

Radical additions to fluoro-olefins. Photochemical mono-fluoroalkylation and sequential bis-fluoroalkylation of oxolane

Oldřich Paleta *, Vladimír Církva, Jaroslav Kvíčala

Department of Organic Chemistry, Prague Institute of Chemical Technology, Technická 5, 16628 Prague 6, Czech Republic

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Abstract

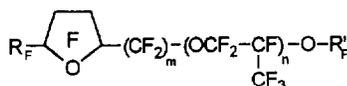
Oxolane was fluoroalkylated by its photoadditions under atmospheric pressure. Monofluoro-alkylations were carried out with hexafluoropropene (**1**) and perfluorovinyl ethers $C_3F_7O-[CF(CF_3)CF_2O]_n-CF=CF_2$ (**2-4**, $n=0-2$) by direct photoexcitation of the olefins to give high yields of addition products **9-12** (81–94%). The reactions were completely regioselective at the oxolane molecule and almost completely regioselective (93–99%) at the double bond of fluoro-olefins; no bis-fluoroalkylated oxolanes were detected. The completely selective introduction of a second fluoroalkyl into position 5 of the oxolane molecule was accomplished by acetone-sensitised photoaddition of 2-fluoroalkylated oxolanes **9, 10** to fluoro-olefins **1** and **2**. Byproducts from reactions of the dimethylketyl radical which is formed in the initiation step were isolated and have given some evidence about the reaction mechanism that is discussed.

Keywords: Radical addition; Regioselectivity; Perfluoroolefins; Oligomerisation of hexafluoropropene-1,2-oxide; Perfluorovinyl ethers; Photo-addition; Sensitised photoaddition; 2-(Fluoroalkyl)oxolanes; 2,5-bis(Fluoroalkyl)oxolanes; Diastereoisomers

1. Introduction

Perfluorinated ethers are known as inert fluids with high solubility for gases [1–3]. Some of them include perfluorinated alkyloxolanes [1–5] that can be used as biocompatible oxygen carriers in medicine. Perfluorinated alkyloxolanes are usually produced by an exhaustive fluorination of non-fluorinated starting compounds, but the processes are not very selective and give low yields of the main products [1–4]. Much better results have been obtained by fluorination of 2-(fluoroalkyl)oxolanes with cobalt trifluoride [6] and electrochemically [7].

Modified and new properties from the point of view of bioinert and oxygen-carrier fluids can be expected in mono- and disubstituted perfluoro-oxolanes having perfluoroalkoxy or perfluoro(polyether) groups in the side chains, as shown in the following general structure:



R_F - perfluoroalkyl, perfluoro(oxaalkyl), polyoxaalkyl)

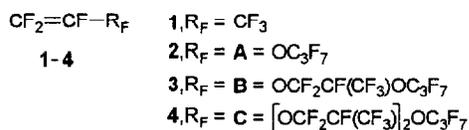
R'_F - perfluoroalkyl

Variations in the side-chain length and structure, as well as the number of ether bonds in it offer broad possibilities of modifying physical and physico-chemical properties of inert compounds of this type that are new to our knowledge. In this paper we studied photochemical preparation of 2,5-bis(fluoroalkylated)oxolanes as intermediates for obtaining the above-discussed structures.

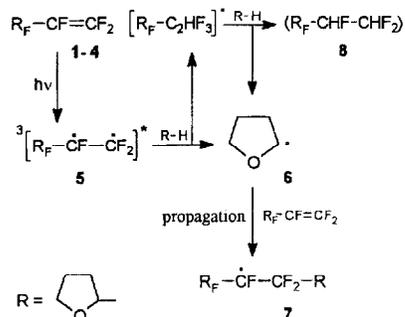
Radical reactions give a good possibility to combine together large building blocks [8,9], for instance by addition reactions in which C–H bonds of addenda are cleaved [8,9]. Some classes of aliphatic and alicyclic oxygen compounds undergo radical additions to aliphatic perfluoro-olefins with three and more carbon atoms in the chain (see, for example, Refs. [10–16]). The addenda used include also oxolane [11–15] whose additions to perfluoroolefins were initiated by dibenzoyl peroxide [11,13] or with γ -rays [11,12,15] to give 2-fluoroalkylated oxolanes. Radical additions of oxygen compounds, in which C–H bonds are cleaved, to perfluoro-olefins can also be initiated photochemically as shown in a series of papers [16–21].

In this paper we studied conditions for a selective sequential photo-fluoroalkylation of oxolane. Photochemical reactions offer several general advantages: first, they are only slightly temperature dependent; second, they can be performed at low temperatures; third, they can be performed

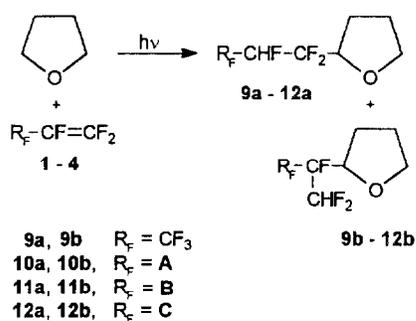
* Corresponding author.



Scheme 1. Fluoro-olefins used.



Scheme 2. Photo-initiation mechanism in the fluoroalkylation of oxolane.



Scheme 3.

under non-pressure conditions; fourth, reaction mixtures are not contaminated with products coming from initiators.

2. Results and discussion

2.1. Photofluoroalkylations of oxolane

We used two kinds of perfluoroolefins for the fluoroalkylations (Scheme 1), namely hexafluoropropene (1) as a representative of volatile perfluoroalkene, and perfluorovinyl ethers 2–4.

Table 1
Photoaddition reactions of oxolane with perfluoro-olefins 1–4

Fluoro-olefin	Oxolane		Time (h)	Conversion of olefin (%)	2-(Fluoroalkyl)oxolanes						
	(g)	(mol)			(g)	(mol)	Product	Diastereoisomer ratio ((%):(%)	Yield (g)	Boiling point (°C/mmHg)	
1	90	0.600	146.5	2.0	15	98	9	9a 56:44	125.1	93.8	80–82/100
2	5.32	0.020	8.64	0.12	2	84	10	10a 56:44	5.50	81.0	94–96/90
3	1.08	0.0025	8.64	0.12	8	100	11	11a 56:32:12	1.11	87.2	91–93/20
4	1.50	0.0025	8.64	0.12	12	100	12	12a 31:27:24:18	1.51	90.0	106–108/10

Photoaddition reactions of oxolane to perfluoroolefins 1–4 were carried out without any initiator or sensitiser [17]. By UV light absorption [22], the olefins are transformed to their triplet excited states [23]. They are of a diradical character (5, Scheme 2) and are able to abstract hydrogen atom from oxolane to form a 2-oxolanyl radical (6) in the initiation step, as shown in Scheme 2. The radical 6 then starts a propagation cycle by its addition in which an adduct-radical 7 is formed.

Dihydrogenalkane 8 is formed in a very low yield as a volatile by-product; we were not able to detect it, but it was detected in a previous paper [16] in connection with the study of radical additions onto hexafluoropropene. The 2-oxolanyl radical was detected in our previous work in the form of its recombination dimer that was formed in a similar photoaddition of oxolane to methyl-2,3,3-trifluoroacrylate [18].

All photoadditions in this work were carried out under atmospheric pressure and the additions took place easily due to the high reactivity of oxolane in radical additions [15]. In the case of hexafluoropropene, the olefin was introduced continuously into the photoreactor, the additions to perfluorovinyl ethers were carried out in quartz cells irradiated from outside.

The monofluoroalkylations accomplished in this paper are depicted in Scheme 3. The reaction scheme shows that pairs of regioisomeric addition products were formed in each addition, but the relative amount of the minor isomers b did not exceed 7% (vide infra). The additions were completely regioselective at the oxolane molecule and no bis-fluoroalkylated oxolanes were detected in the reaction mixture.

