluoroalkylations of butane-1,4-diol with hexafluoropropene gave mono- and bis-fluoroalkylated products under both photochemical, and peroxide initiation in low preparative yields. 1,2- and 1,3-Diols as well as diethylene glycol were completely unreactive under the conditions. Radical fluoroalkylations can be performed in tert.butyl alcohol, methyl tert.butyl ether and 2,2,2-trifluoroethanol which appeared to be inert solvents; acetonitrile quenched radical reactions under both photochemical and peroxide initiation. Surprisingly, in acetonitrile nucleophilic addition of butane-1,4-diol to hexafluoropropene under atmospheric pressure proceeded easily if sodium carbonate was present and the mixture was irradiated with UV light.

4. Experimental details

4.1. General comments

The temperature data were uncorrected. GC analyses were performed on a Chrom 5 instrument (Laboratorní přístroje, Prague; FID, 380×0.3 cm packed column, silicone elastomer E-301 on Chromaton N-AW-DMCS (Lachema, Brno), nitrogen). NMR spectra were recorded on a Bruker 400 AM (FT, ^{19}F at 376.5 MHz) and a Bruker WP 80 SY (FT, ^{19}F at 75 MHz) instruments: TMS and $CFCl_3$ as the internal standards, chemical shifts in ppm (is singlet, bs broad singlet, d doublet, t triplet, q quadruplet, qi quintuplet, m multiplet), coupling constants J in Hz, solvents $CDCl_3$, acetone-d_6 and DMSO-d_6. Mass spectra were scanned on a Finnigan MAT-44S (single focus, 70 eV, direct heated inlet) apparatus.

Chemicals used were as follows. Silicagel L40/100 (Merck), hexafluoropropene and hexafluoropropene-1,2-oxide were purchased from Fluorochem Limited and used without further purification. Oxolane (Fluka) was purified according to the described procedure [38]. Acetonitrile (Fluka) was purified according to the described procedure [39,40]. Methanol, ethanol, 2-propanol, propane-1,2-diol, butane-1,3-diol and butane-1,4-diol were purified according to literature procedures [39,40]. Dibenzoyl peroxide was precipitated from its chloroform solution by methanol and dried in vacuo. 1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahex-1-ene (**4**) and 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-3,6-dioxa-5-trifluoromethyl-non-1-ene (**5**) were prepared according to the described procedures [23].

*4.2. Photochemical addition reactions of alkanols with perfluoro vinyl ethers **4**, **5***

Apparatus: The reactions were carried out in a round-shaped two-necked (sealed with septa) quartz cell with a volume of about 20 ml (diameter 5 cm, thickness 1 cm, plane-parallel sites) irradiated from outside by a medium pressure UV lamp (Tesla, RVK 250 W), placed in a reflecting-metal cylindrical housing, through a round window (diameter 5 cm) with a quartz lens.

Reaction: The reaction mixture consisted of alkanol and perfluoroolefin (**4**, **5**) (amounts viz. Table 1) was 0.5 h deoxygenated at about −40 °C with a stream of argon (inlet-outlet by needles through the septa). The mixture was then irradiated at room temperature while stirring (magnetic spin-bar) and the conversion of the olefin was monitored by GC. Alkanol was then distilled off and the residue was distilled under the reduced pressure to give the product (yields and boiling points viz. Table 1).

*4.2.1. Reaction of 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (**4**) with methanol*

Analysis (**6a** + **6b**): Found: C, 26.80; H, 1.19; F, 64.47%. $C_6H_4F_{10}O_2$ requires: C, 24.18; H, 1.35; F, 63.74%. M, 298.08.

2,2,3,5,5,6,6,7,7,7-Decafluoro-4-oxaheptan-1-ol (**6a**) ($CH_2(OH)CF_2CHFOC_3F_7$): ^1H NMR ($CDCl_3$) δ: 3.46 (s, 1H, OH); 3.92 and 3.98 (2×dqi, 2H, CH_2, $^2J_{HH}={}^3J_{HF}={}^4J_{HF}=13$, $^4J_{HH}=2.4$ or 0.6); 6.11 (dt, 1H, CHF, $^2J_{HF}=54$, $^3J_{HF}=5.2$) ppm.

^{19}F NMR ($CDCl_3$) δ: −82.04 (t, 3F, CF_3, $^3J_{FF}=7$); −85.64 and −87.80 (2×dm, 2F, CF_2O, $^2J_{FF}=147$); −125.34 (ddt, 1F(a), CF_2, $^2J_{FF}=272$, $^3J_{HF}=14$ and 4.5); −126.85 (dtt, 1F(b), CF_2, $^2J_{FF}=272$, $^3J_{HF}=11$ and 6, $^3J_{FF}=6$); −130.43 (s, 2F, CF_2–CF_3); −147.07 (dd, 1F, CHF, $^2J_{HF}=54$, $^3J_{FF}=6$) ppm.

2-Difluoromethyl-2,4,4,5,5,6,6,6,-octafluoro-3-oxahexan-1-ol (**6b**) ($CH_2(OH)CF(CHF_2)O–C_3F_7$):

^{1}H NMR ($CDCl_3$) δ: 3.46 (s, 1H, OH); 4.07 and 4.11 (2×dd, 2H, CH_2, $^2J_{HH}=7$, $^3J_{HF}=3$); 6.02 (dt, 1H, CHF_2, $^2J_{HF}=53.7$, $^3J_{HF}=3.5$) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.93 (t, 3F, CF_3, $^3J_{FF}=7$); −80.60 and −82.95 (2×dm, 2F, CF_2O, $^2J_{FF}=147$); −130.32 (s, 2F, $CF_2–CF_3$); −136.92 (dqi, 1F, CF, $^3J_{FF}={}^3J_{HF}=15$, $^3J_{HF}=3.5$); −137.14 and −139.63 (2×ddd, 2F, CHF_2, $^2J_{FF}=299.5$, $^2J_{HF}=53.7$, $^3J_{FF}=15$) ppm.

4.2.2. Reaction of 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (4) with ethanol

Analysis (**7a**+**7b**): Found: C, 27.30; H, 1.87; F, 61.26%. $C_7H_6F_{10}O_2$ requires: C, 26.94; H, 1.94; F, 60.87%. M, 312.11.

3,3,4,6,6,7,7,8,8,8-Decafluoro-5-oxaoctan-2-ol (**7a**) ($CH_3CH(OH)CF_2CHFOC_3F_7$): ^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (53% rel.), B (47% rel.): 1.37 (d, 3H, CH_3, $^3J_{HH}=6.6$); 2.38 and 2.43 (2×d, 1H (A,B), OH, $^3J_{HH}=7.7$ or 7.1); 4.12 (m, 1H, CH); 6.19 (dd, 1H (B), CHF, $^2J_{HF}=53.4$, $^3J_{HF\,(a)}=9$); 6.20 (ddd, 1H (A), CHF, $^2J_{HF}=54$, $^3J_{HF\,(a)}=7.5$, $^3J_{HF\,(b)}=2.7$) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.93 and −81.97 (2×t, 3F, CF_3, $^3J_{FF}=7.6$); −85.46, −85.57, −87.48, −87.95 (4×dm, 2F, CF_2O, $^2J_{FF}=147$); −128.97 (dq, 1F (F(a), A), CF_2CH_2, $^2J_{FF}=269$, $^3J_{FF}={}^3J_{HF}=7.5$); −130.34 and −130.37 (2×s, 2F, $CF_2–CF_3$); −130.55 (ddt, 1F (F(a), B), CF_2CH_2, $^2J_{FF}=271$, $^3J_{HF}={}^3J_{FF}=11$, $^3J_{HF}=2.8$); −132.54 (dddd, 1F (F(b), A), $-CF_2CH_2-$), $^2J_{FF}=269$, $^3J_{HF}=14.8$ and 2.7, $^3J_{FF}=11$); −133.57 (dd, 1F (F(b), B, $-CF_2CH_2-$), $^2J_{FF}=271$, $^3J_{HF}=19$); −144.86 (ddt, 1F(B), CHF, $^2J_{HF}=53.4$, $^4J_{FF}=9.7$, $^3J_{FF}=6.3$); −149.77 (dtt, 1F(A), CHF, $^2J_{HF}=54$, $^4J_{FF}=12$, $^3J_{FF}=6$) ppm.

3-Difluoromethyl-3,5,5,6,6,7,7,7-octafluoro-4-oxaheptan-2-ol (**7b**) ($CH_3CH(OH)-CF(CHF_2)O-C_3F_7$):

^{1}H NMR ($CDCl_3$) δ, 2 diastereoisomers, A (50% rel.), B (50% rel.): 1.39 (d, 3H, CH_3, $^3J_{HH}=6.5$); 2.40 and 2.42 (2×d, 1H, OH, $^3J_{HH}=7$); 4.27 (m, 1H, CH); 6.23 and 6.26 (2×dd, 1H, CHF_2, $^2J_{HF}=53$, $^3J_{HF}=3.4$) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.78 and −81.83 (2×t, 3F, CF_3, $^3J_{FF}=7$); −85.50 and −88.00 (m, 2F, CF_2O); −130.30 (s, 2F, $CF_2–CF_3$); −134.81 and −135.02 (2×ddd, 1F(a), CHF_2, $^2J_{FF}=300$, $^2J_{HF}=53$, $^3J_{FF}=4$); −136.18 and −141.08 (2×ddd, 1F(b), CHF_2, $^2J_{FF}=300$, $^2J_{HF}=53$, $^3J_{FF}=9$); −138.15 and −143.82 (2×m, 1F, CF) ppm.

4.2.3. Reaction of 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (4) with 2-propanol

Analysis (**8a**+**8b**): Found: C, 29.73; H, 2.26; F, 60.29%. $C_8H_8F_{10}O_2$ requires: C, 29.46; H, 2.47; F, 58.25%. M, 326.13.