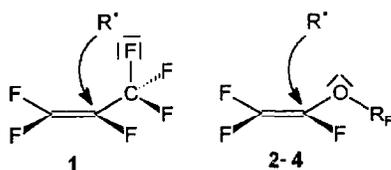
Reaction conditions are summarised in Table 1. The data show that relatively high concentrations of perfluoro-olefins can be used and that the conversion of olefins was almost complete. The products 9a–12a, and 9b–12b were mixtures of diastereoisomeric racemates. It was possible to distinguish the signals of some of the diastereoisomers in the a regioisomers in the ^{19}F NMR spectra and to determine their relative amount, as shown in Table 1.

In the NMR spectra of the products 9a–12a (Scheme 3) we observed signals of a low intensity that could be assigned to groups CHF_2- and $-\text{CF}-$ of the regioisomeric adducts 9b–12b (Scheme 3, Table 2). The formation of a small amount

Table 2
Regioselectivity of the additions of oxolane onto perfluoro-olefins 1–4 (Scheme 3)

Olefin	Minor adduct	
	b	(% rel.)
1	9b	0 ^a 0.8
2	10b	7
3	11b	6
4	12b	5

^a Previous papers [11–15].



Scheme 4.

of regioisomeric adducts (2–4.5% rel.) has been reported for the radical addition of methanol to hexafluoropropene [16] and we confirmed this observation in a non-pressure photochemical reaction (2% rel. of regioisomer [24]). Previous papers on additions of oxolane to hexafluoropropene [11–15] have not reported the formation of the regioisomeric adduct **9b**.

It is curious that the relative amounts of the minor regioisomers are higher in the reactions of perfluorovinyl ethers **2–4** (Table 2) than in the reaction of hexafluoropropene (**1**). This difference in regioselectivity can be caused both by steric and polar factors [25–27]. The olefin **1** as one type and the perfluorovinyl ethers **2–4** as the second type of perfluoroolefins undoubtedly differ in the electronic structure of their double bond and this difference can contribute to different regioselectivity of the additions. A steric effect can also influence significantly the regioselectivity of the additions as depicted in Scheme 4.

If we consider a radical attack to the double bond by radical species (Scheme 4) it can be seen that the access to C2 in perfluorovinyl ethers (**2–4**) can be more easy for steric reasons connected with a favourable OR_F chain conformation. Additionally, repulsive forces can be induced between a nucleophilic radical and non-bonded electrons at fluorine atoms of the CF₃ group causing reduced formation of the regioisomer **9b** in comparison with olefins **2–4**. The formation of regioisomeric adducts also indicates that the values of activation energies for the radical attack at C1 and C2 in both

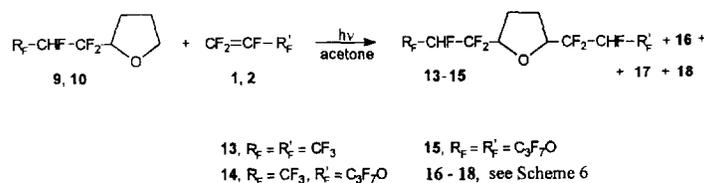
olefinic species are close [25–27]. An effect of the chain length on the regioselectivity can also be observed (Table 2): the relative amount of regioisomers **10b–12b** decreases with the chain length of perfluoroalkyls R_F in fluoro-olefins **2–4** (Table 2). This effect can be caused by a steric shielding of the reactivity site at C2 in the olefins by a conformational movement of the longer perfluorinated chain.

2.2. Photo-fluoroalkylations of 2-(fluoroalkyl)oxolanes

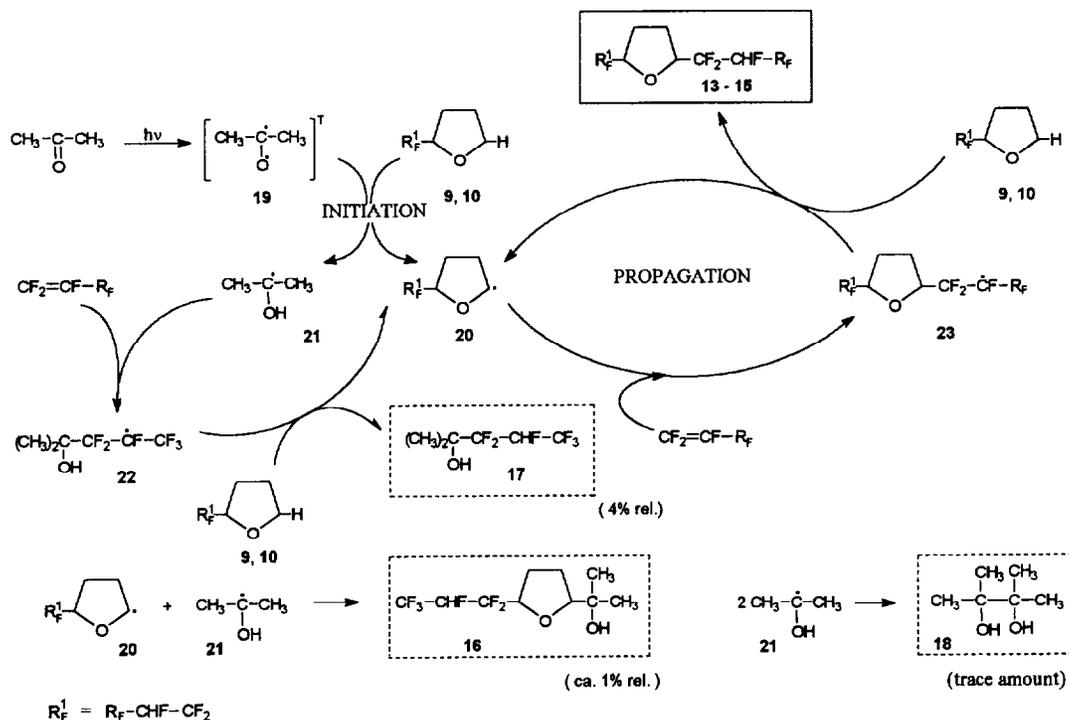
Doubly 2,5-fluoroalkylated cyclic ethers were sometimes obtained in one-pot reactions of the ethers with perfluoro-olefins under the peroxide and γ -ray [11,12] initiations. In our photochemical reactions we have never detected even small amounts of these products in the reaction mixtures. Even when isolated 2-(fluoroalkyl)oxolanes **9–12** were reacted in new runs with the olefins **1–4**, no bis-fluoroalkylated products were obtained.

The non-reactivity of 2-(fluoroalkyl)oxolanes in the subsequent fluoroalkylation can be explained by properties of the excited fluorolefin **5** (Scheme 2) which is not able to abstract hydrogen from fluoroalkylated oxolanes **9–12** because of increased bond dissociation energy of the C5–H bonds [28]. Therefore we used acetone as a photochemical sensitizer of the addition reactions: acetone displays an absorption band at longer wavelengths than perfluoroolefins **1–4** and is easily excited to a triplet state which is of diradical character [23]. Moreover, acetone has been shown to be an efficient photo-sensitizer in additions of alcohols to olefinic compounds [21]. The reactions then took place to give 2,5-bis-fluoroalkylated oxolanes **13–15** as shown in Scheme 5.

Hexafluoropropene (**1**) reacted with 2-(hexafluoropropyl)oxolane (**9**) in a flow-in system with almost total conversion (99%, product **13**), the conversions achieved in the reactions of perfluorovinyl ether **2** were 25–36% (products **14**, **15**). Minor byproducts appeared in the reaction mixtures and analyses showed that they could be formed from acetone. To prepare some of these minor compounds **16–18** (for structures see Scheme 6) formed in the fluoroalkylation of hexafluoropropyl oxolane **9** with hexafluoropropene, we accomplished the photoreaction of acetone with the oxolane (**9**) that afforded compound **16** (10% yield), pinacol (**18**) and some amount of unidentified compound. Similar results were obtained in the former photoreaction of oxolane with acetone [29]. The minor product **17** was prepared independently by the photoaddition of 2-propanol to hexafluoropropene [24]. All the minor products **16–18** have their origin in reactions of dimethyl ketyl radical (**19**, Scheme 6): compounds **16**, **18**



Scheme 5. Second step in the sequential photo-fluoroalkylation of oxolane.