3,3,4,6,6,7,7,8,8,8-Decafluoro-2-methyl-5-oxaoctan-1-ol (**8a**) ($(CH_3)_2C(OH)CF_2CHFOC_3F_7$): ^{1}H NMR ($CDCl_3$) δ: 1.40 (s, 6H, $2CH_3$); 2.07 (s, 1H, OH), 6.26 (ddd, 1H, CHF, $^2J_{HF}=53.3$, $^3J_{HF}=9$ and 3.4) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.85 (t, 3F, CF_3, $^3J_{FF}=7$); −85.37 and −87.41 (2×dm, 2F, CF_2O, $^2J_{FF}=147$); −125.72 (dd, 1F(a), CF_2, $^2J_{FF}=270.5$, $^3J_{HF}=3.4$); −130.26 (s, 2F, CF_2--CF_3); −130.46 (dt, 1F(b), CF_2, $^2J_{FF}=270.5$, $^3J_{FF}={}^3J_{HF}=10$); −141.09 (dd, 1F, CHF, $^2J_{HF}=54$, $^3J_{FF\,(b)}=10$) ppm.

3-Difluoromethyl-3,5,5,6,6,7,7,7-octafluoro-2-methyl-4-oxaheptan-2-ol (**8b**) ($(CH_3)_2C(OH)-CF(CHF_2)OC_3F_7$):

^{1}H NMR ($CDCl_3$) δ: 1.38 (s, 6H, $2CH_3$); 2.08 (s, 1H, OH), 6.41 (t, 1H, CHF_2, $^2J_{HF}=53$) ppm.

^{19}F NMR ($CDCl_3$) δ: −81.73 (t, 3F, CF_3, $^3J_{FF}=7$); −85.30 and −87.40 (2×dm, 2F, CF_2O, $^2J_{FF}=147$); −130.26 (s, 2F, $CF_2–CF_3$); −135.22 (ddd, 2F, CHF_2, $^2J_{HF}=53$, $^3J_{FF}=6$, $^3J_{HF}=3$); −142.20 (m, 1F, CF) ppm.

4.2.4. Reaction of 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-3,6-dioxa-5-trifluoromethyl-non-1-ene (5) with methanol

Analysis (**9a**+**9b**): Found: C, 23.52; H, 1.04; F, 66.16%. $C_9H_4F_{16}O_3$ requires: C, 23.29; H, 0.87; F, 65.50%. M, 464.10.

2,2,3,5,5,6,8,8,9,9,10,10,10-Tridecafluoro-4,7-dioxa-6-trifluoromethyldecan-1-ol (**9a**) ($CH_2(OH)CF_2CHFOCF_2-CF(CF_3)OC_3F_7$): ^{1}H NMR (acetone-$d_6$) δ: 4.00 (m, 2H, CH_2); 5.11 (t, 1H, OH, $^3J_{HH}=6.3$); 6.66 (dt, 1H, CHF, $^2J_{HF}=54$, $^3J_{HF}=5$) ppm.

^{19}F NMR (acetone-d_6) δ: −80.65 (s, 3F, CF_3-CF); −81.94 (s, 3F, $CF_3–CF_2$); −80.68 and −82.39 (2×dm, 2F, $CF_2–CF_2O$, $^2J_{FF}=140$); −84.21 and −86.29 (2×dm, 2F, $CF–CF_2O$, $^2J_{FF}=147$); −125.49 (dt, 1F(a), CF_2CH_2, $^2J_{FF}=271$, $^3J_{HF}=12$); −127.63 (ddt, 1F(b), CF_2CH_2, $^2J_{FF}=271$, $^3J_{FF}={}^3J_{HF}=6$, $^3J_{HF}=12$); −130.15 (s, 2F, $CF_2–CF_3$); −145.41 (t, 1F, CF, $^3J_{FF}=18$); −147.93 (dm, 1F, CHF, $^2J_{HF}=54$) ppm.

2-Difluoromethyl-2,4,4,5,7,7,8,8,9,9,9-undecafluoro-3,6-dioxa-5-trifluoromethylnonan-1-ol (**9b**) ($CH_2(OH)CF-(CHF_2)OCF_2CF(CF_3)–OC_3F_7$):

^{1}H NMR (acetone-d_6) δ, 2 diastereoisomers, A (52% rel.), B (48% rel.): 4.00 (m, 2H, CH_2); 5.28 (t, 1H, OH, $^3J_{HH}=6$); 6.43 and 6.53 (2×dt, 1H(A,B), CHF_2, $^2J_{HF}=54$ and 55, $^3J_{HF}=4$) ppm.

^{19}F NMR (acetone-d_6) δ: −80.63 (s, 3F, $CF_3–CF$); −81.94 (s, 3F, $CF_3–CF_2$); −80.70 and −82.40 (2×dm, 2F, $CF_2–CF_2O$, $^2J_{FF}=140$); −84.20 and −86.30 (2×dm, 2F, $CF–CF_2O$, $^2J_{FF}=147$); −129.84 (s, 2F, $CF_2–CF_3$); −136.91 (m, 1F, $CF–CH_2$); −139.05 (d, 1F(a), CHF_2, $^2J_{HF}=54$); −140.50 (dd, 1F(b), CHF_2, $^2J_{HF}=55$, $^3J_{FF}=5$); −145.41 (t, 1F, $CF–CF_2$, $^3J_{FF}=18$) ppm.

4.2.5. Reaction of 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-3,6-dioxa-5-trifluoromethyl-non-1-ene (5) with ethanol

3,3,4,6,6,7,9,9,10,10,11,11,11-Tridecafluoro-5,8-dioxa-7-trifluoromethylundecan-2-ol (**10a**) ($CH_3CH(OH)CF_2CH-FOCF_2CF(CF_3)OC_3F_7$):

Analysis: Found: C, 25.74; H, 1.51; F, 64.23%. $C_{10}H_6F_{16}O_3$ requires: C, 25.12; H, 1.26; F, 63.58%. M, 478.13.