Scheme 6. Mechanism of the acetone sensitised photo-fluoroalkylation of 2-(fluoroalkyl)oxolanes.

are products of termination reactions, and byproduct **17** is formed in a competitive reaction of the radical **19** with fluoroolefin (Scheme 6). The byproducts **16–18** contain hydroxyl groups and therefore can be easily separated from the main products by column chromatography.

On the bases of the identified minor products **16–18** we suggest a general scheme of simple reactions for the sensitised fluoroalkylation as depicted in Scheme 6: the incident UV light is absorbed by acetone which is transformed to a triplet state (**19**). This diradical [**22**] abstracts hydrogen from 2-(fluoroalkyl)oxolanes (**9, 10**) to form two radicals (**20, 21**) in the initiation step.

2-(Fluoroalkyl)oxolan-5-yl (**20**) reacts with a fluoro-olefin (**1, 2**) to furnish adduct-radical **23** in the first reaction of the propagation step. The second radical from the initiation step, the dimethylketyl radical (**21**) causes the formation of byproducts **16–18** as discussed above.

3. Conclusions

The non-sensitised photoinitiated addition reaction of oxolane with hexafluoropropene and perfluorovinyl ethers under atmospheric pressure leads exclusively to 1:1 adducts, i.e. 2-(fluoroalkyl)oxolanes; the conversions of perfluoro-olefins under the conditions employed were complete. The additions of oxolane were not completely regioselective and small amounts of regioisomeric adducts, whose portions were apparently higher in the case of perfluorovinyl ethers than to hexa-fluoropropene, were detected in the all additions. This new observation has been explained by steric effects.

The introduction of a second fluoroalkyl into 2-(fluoroalkyl)oxolanes was achieved by acetone-sensitised photo-addition of the 2-(fluoroalkyl)oxolanes onto hexafluoropropene and perfluoro(propyl vinyl) ether, respectively. The reactions enable introduction of different fluoroalkyls into position 5 of the 2-(fluoroalkyl)oxolanes. The additions were not chemoselective as two byproducts were formed in reactions of the dimethyl ketyl radical that is generated from acetone in the initiation step. More convenient sequential fluoroalkylations of oxolane can be accomplished in such way that monofluoroalkylation is carried out photochemically and the introduction of a second fluoroalkyl is performed under radical, e.g. peroxide initiation.

4. Experimental details

4.1. General comments

The temperature data were uncorrected. GC analyses were performed on a Chrom 5 instrument (Laboratorní pøístroje, 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, ^{13}C at 100.6 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 (s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quadruplet; qi, quintuplet; sex, sextuplet; sep, septuplet; m, multiplet), coupling constants J in Hz, solvents CDCl_3 and DMSO-d_6 . Mass spectra were scanned on a GC-Mass Spectrometer tandem JEOL

DX-303 (JMA 5000, single focus, 70 eV, helium), GC inlet via a 1 m capillary column coated with silicone elastomer.

The chemicals used were as follows. Hexafluoropropene and hexafluoropropene-1,2-oxide were purchased from Fluorochem Limited. Oxolane (Fluka) was purified according to the described procedure [30].

4.2. Preparation of perfluorovinyl ethers 2–4

4.2.1. Ionic oligomerisation of hexafluoropropene-1,2-oxide

The compounds were synthesized on the basis of oligomerisation of hexafluoropropene-1,2-oxide, as described in the literature [31–35]. A typical procedure used was as follows. An oven-heated 0.5 l flask equipped with efficient gas-tight mechanical stirrer, low-temperature reflux condenser, gas inlet and bottom outlet was charged under dry conditions with 10 g of vacuum-dried potassium fluoride, 150 ml of diethyleneglycol dimethyl ether (diglyme, DG) and 21.5 g of ethyl fluoroacetate, flushed with dry nitrogen and cooled to -25°C . Gaseous hexafluoropropene was introduced into the reaction mixture so that only mild reflux occurred (about 2 ml s^{-1}). The bottom fluoro-oligomer layer was periodically removed through the outlet. Over 14 h altogether 298 g of hexafluoropropene-1,2-oxide was thus added and 212 g of oligomer (dimer to heptamer) mixture was obtained. Fraction distillation over a 30 cm column packed with Berle saddles furnished 2.20 g of 2,4,4,5,5,6,6,6-octafluoro-3-oxa-2-(trifluoromethyl)hexanoyl fluoride (dimer, b.p. $40\text{--}48^{\circ}\text{C}$), 3.64 g of 2,4,4,5,7,7,8,8,9,9,9-undecafluoro-3,6-dioxa-2,5-bis(trifluoromethyl)nonanoyl fluoride (trimer, b.p. $10\text{--}20^{\circ}\text{C}/5\text{ kPa}$), 9.50 g of 2,4,4,5,7,7,8,10,10,11,11,12,12,12-tetradecafluoro-3,6,9-trioxa-2,5,8-tris(trifluoromethyl)dodecanoyl fluoride (tetramer, b.p. $68\text{--}74^{\circ}\text{C}/5\text{ kPa}$), 39.50 g of 2,4,4,5,7,7,8,10,10,11,13,13,14,14,15,15,15-heptadecafluoro-3,6,9,12-tetraoxa-2,5,8,11-tetrakis(trifluoromethyl)pentadecanoyl fluoride (pentamer, b.p. $108\text{--}117^{\circ}\text{C}/5\text{ kPa}$), 45.90 g of 2,4,4,5,7,7,8,10,10,11,13,13,14,16,16,17,17,18,18,18-eicosafluoro-3,6,9,12,15-pentaoxa-2,5,8,11,14-pentakis(trifluoromethyl)octadecanoyl fluoride (hexamer, b.p. $87\text{--}92^{\circ}\text{C}/200\text{ Pa}$) and 15.54 g of 2,4,4,5,7,7,8,10,10,11,13,13,14,16,16,17,19,19,20,20,21,21,21-tricosfluoro-3,6,9,12,15,18-hexacos-2,5,8,11,14,17-hexakis(trifluoromethyl)heneicosanoyl fluoride (heptamer, b.p. $79\text{--}89^{\circ}\text{C}/50\text{ Pa}$).

4.2.2. 1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahex-1-ene (2) [31–36]

2,4,4,5,5,6,6,6-Octafluoro-3-oxa-2-trifluoromethyl hexanoyl fluoride ($\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COF}$) (22 g; 65 mmol) was neutralised with 10% solution of sodium hydroxide. The solution of sodium salts was evaporated to dryness (rotary evaporator, 25 mm Hg) and then dried for 3 h in vacuo (0.3 mm Hg) at 100°C . The dry mixture of sodium 2,4,4,5,5,6,6,6-octafluoro-2-trifluoromethyl-3-oxahexanoate and sodium

fluoride in a flask of a distillation set equipped with dry-ice cooled trap and hydraulic seal (sulfuric acid) was rapidly heated up to 310°C on a Wood's-metal bath and the distillate was collected. The raw product **2** (14.6 g) was then fractionally distilled on a short packed column (11 cm, stainless-steel coils) to obtain olefin **2** in the yield of 10.1 g (57%), b.p. $34\text{--}36^{\circ}\text{C}$ (lit. value [37], b.p. 33°C), purity 97%.