^{1}H NMR (CDCl$_3$) δ, 2 diastereoisomers, A (52% rel.), B (48% rel.): 1.38 (d, 3H, CH$_3$, $^3J_{HH}=6.4$); 2.16 (bs, 1H, OH); 4.10 (m, 1H, CH); 6.19 (dd, 1H (B), CHF, $^2J_{HF}=54$, $^3J_{HF\,(a)}=10$); 6.20 (ddd, 1H (A), CHF, $^2J_{HF}=54$, $^3J_{HF\,(a)}=8$, $^3J_{HF\,(b)}=3$) ppm.

^{19}F NMR (CDCl$_3$) δ: −80.60 (dm, 3F, CF_3CF, $^3J_{FF}=5$); −81.90 (s, 3F, CF_3CF$_2$); −80.20 and −82.41 (2×dm, 2F, CF$_2$CF_2O, $^2J_{FF}=141$); −84.19 and −86.30 (2×dm, 2F, CFCF_2O, $^2J_{FF}=147$); −128.81 (dq, 1F (F(a), A), CF$_2$CH$_2$, $^2J_{FF}=270$, $^3J_{FF}={}^3J_{HF}=7.5$); −129.94 and −130.12 (2×s, 2F, CF_2–CF$_3$); −131.01 (dm, 1F (F(a), B), CF$_2$CH$_2$, $^2J_{FF}=271$); −133.18 (dm, 1F (F(b), A), CF$_2$CH$_2$, $^2J_{FF}=270$); −134.23 (dd, 1F (F(b), B), CF$_2$CH$_2$, $^2J_{FF}=271$, $^3J_{HF}=17$); −145.11 (ddt, 1F(B), CHF, $^2J_{HF}=54$, $^4J_{FF}=9$, $^3J_{FF}=8$); −145.45 (t, 1F, CF, $^3J_{FF}=19$); −149.92 (dtt, 1F(A), CHF, $^2J_{HF}=54$, $^4J_{FF}=11$, $^3J_{FF}=6$) ppm.

4.2.6. *Reaction of 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-3,6-dioxa-5-trifluoromethyl-* non-1-ene (**5**) with 2-propanol

3,3,4,6,6,7,9,9,10,10,11,11,11-Tridecafluoro-2-methyl-5,8-dioxa-7-trifluoromethylundecan-2-ol (**11a**) ((CH$_3$)C(OH)CF$_2$CHFOCF$_2$CF(CF$_3$)-OC$_3$F$_7$):

^{1}H NMR (CDCl$_3$) δ, 2 diastereoisomers, A (76% rel.), B (24% rel.): 1.40 (s, 6H, 2CH$_3$); 2.03 (bs, 1H, OH), 6.03 (dq, 1H(B), CHF, $^2J_{HF}=53$, $^3J_{HF}={}^4J_{HF}=2.8$); 6.26 (ddd, 1H(A), CHF, $^2J_{HF}=53$, $^3J_{HF}=9.4$ and 2.6) ppm.

^{19}F NMR (CDCl$_3$) δ: −80.57 (dm, 3F, CF_3CF, $^3J_{FF}=5$); −81.91 (s, 3F, CF_3CF$_2$); −80.71 and −82.32 (2×dm, 2F, CF$_2$CF_2O, $^2J_{FF}=141$); −84.20 and −86.25 (2×dm, 2F, CFCF_2O, $^2J_{FF}=147$); −125.44 (dd, 1F(a), CF$_2$CH$_2$, $^2J_{FF}=272$, $^3J_{FF}=14.6$); −130.10 (s, 2F, CF_2–CF$_3$); −131.09 (dt, 1F(b), CF$_2$CH$_2$, $^2J_{FF}=272$, $^3J_{FF}={}^3J_{HF}=11$); −141.01 (dm, 1F(A), CHF, $^2J_{HF}=53$); −145.32 (t, 1F, CF, $^3J_{FF}=20$); −146.27 (dm, 1F(B), CHF, $^2J_{HF}=54$) ppm.

4.3. *Radical addition reactions of 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (4) with oxolane in solvents*

For the amount of reactants and solvents see Table 3. The reactants, dibenzoyl peroxide and a solvent were refluxed; the internal temperature of the mixture was measured with reaction time, was measured. The conversion of olefin **4** was determined by GC (purity 99%).

2-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahex-1-yl)oxolane (**12**): Elemental analysis or a NMR spectra see Ref. [23].

4.4. *Radical fluoroalkylations of alkane diols with perfluoroolefins 3, 4*

4.4.1. *Reaction of hexafluoropropene with butane-1,4-diol*

Apparatus: An immersion-well photoreactor cooled from outside to −15 to 0 °C, a medium-pressure UV lamp (Tesla, RVK 125) in a water-cooled double jacket (quartz and Simax® glass, gas inlet of sintered-glass at the bottom of the reactor), and of dry-ice cooled spiral cooler with hydraulic seal (silicone oil) connected with dry-ice cooled trap that was connected with atmosphere through a hydraulic seal with sulfuric acid.

Reaction: Prior to the reaction, a mixture of butane-1,4-diol (30.6 g, 0.34 mol) and methanol (60 ml, 48.8 g, 1.52 mol) was bubbled through with pure nitrogen for 1 h. The reactor was then cooled to −5 to −15 °C in dry-ice bath (ethanol) and hexafluoropropene (6.0 g, 40 mmol) was 20 h introduced into the photoreactor with the conversion of 45%. Methanol was then distilled off, then a fraction 65–120 °C was taken (80% 2,2,3,4,4,4-hexafluorobutanol, **14**) that was fractioned on a packed column (15 cm, Berle saddles, heated jacket) to yield the product **14** (1.59 g, 21.9%, b.p. 113–114 °C (lit. value [16], b.p. 114 °C)). The residue from the main distillation was distilled trap-to-trap and a fraction 99–110 °C 0.1 mmHg^{-1} (13.3 kPa) was taken (3.18 g) containing a mixture of products **16** and **18** that were separated by column chromatography (column 2.5×40 cm, silicagel, diethyl ether) with the following yields: monofluoroalylated diol **16**, 1.03 g (10.7%), GC purity 97%; bis-fluoroalylated diol **18**, 0.99 g (6.4%), GC purity 98%.

5,5,6,7,7,7-Hexafluoroheptane-1,4-diol (**16**) (CF$_3$CHFCF$_2$CH(OH)(CH$_2$)$_2$CH$_2$OH):

Analysis: Found: C, 35.64; H, 4.48; F, 47.01%. C$_7$H$_{10}$F$_6$O$_2$ requires: C, 35.01; H, 4.20; F, 47.47%. M, 240.15.

^{1}H NMR (CDCl$_3$) δ, 2 diastereoisomers, A (56% rel.), B (44% rel.): 1.72 (m, 2H, CH_2–CH$_2$OH); 1.82 and 1.93 (2×m, 2H (A, B), CH–CH_2); 3.18 (bs, 1H, CH–OH); 3.67 and 3.79 (2×m, 2H, CH_2–OH); 3.93 and 3.97 (2×m, 1H (A, B), CH–OH); 4.84 (bs, 1H, CH$_2$–OH); 5.17 and 5.21 (2×dm, 1H (A, B), CHF, $^2J_{HF}=43$) ppm.

^{19}F NMR (CDCl$_3$) δ: −74.51 and −74.98 (2×ddm, 3F (B, A), CF$_3$, $^3J_{FF}=11$, $^3J_{HF}=6$); −120.53, −125.31 and −126.00, −130.61 (4×ddm, 2F (A, B), CF$_2$, $^2J_{FF}=268$, $^3J_{FF}=9$ or 11); −213.72 and −216.53 (2×dm, 1F (B, A), CHF, $^2J_{HF}=43$) ppm.

1,1,1,2,3,3,8,8,9,10,10,10-Dodecafluoro-4,7-decane-4,7-diol (**18**) (CF$_3$CHFCF$_2$CH(OH)-(CH$_2$)$_2$CH(OH)CF$_2$CHFCF$_3$):

Analysis (**18**): Found: C, 31.27; H, 2.74; F, 59.26%. C$_{10}$H$_{10}$F$_{12}$O$_2$ requires: C, 30.78; H, 2.58; F, 58.43%. M, 390.17.

^{1}H NMR (CDCl$_3$) δ, 4 diastereoisomers and 2 mesoforms, A (38% rel.), B (15% rel.), C (15% rel.), D (12% rel.), E (10% rel.), F (10% rel.): 1.92 (m, 4H, 2 CH$_2$); 2.67 and 3.08 (2×bs, 2H, 2 OH); 4.08 (m, 2H, 2 CH); 5.17 (dm, 2H, 2 CHF, $^2J_{HF}=43$) ppm.

^{19}F NMR (CDCl$_3$) δ: −74.81, −74.40, −74.80, −74.81, −74.40, −74.41 (6×ddm, 6F (A,B,C,D,E,F), 2 CF$_3$, $^3J_{FF}=10$, $^3J_{HF}=6$); −120.00, −125.05 and −119.81, −124.80 and −119.82, −124.83 and −125.73, −129.91 and −125.52, −129.70 and −125.21, −129.43 (12×ddm, 4F (A,B,C,D,E,F), 2 CF$_2$, $^2J_{FF}=274$, $^3J_{FF}=10$); −214.91, −213.32, −214.30, −214.31, −213.32, −213.40 (6×dm, 2F (A,B,C,D,E,F), 2 CHF, $^2J_{HF}=43$) ppm.

*4.4.2. Reaction of 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (**4**) with butane-1,4-diol*

Photochemical initiation: For apparatus and general procedure see 4.2. A homogenous mixture of olefin **4** (2.55 g, 9.58 mmol), butane-1,4-diol (3.58 g, 39.7 mmol) and 2,2,2.trifluoro-ethanol (7.3 g, 72.5 mmol) was irradiated for 11.5 h while stirring; the conversion of the olefin was 24%. From the yellowish reaction mixture were then distilled off lower-boiling fractions up to 170 °C in oil bath and 100 mmHg. The residue (0.9 g) that contained products **17** and **19** in relative amount 11:89 (GC) was purified by column chromatography (10 g of silicagel, column 25 × 2.5 cm, diethyl ether); purified mixture of **17**, **19** was dissolved in chloroform (3 ml) and petroleum ether (2 ml) was added. White crystals (compound **17**) precipitated from the solution over night and the addition of petroleum ether was twice repeated. The crystals were purified by dissolving in boiling acetone and precipitation with petroleum ether; after drying in vacuo, the yield of the product **17** was 32 mg (2.57%), GC purity 96%, m.p. 116–118 °C. Mother liquors were combined and evaporated in vacuo to give 236 mg (16.8%) of product **19**, GC purity 97%.