4.2.3. 1,1,2,4,4,5,7,7,8,8,9,9,9-Tridecafluoro-3,6-dioxa-5-trifluoromethyl-non-1-ene (3) [34,35,38]

The olefin **3** was prepared from 2,4,4,5,7,7,8,8,9,9,9-undecafluoro-3,6-dioxa-2,5-bis(trifluoromethyl)nonanoyl fluoride ($\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{COF}$) (29.9 g; 60 mmol) in the same manner as compound **2** in yield of 15.3 g (59%), purity 98%, b.p. $101\text{--}103^{\circ}\text{C}$ (lit. value [38], b.p. 103°C). ^{19}F NMR (CDCl_3) δ : -80.45 (m, 3F, CF_3CF); -81.87 (m, 3F, CF_3CF_2); -82.33 (m, 2F, $\text{CF}_2\text{--CF}_2\text{O}$); -85.27 (m, 2F, $\text{CF--CF}_2\text{O}$); -113.54 (dd, 1F, $\text{CF}_2\text{--}$, F_B , $^2J_{\text{FF}} = 83$, $^3J_{\text{FF}} = 66$); -122.02 (dd, 1F, $\text{CF}_2\text{--}$, F_A , $^2J_{\text{FF}} = 83$, $^3J_{\text{FF}} = 111$); -130.04 (m, 2F, CF_2); -136.0 (ddt, 1F, --CF-- , $^3J_{\text{FF}} = 66$ and 111 , $^4J_{\text{FF}} = 6$); -145.27 (t, 1F, CF , $^3J_{\text{FF}} = 20$) ppm.

When the mixture of sodium salts, prepared from the acid fluoride (10 g; 20 mmol) was pyrolysed after the evaporation of water without subsequent drying in vacuo then the saturated product was obtained, i.e. 1,1,1,2,2,3,3,5,6,6,8,9,9,9-tetradecafluoro-4,7-dioxa-5-(trifluoromethyl)-nonane ($\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCHF}(\text{CF}_3)$) in high yield of 7.3 g (80%), b.p. $103\text{--}105^{\circ}\text{C}$ (lit. value [39], b.p. 104.4°C), purity 96%. ^1H NMR ($\text{CDCl}_3 + \text{Et}_2\text{O}$, 10:1) δ : 5.82 and 6.00 (2 \times d, 1H, OCHF, $^2J_{\text{HF}} = 54$) ppm. ^{19}F NMR ($\text{CDCl}_3 + \text{Et}_2\text{O}$, 10:1) δ : -80.65 (m, 3F, CF_3CF); -82.00 (m, 3F, CF_3CF_2); -84.51 (m, 3F, CF_3CHF); -81.62 and -82.95 (2 \times dm, 2F, $\text{CF}_2\text{--CF}_2\text{O}$, $^2J_{\text{FF}} = 140$); -84.20 and -86.49 (2 \times dm, 2F, $\text{CF--CF}_2\text{O}$, $^2J_{\text{FF}} = 144$); -130.22 (m, 2F, CF_2); -145.42 (t, 1F, CF , $^3J_{\text{FF}} = 19$); -146.38 (dm, 1F, CHF , $^2J_{\text{FF}} = 54$) ppm.

4.2.4. 1,1,2,4,4,5,7,7,8,10,10,11,11,12,12,12-Hexadecafluoro-3,6,9-trioxa-5,8-bis(trifluoromethyl)dodec-1-ene (4) [34,35]

The olefin **4** was prepared from 2,4,4,5,7,7,8,10,10,11,11,12,12,12-tetradecafluoro-3,6,9-trioxa-2,5,8-tris(trifluoromethyl)dodecanoyl fluoride ($\text{C}_3\text{F}_7\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_2\text{CF}(\text{CF}_3)\text{COF}$) (21.7 g; 33 mmol) in a similar manner as compound **2**. The dried sodium dodecanoate was rapidly heated from 100°C up to 360°C on a Wood's-metal bath. The raw product **4** (15.4 g) was then fractionally distilled and olefin **4** was obtained in a yield of 10.5 g (54%), b.p. $68^{\circ}\text{C}/25\text{ mm Hg}$ (lit. value [40], b.p. 163°C), purity 97%.

4.3. Fluoroalkylations of oxolane

4.3.1. With hexafluoropropene

Apparatus: An immersion-well photoreactor cooled from outside to -15 to 0°C , a UV lamp (Tesla, RVK 125) in a water-cooled double jacket (quartz and Simax[®] glass, gas

sintered-glass inlet at the bottom of the reactor), and with a 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, the whole apparatus filled with oxolane was carefully flushed with pure nitrogen. Hexafluoropropene (90 g; 0.6 mol) was introduced into the oxolane (146.5 g; 2 mol) over 15 h in the photoreactor at such a flow-rate that it was almost totally consumed (conversion 98.3%). Oxolane was then distilled off and the raw product **9** was fractioned on a packed column (15 cm, Berle saddles, heated jacket): 125 g (93.8%) yield of the product **9**, b.p. 80–82°C/100 Torr (13.33 kPa) (lit. value [12,15], b.p. 136–137°C), purity 99%.

Analysis (9a + 9b): Found: C, 37.55; H, 3.76; F, 51.80%. $C_7H_8F_6O$ requires: C, 37.85; H, 3.63; F, 51.32%. M, 222.13.

2-(1,1,2,3,3,3-Hexafluoroprop-1-yl)oxolane (**9a**). 1H NMR and ^{19}F NMR spectra in Refs. [11,13,16].

2-(1,1,2,3,3,3-Hexafluoroprop-2-yl)oxolane (**9b**, 0.8% rel.). 1H NMR ($CDCl_3$) δ , 2 diastereoisomers, A (57% rel.), B (43% rel.): 2.00 (m, 4H, $2CH_2$); 3.89 (m, 2H, CH_2O); 4.46 and 4.55 ($2 \times dm$, 1H (A,B), $-CH-$, $^3J_{HF} = 25$ and 23); 6.21 and 6.22 ($2 \times dt$, 1H (A,B), $-CHF_2$, $^2J_{HF} = 52$ and 55, $^3J_{HF} = 6$ and 7) ppm. ^{19}F NMR ($CDCl_3$) δ : -74.49 and -74.97 ($2 \times dt$, 3F (A,B), CF_3 , $^3J_{FF} = 3$ and 7, $^4J_{FF} = 10$); -134.65 and -136.39 ($2 \times ddq$, 2F (A,B), $-CHF_2$, $^2J_{HF} = 52$ and 55, $^3J_{FF} = 3$ and 7, $^4J_{FF} = 10$); -189.46 (dsep, 1F (B), $-CF-$, $^3J_{HF} = 23$ and 7, $^3J_{FF} = 7$); -197.52 (ddsex, 1F (A), $-CF-$, $^3J_{HF} = 25$ and 6, $^3J_{FF} = 3$) ppm.

4.3.2. With 1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahex-1-ene (2)

Apparatus: The reaction was carried out in a round-shaped two-necked (with septa) quartz cell of volume ca. 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, with a round window (5 cm diameter) with a quartz lens.

Reaction: The reaction mixture consisted of oxolane (8.64 g; 0.12 mol) and the olefin **2** (5.32 g; 3.81 mmol) was deoxygenated for 0.5 h at ca. -40°C with a stream of argon (inlet-outlet by needles through the septa). The mixture was irradiated for 2 h (84% conversion of the olefin, monitoring by GC) while stirring (magnetic spinbar). Oxolane was then distilled off (5 cm Vigreux column) and the raw product was distilled to afford product **10**, 5.5 g (81%) yield, b.p. 94–96°C/90 Torr (12.0 kPa), purity 98.5%.

Analysis (10a + 10b): Found: C, 31.82; H, 2.25; F, 57.02%. $C_9H_8F_{10}O_2$ requires: C, 31.97; H, 2.38; F, 56.18%. M, 338.2.