Peroxide initiation: A homogenous mixture of olefin **4** (2.66 g, 10 mmol), butane-1,4-diol (4.51 g, 50 mmol), 2,2,2.trifluoroethanol (5 g) and dibenzoyl peroxide (0.24 g, 1 mmol) was refluxed in a flask (equipped with a reflux condenser with a dry-ice cooler at the top) in nitrogen atmosphere on oil bath (110–120 °C) for 12.5 h. After distillation of the lower boiling components, the residue (0.758 g) was purified as above. The relative amount of products **17**, **19** in the residue was 74:26, calculated yields (GC) after the purification were 18% and 4.6%, respectively.

5,5,6,8,8,9,10,10,10-Decafluoro-7-oxadecane-1,4-diol (**17**) ($C_3F_7OCHFCF_2CH(OH)$-$(CH_2)_2CH_2OH$):

Analysis: Found: C, 30.24; H, 2.56%. $C_9H_{10}F_{10}O_3$ requires: C, 30.35; H, 2.83; F, 53.34%. M, 356.16.

^{1}H NMR (DMSO-d_6) δ, 2 diastereoisomers, A (55% rel.), B (45% rel.): 1.43 (m, 2H, CH_2–CH_2OH); 1.68 (m, 2H, CH–CH_2); 3.35 (bs, 1H, CH–OH); 3.72 and 3.88 (2 × m, 2H, CH_2–OH); 3.98 and 4.10 (2 × m, 1H, CH); 4.38 and 4.49 (2 × t, 1H, CH_2OH, $^3J_{HH}=5$); 5.97 and 6.07 (2 × ddd, 1H, CHF, $^2J_{HF}=53$, $^3J_{HF}=16$ and 10) ppm.

^{19}F NMR (DMSO-d_6) δ: -81.20 (t, 3F, CF_3, $^3J_{HF}=7$); -84.22 and -85.81 (2 × dm, 2F, CF_2O, $^2J_{FF}=147$); -129.00 (ddd, 1F (a), CF_2, $^2J_{FF}=272$, $^3J_{HF}=16$, $^3J_{FF}=9$); -129.24 (s, 2F, CF_2CF_3); -130.85 (dd, 1F (b), CF_2, $^2J_{FF}=272$, $^3J_{HF}=10$); -144.77 and -144.88 (2 × ddd, 1F, CHF, $^2J_{HF}=53$, $^3J_{FF}=9$ and 7) ppm.

MS m/z (% rel. int.): 356 (1.3, M^+); 355 (16, $(M-1)^+$); 337 (37, $(M-F)^+$); 225 (4); 217 (3, $C_4HF_8O^+$); 215 (4); 185 (1, $C_3F_7O^+$); 169 (27, $C_3F_7^+$); 149 (42); 123 (18); 119 (12, $C_2F_5^+$); 103 (57); 91 (45); 77 (46); 73 (30); 69 (100, CF_3^+); 59 (63, $C_3H_7O^+$); 57 (35, $C_3H_5O^+$); 55 (24, $C_3H_3O^+$); 47 (30).

1,1,1,2,2,3,3,5,6,6,11,11,12,14,14,15,15,16,16,16-eicosafluoro-4,13-dioxahexadecane-7,10-diol (**19**) ($C_3F_7OCHFCF_2CH(OH)(CH_2)_2CH(OH)CF_2CHFOC_3F_7$):

Analysis: Found: C, 26.39; H, 1.70; F, 60.97%. $C_{14}H_{10}F_{20}O_4$ requires: C, 27.03; H, 1.62; F, 61.07%. M, 622.20.

^{1}H NMR ($CDCl_3$) δ, diastereoisomers, A (64% rel.), B (36% rel.): 1.90 (m, 4H, 2 CH_2); 2.70 and 3.00 (2 × bs, 2H, 2 OH); 4.10 (m, 2H, 2 CH); 6.20 and 6.23 (2 × dd, 2H, 2 CHF, $^2J_{HF}=53$, $^3J_{HF}=3$) ppm.

^{19}F NMR ($CDCl_3$) δ: -81.89 (t, 6F, 2 CF_3, $^3J_{FF}=7$); -85.02 and -85.20 (2 × dm, 2F (a), 2 CF_2O, $^2J_{FF}=147$); -87.61 and -88.95 (2 × dm, 2F (b), 2 CF_2O, $^2J_{FF}=147$); -126.51 and -126.57 (2 × ddm, 2F (a), 2 CF_2, $^2J_{FF}=272$, $^3J_{FF}=5$); -130.21 (s, 4F, 2 CF_2CF_3); -130.82 (ddm, 2F (b), 2 CF_2, $^2J_{FF}=272$, $^3J_{FF}=8$); -144.69 and -148.87 (2 × ddm, 2F (B,A), 2 CHF, $^2J_{HF}=53$, $^3J_{FF}=5$) ppm.

4.4.3. Attempts to react of hexafluoropropene with propane-1,2-diol, with butane-1,3-diol and with diethylene glycol

Reaction with propane-1,2-diol: For apparatus and general procedures see 4.4.1. In a mixture of propane-1,2-diol (62.4 g, 0.82 mol), methanol (30 ml, 23.7 g, 0.741 mol) hexafluoropropene (6 g, 40 mmol) was introduced in the photoreactor for 20 h under irradiation. Only a very small amount of hexafluorobutanol **14** (less than 0.5%) was detected in the reaction mixture by GC.

Reaction with butane-1,3-diol: Into a mixture of the diol (30.2 g, 0.34 mmol), methanol (60 ml, 47.5 g, 1.48 mol) hexafluoropropene (6 g, 40 mmol) was introduced for 20 h under irradiation. No hexafluorobutanol **14** and no other products were detected in the reaction mixture by GC.

Reaction with diethylene glycol: Into a mixture of the glycol (67.1 g, 0.63 mol), methanol (30 ml, 23.7 g, 0.741 mol) hexafluoropropene (6 g, 40 mmol) was introduced in the photoreactor for 20 h under irradiation. No hexafluorobutanol **14** or other products were detected in the reaction mixture by GC.

*4.5. Attempts to react perfluoro vinyl ethers **4** and **5** with propane-1,2-diol*

Reaction of vinyl ether **4**: A mixture of 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (**4**; 2.66 g, 10 mmol), propane-1,2-diol (3.81 g, 50 mmol), 2,2,2-trifluoroethanol (5 g, 50 mmol) and dibenzoyl peroxide (0.24 g, 1 mmol) in flask with reflux condenser equipped with hydraulic seal with conc. sulfuric acid, was refluxed in nitrogen atmosphere for 8 h. Additional amount of dibenzoyl peroxide (0.24 g, 1 mmol) was then added and refluxing was continued for 2 h. No product was detected in the reaction mixture by GC.

Reaction of vinyl ether **5**: A mixture of 1,1,2,4,4,5,7,7,8,8,9,9,9-tridecafluoro-3,6-dioxa-5-trifluoromethylnon-1-ene (**5**; 1.2 g, 2.7 mmol), propane-1,2-diol (0.647 g, 8.5 mmol), 2,2,2-trifluoroethanol (2.06 g, 20.5 mmol) and dibenzoyl peroxide (0.048 g, 0.2 mmol) was refluxed as above; additional amount of dibenzoyl peroxide (0.048 g, 0.2 mmol) was added. No product was detected in the reaction mixture by GC.

4.6. Photo-assisted nucleophilic addition of butane-1,4-diol to hexafluoropropene

For apparatus and general procedure see 4.4.1. Hexafluoropropene (6 g, 40 mmol) was introduced for 2 h into the irradiated mixture of butane-1,4-diol (30.6 g, 0.34 mol), sodium carbonate (2.0 g, 19 mmol) and acetonitrile (60 ml). Solvent acetonitrile, oxolane was then distilled off and the residue was distilled in vacuo to give 2 fractions, fraction 1, 4.7 g of b.p. 55–80 °C 20 mmHg^{-1} (2.7 kPa) that contained starting diol and products **20**, **21**, and fraction 2, 9.2 g of b.p. 80–95 °C 20 mmHg^{-1} (2.7 kPa) that contained products **20**, **21** (85% rel.) and about 2% of product **22**. Separation of products by chromatography: silicagel, column 2.5 × 40 cm, injections 4.7 g and 7.6 g, firstly benzene to elute **20**, then diethyl ether to **21**; yields: **20**, 1.79 g (11.4%), GC purity 98%; **21**, 5.02 g (52.3%), GC purity 97%.

Preparation of **22**: A mixture of fraction 2 (1.05 g) and sulfuric acid (0.5 ml, 50%) was heated at 100–120 °C for 6 h while stirring. The mixture was then diluted with diethyl ether, neutralised with sodium hydrogen carbonate, the solution was then dried (magnesium sulfate) and the solvent evaporated. Chromatography: silicagel, benzene; yield of **22**, 0.52 g (about 55%), GC purity 97.5%.

6,6,7,8,8,8-Hexafluoro-5-oxaoctan-1-ol (**20**) (CF_3CHF-CF_2-$O(CH_2)_4OH$):

Analysis: Found: C, 35.77; H, 4.14; F, 47.34%. $C_7H_{10}F_6O_2$ requires: C, 35.01; H, 4.20; F, 47.47%. M, 240.15.

^{1}H NMR ($CDCl_3$) δ: 1.64 (m, 2H, CH_2–CH_2OH); 1.77 (m, 2H, CH_2–CH_2–O); 2.39 (bs, 1H, OH); 3.66 (t, 2H, CH_2OH, $^{3}J_{\mathrm{HH}}=6.3$); 4.03 (t, 2H, CH_2O-, $^{3}J_{\mathrm{HH}}=6.4$); 4.78 (dddq, 1H, CHF, $^{2}J_{\mathrm{HF}}=44$, $^{3}J_{\mathrm{HF}}=5.8$, $^{3}J_{\mathrm{HF\,(b)}}=6.7$, $^{3}J_{\mathrm{HF\,(a)}}=4.1$) ppm.