2-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahex-1-yl)oxolane (**10a**). 1H NMR ($CDCl_3$) δ , 2 diastereoisomers, A (56% rel.), B (44% rel.): 1.93 and 1.99 ($2 \times m$, 2H (A,B), CH_2-CH_2-O); 2.11 and 2.16 ($2 \times m$, 2H (A,B), CH_2-CH-); 3.87 (dm, 2H, $-CH_2-O$); 4.18 and 4.30 ($2 \times dm$, 1H (A,B), $-CH-$, $^3J_{HF (b)} = 22$); 6.14 and 6.15 ($2 \times dd$, 1H (B,A), -

$CHF-$, $^2J_{FF} = 50$ and 55, $^3J_{HF (a)} = 11$ and 9) ppm. ^{19}F NMR (**10a**, $CDCl_3$) δ : -81.81 and -81.87 ($2 \times t$, 3F (A,B), CF_3 , $^3J_{FF} = 7.1$); -85.23, -85.48, -87.19 and -87.97 ($4 \times dm$, 2F (A,B), CF_2-O , $^2J_{FF} = 146.7$); -129.21 (dt, 1F (F(a), A), CF_2-CH , $^2J_{FF} = 266$, $^3J_{FF} = ^3J_{HF} = 9$); -130.96 (dt, 1F (F(a), B), CF_2-CH , $^2J_{FF} = 268.5$, $^3J_{FF} = ^3J_{HF} = 11$); -131.41 (ddd, 1F (F(b), A), CF_2-CH , $^2J_{FF} = 266$, $^3J_{HF} = 22$, $^3J_{FF} = 12$); -132.22 (dd, 1F (F(b), B), CF_2-CH , $^2J_{FF} = 268.5$, $^3J_{HF} = 22.5$); -130.28 and -130.31 ($2 \times m$, 2F (A,B), $-CF_2-CF_3$); -144.65 (dd, 1F (B), $-CHF-$, $^2J_{HF} = 50$, $^3J_{HF (a)} = 11$); -152.20 (ddd, 1F (A), $-CHF-$, $^2J_{HF} = 55$, $^3J_{FF (b)} = 12$, $^3J_{FF (a)} = 9$) ppm.

2-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahex-2-yl)oxolane (**10b**, 7% rel.). 1H NMR ($CDCl_3$) δ , 2 diastereoisomers, A (50% rel.), B (50% rel.): 1.90–2.30 (m, 4H, $2CH_2$); 3.88 (m, 2H, CH_2O); 4.40 (m, 1H, $-CH-O$); 6.05 (dt, 1H (B), CHF_2 , $^2J_{HF} = 53$, $^3J_{HF} = 7$); 6.07 (t, 1H (A), CHF_2 , $^2J_{HF} = 54$) ppm. ^{19}F NMR (**10b**, $CDCl_3$) δ : -81.65 and -81.74 ($2 \times t$, 3F (A,B), CF_3 , $^3J_{FF} = 7$); -85.15 and -88.17 ($2 \times m$, 2F (A,B), CF_2-O); -129.95 and -130.12 ($2 \times m$, 2F (A,B), CF_2-CF_3); -134.48 (ddd, 1F (F(a), A), $-CHF_2$, $^2J_{FF} = 301$, $^2J_{HF} = 54$, $^3J_{FF} = 4$); -135.32 (ddd, 1F (F(a), B), $-CHF_2$, $^2J_{FF} = 300$, $^2J_{HF} = 53$, $^3J_{FF} = 4$); -136.24 (ddd, 1F (F(b), B), $-CHF_2$, $^2J_{FF} = 300$, $^2J_{HF} = 53$, $^3J_{FF} = 9$); -137.33 (m, 1F (B), $-CF-$); -139.37 (dddt, 1F (F(b), A), $-CHF_2$, $^2J_{FF} = 301$, $^2J_{HF} = 54$, $^3J_{HF} = 23$, $^3J_{FF} = 8$); -145.12 (m, 1F (A), $-CF-$) ppm.

4.3.3. With 1,1,2,4,4,5,7,7,8,8,9,9,9-Tridecafluoro-3,6-dioxa-5-(trifluoromethyl)non-1-ene (3)

For apparatus and procedure see Section 4.3.2. The heterogeneous mixture of oxolane (8.64 g; 0.12 mol) and the olefin **3** (1.08 g; 2.5 mmol) was irradiated for 8 h while stirring intensively (complete conversion of the olefin, monitoring by GC). The main fraction from micro-distillation scale afforded product **11**, 1.1 g (87%) yield, b.p. 91–93°C/20 Torr (2.67 kPa), purity 98%.

Analysis (11a + 11b): Found: C, 28.33; H, 1.71; F, 60.95%. $C_{12}H_8F_{16}O_3$ requires: C, 28.59; H, 1.60; F, 60.29%. M, 504.2.

2-[1,1,2,4,4,5,7,7,8,8,9,9,9-Tridecafluoro-3,6-dioxa-5-(trifluoromethyl)non-1-yl]oxolane (**11a**). 1H NMR ($CDCl_3$) δ , 4 diastereoisomers, A,B (56% rel.), C (32% rel.), D (12% rel.): 1.97 (m, 2H, CH_2-CH_2-O); 2.11 (m, 2H, CH_2-CH-O); 3.91 (m, 2H, CH_2-O); 4.15 (ddt, 1H (A,B), $-CH-O$, $^3J_{HF} = 20$ and 8, $^3J_{HH} = 5.5$); 4.30 (dm, 1H (C,D), $-CH-O$, $^3J_{HF} = 20$); 6.09 and 6.26 (ddd, 1H (C,D), $-CHF-$, $^2J_{HF} = 53$, $^3J_{HF (a)} = 12$, $^3J_{HF (b)} = 1$); 6.11 (ddd, 1H (A,B), $-CHF-$, $^2J_{HF} = 55$, $^3J_{HF (a)} = 12$, $^3J_{HF (b)} = 2$) ppm. ^{19}F NMR (**11a**, $CDCl_3$) δ : -80.51, -80.53, -80.61, -80.64 ($4 \times d$, 3F (A,B,C,D), CF_3-CF); -81.82, -81.84, -81.85, -81.87 ($4 \times t$, 3F (A,B,C,D), CF_3-CF_2); -81.92 and -82.44 ($2 \times dm$, 2F, CF_2-CF_2-O , $^2J_{FF} = 139$); -83.78, -83.85, -84.46, -86.02 ($4 \times dm$, 1F (F(a), A,B,C,D), $CF-CF_2-O$, $^2J_{FF} = 143$); -84.39, -86.26, -86.55, -87.22 ($4 \times dm$, 1F (F(b), A,B,C,D), $CF-CF_2-O$,

$^2J_{\text{FF}} = 143$); -128.96 and -129.22 ($2 \times \text{ddt}$, 1F (F(a), A,B), $-\text{CF}_2-\text{CH}$, $^2J_{\text{FF}} = 268$, $^3J_{\text{HF}} = 12$ and 9 , $^3J_{\text{FF}} = 9$); -130.15 and -130.20 ($2 \times \text{m}$, 2F (A,B,C,D), $-\text{CF}_2-\text{CF}_3$); -131.19 and -131.47 ($2 \times \text{dddd}$, 1F (F(b), A,B), $-\text{CF}_2-\text{CH}$, $^2J_{\text{FF}} = 268$, $^3J_{\text{FF}} = 19$, $^3J_{\text{HF}} = 11$ and 2); -132.22 (dt, 2F (C,D), CF_2-CH , $^3J_{\text{FF}} = 12$, $^3J_{\text{HF}} = 12$ and 1); -144.45 and -144.54 ($2 \times \text{dt}$, 1F (C,D), $-\text{CHF}-$, $^2J_{\text{HF}} = 53$, $^3J_{\text{FF}} = 12$); -145.69 (t, 1F (A,B,C,D), $-\text{CF}-$, $^3J_{\text{FF}} = 22$); -151.45 and -151.67 ($2 \times \text{ddd}$, 1F (A,B), $-\text{CHF}-$, $^2J_{\text{HF}} = 55$, $^3J_{\text{FF(a)}} = 9$, $^3J_{\text{FF(b)}} = 19$) ppm.

2-[1,1,2,4,4,5,7,7,8,8,9,9,9-Tridecafluoro-3,6-dioxo-5-(trifluoromethyl)non-2-yl]oxolane (**11b**, 6% rel.). ^1H NMR (CDCl_3) δ , 4 diastereoisomers, A,B (65% rel.), C,D (35% rel.): 1.95–2.15 (m, 4H, 2- CH_2-); 3.91 (m, 2H, CH_2-O); 4.40 (m, 1H, $\text{CH}-\text{O}$); 6.05, 6.07, 6.20, 6.22 ($4 \times \text{dt}$, 1H (A,B,C,D), $-\text{CHF}_2$, $^2J_{\text{HF}} = 53$, $^3J_{\text{HF}} = 12$) ppm. ^{19}F NMR (CDCl_3) δ : -80.10 , -80.30 ($2 \times \text{m}$, 3F, CF_3-CF); -81.80 , -81.90 ($2 \times \text{m}$, 3F, CF_3-CF_2); -82.30 (m, 2F, $\text{CF}_2-\text{CF}_2-\text{O}$); -87.30 (m, 2F, $\text{CF}-\text{CF}_2-\text{O}$); -130.11 (m, 2F, CF_2-CF_3); -134.75 (ddd, 1F (F(a), A,B), $-\text{CHF}_2$, $^2J_{\text{FF}} = 301$, $^2J_{\text{HF}} = 53$, $^3J_{\text{FF}} = 12$); -135.92 (dm, 2F (C, D), $-\text{CHF}_2$, $^2J_{\text{HF}} = 53$); -136.50 (m, 1F (A, B), $-\text{CF}-$); -139.91 (ddm, 1F (F(b), A,B), $-\text{CHF}_2$, $^2J_{\text{FF}} = 301$, $^2J_{\text{HF}} = 53$); -140.89 (m, 1F (C,D), $-\text{CF}-$); -145.50 (m, 1F, CF_3-CF) ppm.

4.3.4. With 1,1,2,4,4,5,7,7,8,10,10,11,11,12,12,12-hexadecafluoro-3,6,9-trioxa-5,8-bis(trifluoromethyl)dodec-1-ene (**4**)

For apparatus and procedure see Section 4.3.2. The heterogeneous mixture of oxolane (8.64 g; 0.12 mol) and the olefin **4** (1.50 g; 2.5 mmol) was irradiated for 12 h while stirring intensively (complete conversion of the olefin, monitoring by GC). The main fraction from micro-distillation afforded product **12**, 1.51 g (90%) yield, b.p. 106–108°C/10 Torr (1.33 kPa), purity 97%.

Analysis (**12a** + **12b**): Found: C, 26.57; H, 1.33; F, 63.91%. $\text{C}_{15}\text{H}_8\text{F}_{22}\text{O}_4$ requires: C, 26.88; H, 1.20; F, 62.37%. M, 670.2.

2-[1,1,2,4,4,5,7,7,8,10,10,11,11,12,12,12-Hexadecafluoro-3,6,9-trioxa-5,8-bis(trifluoro-methyl)dodec-1-yl]oxolane (**12a**). ^1H NMR (CDCl_3) δ , 4 diastereoisomers, A (31% rel.), B (27% rel.), C (24% rel.), D (18% rel.): 1.98–2.13 (m, 4H, 2- CH_2-); 3.90 (m, 2H, CH_2-O); 4.17 (ddt, 1H (A,B), $-\text{CH}-\text{O}$, $^3J_{\text{HF}} = 20$ and 8 , $^3J_{\text{HH}} = 5.5$); 4.31 (dm, 1H (C,D), $-\text{CH}-\text{O}$, $^3J_{\text{HF}} = 20$); 6.11 and 6.14 ($2 \times \text{dm}$, 1H (C,D and A,B), $-\text{CHF}-$, $^2J_{\text{HF}} = 55$ and 53) ppm. ^{19}F NMR (CDCl_3) δ : -78.46 , -79.32 , -81.25 , -81.37 ($4 \times \text{dm}$, 2F, $\text{CF}-\text{CF}_2-\text{O}$, $^2J_{\text{FF}} = 147$); -80.65 , -80.69 ($2 \times \text{s}$, 6F, $2 \times \text{CF}-\text{CF}_3$); -82.04 (s, 3F, CF_2-CF_3); -82.08 , -82.63 ($2 \times \text{dm}$, 2F, $\text{CF}_2-\text{CF}_2-\text{O}$, $^2J_{\text{FF}} = 140$); -84.31 , -84.53 , -86.05 , -86.57 ($4 \times \text{dm}$, 2F, $\text{CF}_2-\text{O}-\text{CHF}$, $^2J_{\text{FF}} = 143$); -128.70 , -128.87 , -130.88 , -130.96 ($4 \times \text{dm}$, 2F (A,B), CF_2-CH , $^2J_{\text{FF}} = 268$); -131.48 , -131.50 , -132.25 , -132.28 ($4 \times \text{dm}$, 2F (C,D), CF_2-CH , $^2J_{\text{FF}} = 268$); -130.33 (s, 2F, CF_2-CF_3); -144.82 ,

-144.97 ($2 \times \text{dm}$, 1F (C,D), $-\text{CHF}-$, $^2J_{\text{HF}} = 55$); -145.80 (m, 2F, $2 \times -\text{CF}-\text{O}$); -151.45 , -151.60 ($2 \times \text{dm}$, 1F (A,B), $-\text{CHF}-$, $^2J_{\text{HF}} = 53$) ppm.

2-[1,1,2,4,4,5,7,7,8,10,10,11,11,12,12,12-Hexadecafluoro-3,6,9-trioxa-5,8-bis(trifluoro-methyl)dodec-2-yl]oxolane (**12b**, 5% rel.). ^1H NMR (CDCl_3) δ , 4 diastereoisomers, A,B (65% rel.), C,D (35% rel.): 1.95–2.15 (m, 4H, 2- CH_2-); 3.91 (m, 2H, CH_2-O); 4.43 (m, 1H, $\text{CH}-\text{O}$); 6.07, 6.09, 6.23, 6.25 ($4 \times \text{dt}$, 1H (A,B,C,D), $-\text{CHF}_2$, $^2J_{\text{HF}} = 53$, $^3J_{\text{HF}} = 12$) ppm. ^{19}F NMR (CDCl_3) δ : -79.80 (m, 2F, $-\text{CF}-\text{CF}_2-\text{O}$, $^2J_{\text{FF}} = 146$); -80.15 , -80.32 ($2 \times \text{m}$, 6F, $2 \times \text{CF}_3-\text{CF}$); -81.83 , -81.95 ($2 \times \text{m}$, 3F, CF_3-CF_2); -82.35 (m, 2F, $\text{CF}_2-\text{CF}_2-\text{O}$); -87.33 (m, 2F, $-\text{CF}_2-\text{O}-\text{CF}$); -130.10 (m, 2F, CF_2-CF_3); -134.65 (ddd, 1F (F(a), A,B), $-\text{CHF}_2$, $^2J_{\text{FF}} = 300$, $^2J_{\text{HF}} = 53$, $^3J_{\text{FF}} = 11$); -135.95 (dm, 2F (C,D), $-\text{CHF}_2$, $^2J_{\text{HF}} = 53$); -136.45 (m, 1F (A,B), $-\text{CF}-$); -139.90 (ddm, 1F (F(b), A,B), $-\text{CHF}_2$, $^2J_{\text{FF}} = 300$, $^2J_{\text{HF}} = 53$); -140.89 (m, 1F (C,D), $-\text{CF}-$); -145.50 (m, 2F, $2 \times \text{CF}_3-\text{CF}$) ppm.

4.4. Fluoroalkylations of 2-(fluoroalkyl)oxolanes

4.4.1. Non-sensitised reaction of 2-(1,1,2,3,3,3-hexafluoroprop-1-yl)oxolane (**9**) with hexafluoropropene

The reaction was carried out in the same apparatus under the same conditions as the preparation of the compound **9** (**9**, 120 g, 0.54 mol; olefin **1**, 6.1 g, 42 mmol; 8 h), but no product was detected in the reaction mixture.

4.4.2. Non-sensitised reaction of 2-(1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-yl)oxolane (**10**) with 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (**2**)

For apparatus and procedure see Section 4.3.2. The homogenous mixture of fluoroalkyloxolane **10** (8.45 g; 0.025 mol) and the olefin **2** (2.66 g; 0.01 mol) was irradiated for 9 h while intensively stirring (4% conversion of the olefin, monitored by GC), no product was observed during further irradiation for 3 h. Product **15** was formed in low conversion and was not isolated (for the preparation see Section 4.4.5.).