^{19}F NMR ($CDCl_3$) δ: -75.77 (dq, 3F, CF_3, $^{3}J_{\mathrm{FF}}={}^{4}J_{\mathrm{FF}}=9$, $^{3}J_{\mathrm{HF}}=5.8$); -80.67 and -83.54 (dddq, 2F, CF_2, $^{2}J_{\mathrm{FF}}=147$, $^{4}J_{\mathrm{FF}}=9$, $^{3}J_{\mathrm{FF}}=3$ or 6, $^{3}J_{\mathrm{HF}}=4.1$ or 6.7); -212.14 (dddq, 1F, CHF, $^{2}J_{\mathrm{HF}}=44$, $^{3}J_{\mathrm{FF}}=9$, $^{3}J_{\mathrm{FF\,(a,b)}}=6$ and 3) ppm.

1,1,1,2,3,3,10,10,11,12,12,12-Dodecafluoro-4,9-dioxadodecane (**21**) (CF_3CHFCF_2-$O(CH_2)_4$-O-CF_2CHFCF_3):

Analysis: Found: C, 31.20; H, 2.40; F, 62.72%. $C_{10}H_{10}F_{12}O_2$ requires: C, 30.78; H, 2.58; F, 58.43%. M, 390.17.

^{1}H NMR ($CDCl_3$) δ: 1.78 (m, 4H, 2 CH_2); 4.03 (m, 4H, 2 CH_2O); 4.75 (dddq, 2H, 2 CHF, $^{2}J_{\mathrm{HF}}=44$, $^{3}J_{\mathrm{HF}}=5.8$, $^{3}J_{\mathrm{HF\,(b)}}=6.7$, $^{3}J_{\mathrm{HF\,(a)}}=4.1$) ppm.

^{19}F NMR ($CDCl_3$) δ: -76.08 (dq, 6F, 2 CF_3, $^{3}J_{\mathrm{FF}}={}^{4}J_{\mathrm{FF}}=9$, $^{3}J_{\mathrm{HF}}=5.8$); -81.00 and -84.03 (dddq, 4F, 2 CF_2, $^{2}J_{\mathrm{FF}}=147$, $^{4}J_{\mathrm{FF}}=9$, $^{3}J_{\mathrm{FF}}=3$ or 6, $^{3}J_{\mathrm{HF}}=4.1$ or 6.7); -212.44 (dddq, 2F, 2 CHF, $^{2}J_{\mathrm{HF}}=44$, $^{3}J_{\mathrm{FF}}=9$, $^{3}J_{\mathrm{FF\,(a,b)}}=6$ and 3) ppm.

6,6,7,8,8,8-Hexafluoro-5-oxaoct-1-yl 2,3,3,3-trifluoropropanoate (**22**)) (CF_3CHFCF_2–$O(CH_2)_4$–OCO–$CHFCF_3$):

Analysis: Found: C, 33.40; H, 3.21; F, 54.29%. $C_{10}H_{10}F_{10}O_3$ requires: C, 32.62; H, 2.74; F, 51.60%. M, 368.17.

^{1}H NMR ($CDCl_3$) δ: 1.81 (m, 4H, 2 CH_2); 4.04 (t, 2H, CH_2O, $^{3}J_{\mathrm{HH}}=6$); 4.33 and 4.38 (2 × dt, 2H, CH_2–OCO, $^{2}J_{\mathrm{HH}}=11$, $^{3}J_{\mathrm{HH}}=6$); 4.78 (dddq, 1H, CHF, $^{2}J_{\mathrm{HF}}=44$, $^{3}J_{\mathrm{HF}}=5.8$, $^{3}J_{\mathrm{HF\,(b)}}=6.6$, $^{3}J_{\mathrm{HF\,(a)}}=4.1$); 5.11 (dq, 1H, CHF–CO, $^{2}J_{\mathrm{HF}}=46.2$, $^{3}J_{\mathrm{HF}}=6.5$) ppm.

^{19}F NMR ($CDCl_3$) δ: -75.82 (dq, 3F, CF_3–CHF–CF_2, $^{3}J_{\mathrm{FF}}={}^{4}J_{\mathrm{FF}}=9$, $^{3}J_{\mathrm{HF}}=5.8$); -76.52 (dd, 3F, CF_3–CHF–CO, $^{3}J_{\mathrm{FF}}=12$, $^{3}J_{\mathrm{HF}}=6.5$); -80.62 and -83.63 (dddq, 2F, CF_2, $^{2}J_{\mathrm{FF}}=147$, $^{4}J_{\mathrm{FF}}=9$, $^{3}J_{\mathrm{FF}}=3$ or 6, $^{3}J_{\mathrm{HF}}=4.1$ or 6.6); -205.06 (dq, 1F, CHF–CO, $^{2}J_{\mathrm{HF}}=46.2$, $^{3}J_{\mathrm{FF}}=12$); -212.22 (dddq, 1F, CHF, $^{2}J_{\mathrm{HF}}=44$, $^{3}J_{\mathrm{FF}}=9$, $^{3}J_{\mathrm{FF\,(a,b)}}=6$ and 3) ppm.

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