4.4.3. Sensitised reaction of 2-(1,1,2,3,3,3-hexafluoroprop-1-yl)oxolane (**9**) with hexafluoropropene

For apparatus and conditions see Section 4.3.1. Hexafluoropropene (23 g; 36 mmol) was introduced over 6 h into the mixture of fluoroalkyloxolane **9** (73.3 g; 0.33 mol) and acetone (2.1 g; 36 mmol) in the photoreactor at such a flow rate that it was almost totally consumed (conversion 98.9%). The mixture was then neutralised with an aqueous solution of sodium hydrogen carbonate and dried with potassium carbonate. The composition of the mixture (GC) was the following (% rel.): acetone 0.2%, starting compound **9** 52.3%, main product **13** 41%, termination products **16–18** 2.5%. Fraction distillation on a packed column (see Section 4.3.1.): product **13**, b.p. 96–99°C/45 Torr (6 kPa) (lit. value [12], b.p. 171–177°C), yield 40.3 g (70.2%), purity 99%. The ratio of products formed (Scheme 6) was calcu-

lated (GC) from fractions and distillation residue and was the following (% rel.): **13**, 70%; **16**, ca. 1%; **17**, 4%; **18**, less than 1%. Minor compounds **16–18** were identified by GC and by comparison of their NMR spectra with standard compounds (preparation of **16**, see Section 4.5.; preparation of **17**, see Refs. [16,24]).

Analysis (**13**): Found: C, 32.53; H, 2.21; F, 60.64%. $C_{10}H_8F_{12}O$ (372.15), requires: C, 32.27; H, 2.17; F, 61.26%.

2,5-bis(1,1,2,3,3,3-Hexafluoropropyl)oxolane (**13**). 1H NMR and ^{19}F NMR in Ref. [11].

4.4.4. Sensitised reaction of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**9**) with 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (**2**)

For apparatus and procedure see Section 4.3.2. The homogenous mixture of fluoroalkyloxolane **9** (6.66 g; 0.03 mol), olefin **2** (4.0 g; 0.015 mol) and acetone (0.5 g, 8.62 mmol) was irradiated for 9 h while stirring intensively (25% conversion of the olefin, monitoring by GC). The main fraction from micro-distillation afforded product **14**, 0.74 g (10%) yield, b.p. 90–92°C/20 Torr (2.67 kPa), purity 97%.

Analysis (**14**): Found: C, 30.85; H, 1.37; F, 62.69%. $C_{12}H_8F_{16}O_2$ requires: C, 29.53; H, 1.65; F, 62.27%. M, 488.2. 2-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahex-1-yl)-5-(1,1,2,3,3,3-hexafluoroprop-1-yl)oxolane (**14**). 1H NMR ($CDCl_3$) δ , 8 diastereoisomers, A (25% rel.), B (17% rel.), C (16% rel.), D (13% rel.), E (10% rel.), F (7% rel.), G (7% rel.), H (5% rel.): 2.29 (m, 4H, 2CH₂); 4.46 (m, 2H, 2CH–O); 4.88 and 5.08 (2 × dtq, 1H, –CHF–, $^2J_{HF} = 44$, $^3J_{HF} = 12$ and 6); 6.01, 6.02, 6.05, 6.07, 6.08, 6.11, 6.12, 6.13 (8 × dm, 1H, –CHF–O, $^2J_{HF} = 55$) ppm. ^{19}F NMR (**14**, $CDCl_3$) δ : –74.33, –74.39, –74.52, –74.58, –74.88, –74.98, –75.08, –75.17 (8 × dq, 3F, CF_3 –CHF, $^3J_{FF} = 4J_{FF} = 11$, $^3J_{HF} = 6$); –81.90 (m, 3F, CF_3 – CF_2); –85.24, –85.50 (2 × dm, 1F (a), – CF_2 –O, $^2J_{FF} = 147$); –87.36, –87.49, –87.56, –87.63, –88.37, –88.38, –88.55, –88.56 (8 × dm, 1F (F(b), C,D,F,E,H,A,G,B), – CF_2 –O, $^2J_{FF} = 147$); –119.38, –119.92, –120.03, –120.05, –125.49, –125.52, –125.55, –125.58 (8 × dddq, 1F (F(a), F,E,D,A,H,G,C,B), – CF_2 –CHF, $^2J_{FF} = 276$, $^3J_{HF} = 12$, $^3J_{FF} = 9$, $^4J_{FF} = 10$); –124.55, –124.75, –124.82, –125.09, –128.05, –128.06, –128.16, –128.18 (8 × dddq, 1F (F(b), E,D,F,A,H,G,C,B), – CF_2 –CHF, $^2J_{FF} = 276$, $^3J_{HF} = 12$, $^3J_{FF} = 10$, $^4J_{FF} = 11$); –128.60, –128.85, –130.07, –130.08, –130.09, –130.10, –130.35, –130.48 (8 × dt, 1F (F(a), D,E,B,F,G,H,A,C), – CF_2 –CHF–O, $^2J_{FF} = 271$, $^3J_{HF} = 3J_{FF} = 11$); –130.29, –130.39 (2 × m, 2F, CF_2 – CF_3); –130.99, –131.00, –131.01, –131.02, –131.33, –131.39, –132.20, –132.40 (8 × ddd, 1F (F(b), B,F,G,H,A,C,E,D), – CF_2 –CHF–O, $^2J_{FF} = 271$, $^3J_{HF} = 21$, $^3J_{FF} = 10$); –143.76, –144.03, –144.04, –144.18, –149.04, –150.38, –151.50, –151.70 (8 × dddd, 1F (E,C,F,D,G,H,A,B), –CHF–O, $^2J_{HF} = 55$, $^3J_{FF} = 20$ and 11, $^4J_{HF} = 5$); –213.07, –213.37, –213.38, –216.76, –217.41, –218.25,

–218.62, –218.63 (8 × dddq, 1F (C,D,A,H,G,B,E,F), –CHF–, $^2J_{HF} = 44$, $^3J_{FF} = 12$ and 3, $^3J_{FF} = 11$) ppm.

4.4.5. Sensitised reaction of 2-(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahex-1-yl)oxolane (**10**) with 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (**2**)

For apparatus and procedure see Section 4.3.2. The homogenous mixture of fluoroalkyloxolane **10** (8.45 g; 0.025 mol), olefin **2** (2.66 g; 0.01 mol) and acetone (0.5 g, 8.62 mmol) was irradiated for 9 h while stirring intensively (36% conversion of the olefin, monitoring by GC). The main fraction from micro-distillation afforded product **15**, 0.97 g (16%) yield, b.p. 100–103°C/5 Torr (0.67 kPa), purity 99%.

Analysis (**15**): Found: C, 28.23; H, 1.35; F, 63.46%. $C_{14}H_8F_{20}O_3$ requires: C, 27.83; H, 1.33; F, 62.89%. M, 604.2.

2,5-bis(1,1,2,4,4,5,5,6,6,6-Decafluoro-3-oxahex-1-yl)oxolane (**15**). 1H NMR ($CDCl_3$) δ , 8 diastereoisomers, A (25% rel.), B (21% rel.), C (21% rel.), D (11% rel.), E (6% rel.), F (6% rel.), G (5% rel.), H (5% rel.): 2.28 (m, 4H, 2CH₂); 4.45 (m, 2H, 2CH–O); 6.00, 6.01, 6.05, 6.08, 6.10, 6.11, 6.13, 6.14 (8 × dm, 2H (F,E,D,H,G,B,A,C), 2 –CHF–, $^2J_{HF} = 54, 52, 46, 55, 55, 55, 55, 53$) ppm. ^{19}F NMR (**15**, $CDCl_3$) δ : –82.03 (m, 6F, 2 CF_3); –85.16, –85.20, –85.25, –85.42, –85.64, –85.65, –85.81, –85.85 (8 × dm, 4F (F(a), B,D,G,A,E,F,H,C), 2 × – CF_2 –O, $^2J_{FF} = 147$); –87.44, –87.85, –87.86, –87.89, –87.99, –88.80, –88.94, –89.00 (8 × dm, 4F (F(b), D,E,F,G,C,A,H,B), 2 × – CF_2 –O, $^2J_{FF} = 147$); –128.76, –128.83, –129.24, –129.27, –129.61, –130.18, –130.20, –130.98 (8 × dt, 4F (F(a), F,C,G,E,B,H,D,A), 2 × – CF_2 –CH, $^2J_{FF} = 269$, $^3J_{FF} = 3J_{HF} = 11$); –130.41, –130.49, –130.51, –131.24, –131.48, –131.95, –132.44, –132.54 (8 × dd, 4F (F(b), H,G,E,D,B,A,F,C), 2 × CF_2 –CH, $^2J_{FF} = 269$, $^3J_{FF} = 22$); –130.37, –130.43, –130.49, –130.54 (4 × s, 4F, 2 × CF_2 – CF_3); –143.98 (ddd, 2F (E), 2 –CHF–, $^2J_{HF} = 52$, $^3J_{FF} = 12$ and 6); –144.08 (dm, 2F (D), 2 –CHF–, $^2J_{HF} = 46$); –144.21 (ddd, 2F (F), 2 –CHF–, $^2J_{HF} = 54$, $^3J_{FF} = 12$ and 6); –144.28 (dd, 2F (C), 2 –CHF–, $^2J_{HF} = 53$, $^3J_{FF} = 5$); –149.92 (ddd, 2F (G), 2 –CHF–, $^2J_{HF} = 55$, $^3J_{FF} = 15$ and 6); –151.12 (ddd, 2F (H), 2 –CHF–, $^2J_{HF} = 55$, $^3J_{FF} = 15$ and 7); –151.77 (dm, 2F (B), 2 –CHF–, $^2J_{HF} = 55$); –152.51 (dd, 2F (A), 2 –CHF–, $^2J_{HF} = 55$, $^3J_{FF} = 10$) ppm.

4.5. Photoreaction of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**9**) with acetone

For apparatus and procedure see Section 4.3.1. A mixture of fluoroalkyloxolane **9** (22.2 g; 0.1 mol) and acetone (5.8 g; 0.1 mol) was irradiated for 16 h to obtain an end-mixture with the following approximate composition: acetone 27%, starting compound **9** 61%, pinacol 3% and product **16** 9%. Starting compounds were separated by fractional distillation on a packed column (see Section 4.3.1.) and the residue was distilled (0.15 Torr; 0.02 kPa) to give two fractions: 90–95°C (3.1 g) and 95–110°C (2.8 g). The first fraction was purified

by column chromatography (Silicagel L40/100, column 35/2.5 cm/cm, benzene-dichloromethane 1:2) to afford product **16**, 2.78 g (9.99%), purity 98%. Pinacol (**18**) was isolated from the second fraction in the form of its hydrate (m.p. 155–158°C; 0.66 g; 1.32%).

Analysis (**16**): Found: C, 42.75; H, 5.28; F, 41.13%. $C_{10}H_{14}F_6O_2$ requires: C, 42.86; H, 5.04; F, 40.68%. M, 280.2.

2-[(1,1,2,3,3,3-Hexafluoropropyl)oxol-5-yl]-2-propanol (**16**). 1H NMR ($CDCl_3$) δ , 4 diastereoisomers, A (43% rel.), B (16% rel.), C (29% rel.), D (12% rel.): 1.14, 1.16, 1.24, 1.25 (4×s, 6H, 2CH₃); 2.06 (m, 4H, 2CH₂-); 2.10 (bs, 1H, OH); 3.86 (m, 1H, -CH-); 4.33 (ddt, 1H (A,B), -CH-CF₂, $^3J_{HF}$ = 24 and 12, $^3J_{HH}$ = 7); 4.41 (ddt, 1H (C,D), -CH-CF₂, $^3J_{HF}$ = 25 and 7, $^3J_{HH}$ = 4); 5.07 (dddq, 1H (A,B), -CHF-, $^2J_{HF}$ = 43, $^3J_{HF}$ = 20 and 3, $^3J_{HF}$ = 6); 5.12 (dddq, 1H (C,D), -CHF-, $^2J_{HF}$ = 44, $^3J_{HF}$ = 11 and 6, $^3J_{HF}$ = 5) ppm. ^{13}C NMR (**16**, $CDCl_3$) δ : 24.51, 27.14 (2×s, 2C, 2CH₃); 25.55, 26.00, 26.02, 26.18 (4×s, 2C, 2CH₂); 71.26 (s, 1C, -C-); 75.74, 76.05 (2×dd, 1C, CF₂-CH-O, $^2J_{CF}$ = 34 and 23); 83.70, 83.73, 85.61, 85.65 (4×dsex, 1C (B,A,D,C), -CHF-, $^1J_{CF}$ = 156, $^2J_{CF}$ = 26); 87.90, 88.01, 88.26, 88.27 (4×s, 1C (A,C,B,D), O-CH-C); 117.27, 117.28, 117.50, 117.69 (4×dt, 1C (D,B,C,A), -CF₂-, $^1J_{CF}$ = 252, $^2J_{CF}$ = 26); 120.85, 120.98, 121.22, 121.23 (4×dq, 1C (D,B,C,A), CF₃, $^1J_{CF}$ = 282, $^2J_{CF}$ = 26) ppm. ^{19}F NMR (**16**, $CDCl_3$) δ : -74.34 (dq, 3F (A,B), CF₃, $^3J_{FF}$ = $^4J_{FF}$ = 12, $^3J_{HF}$ = 6); -74.81 (ddt, 3F (C,D), CF₃, $^3J_{FF}$ = $^4J_{FF(a)}$ = 11, $^4J_{FF(b)}$ = 10, $^3J_{HF}$ = 5); -119.78, -120.25 (2×ddsex, 1F (F(a), C,D), -CF₂-, $^2J_{FF}$ = 271, $^3J_{FF}$ = 11, $^4J_{FF}$ = 11, $^3J_{HF}$ = 11 and 7); -123.83, -124.50 (2×dddq, 1F (F(b), C,D), -CF₂-, $^2J_{FF}$ = 271, $^3J_{FF}$ = 11, $^4J_{FF}$ = 10, $^3J_{HF}$ = 25 and 6); -125.41, -126.22 (2×ddsex, 1F (F(a), B,A), -CF₂-, $^2J_{FF}$ = 271, $^3J_{FF}$ = 12, $^4J_{FF}$ = 12, $^3J_{HF}$ = 20 and 12); -129.75, -130.79 (2×dddq, 1F (F(b), A,B), -CF₂-, $^2J_{FF}$ = 271, $^3J_{HF}$ = 24 and 3, $^4J_{FF}$ = 12); -213.00, -213.28 (2×dqi, 1F (B,A), -CHF-, $^2J_{HF}$ = 43, $^3J_{FF}$ = $^3J_{FF(a)}$ = 12); -217.41, -217.70 (2×dsex, 1F (D,C), -CHF-, $^2J_{HF}$ = 44, $^3J_{FF(a)}$ = $^3J_{FF(b)}$ = $^3J_{FF}$ = 11) ppm.

4.6. Peroxide initiated reaction of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**9**) with 1,1,2,4,4,5,5,6,6,6-decafluoro-3-oxahex-1-ene (**2**)

Apparatus: The reaction was carried out in a flask (25 ml) equipped with a dry-ice cooled spiral reflux condenser with a hydraulic seal (sulfuric acid).

Reaction: The homogenous mixture of fluoroalkyloxolane **9** (6.66 g; 0.03 mol), olefin **2** (4.0 g; 0.015 mol) and dibenzoyl peroxide (0.484 g; 2 mmol) was deoxygenated for 0.5 h at ca. -40°C with a stream of argon (inlet-outlet by needles through the septa). The mixture was heated at 90°C for 9 h while stirring intensively (20% conversion of the olefin, monitoring by GC). The main fraction from micro-distillation afforded product **14**, 0.74 g (10%) yield, b.p. 91–93°C/20 Torr (2.67 kPa), purity 96%.

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