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Radical addition reactions of fluorinated species Part 6. [1] Regioselectivity of the addition of nucleophilic radicals to halogenopropenes and evidence for a steric effect of the chlorine substituent [2]

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Abstract

Nucleophilic radicals derived from alkanols and cyclic ethers (oxolane, 1,3-dioxolane, 2,2-dimethyl-1,3-dioxolane) were employed to test the regioselectivity of addition to 3-chloro-1,1,2,3,3-pentafluoropropene (**1**), 1,3-dichloro-1,2,3,3-tetrafluoropropene (**2**), 1,1,3-trichloro-2,3,3-trifluoropropene (**3**) and 1,3-dichloro-2,3,3-trifluoropropene (**4**). The regioselectivity was strongly dependent on the number of chlorine atoms at the terminal position and on the character of the additive. Thus the two chlorine atoms in **3** completely reversed the regioselectivity to an anti-Kharasch mode. The relative reaction rates were dramatically decreased with increasing number of terminal chlorine atoms in olefins **1–3**. The allylic chlorine atom in **1** appeared to mimic a longer perfluoroalkyl chain. Experimental results were compared with the shapes of frontier orbitals and electron densities calculated using PM3 and ab initio (3-12G and 6-311 + G**) methods. The transformations of the adducts to chlorofluoroalkyl methacrylates and fluorinated pentane-1,2-diol are reported. © 1997 Elsevier Science S.A.

Keywords: Halogenopropenes; Nucleophilic radical addition; Regioselectivity; Steric effect of chlorine; Quantum chemical calculations

1. Introduction

Radical additions to double bonds are a powerful chemical tool for the formation of new C–C bonds. In organic syntheses [6], including stereoselective reactions [7a,7b], large reaction partners can be combined by this method. Radical additions to fluorine-containing, three-carbon and higher olefins are of practical importance, because the reaction products can be employed as useful synthetic intermediates [8a–8c], as special monomers [9a,9b], e.g. highly sensitive electron-beam and X-ray resists for microlithography, or comonomers [5,9a,9b] and as biocompatible materials with improved oxygen transport capacity. Therefore it is of interest to investigate the effects of the chlorine atoms on the regioselectivity of addition and on the relative reactivity of chlorofluoropropenes in radical addition. Moreover, the effects of chlorine substituents on the regioselectivity of addition are of interest with regard to the general scope of radical addition.

In the series of chlorine- and fluorine-containing ethylenes, the fluorine and chlorine substituents can dramatically influence the regioselectivity, as demonstrated by the following examples of electrophilic CF_3 radical additions [10a,10b, 11a–11c]

$\underset{100\%}{CH_2{=}CH-Cl}$ $\quad$ $\underset{100\%}{CF_2{=}CH_2}$ $\quad$ $\underset{92\%}{CF_2{=}}\underset{8\%}{CH-Cl}$

The regioselectivities can be explained using the general rules [11a–11c,12a,12b] of radical addition to ethylenes substituted with p- and π-electron-active substituents and groups. In contrast, the prediction of the regioselectivity of addition in the series of fluorine-containing propenes is less clear as documented by the following experimental data from the reactions of CF_3 radicals [6,11a–11c,12a,12b]

$\underset{8\%}{CH_3-CH}{=}\underset{92\%}{CH_2}$ $\quad$ $CH_3-\underset{100\%}{CH}{=}CF_2$ $\quad$ $CF_3-\underset{2\%}{CH}{=}\underset{98\%}{CH_2}$

$\underset{25\%}{CF_3-CH}{=}\underset{75\%}{CH-F}$ $\quad$ $\underset{5\%}{CF_3-CF}{=}\underset{95\%}{CF_2}$

The influence of a chlorine substituent on the regioselectivity of radical addition to fluorine-containing propenes and higher terminal olefins would be expected to be great, because it

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[1] Part 1, Refs. [1a,1b]. Part 2, Ref. [2]. Part 3, Ref. [3]. Part 4, Ref. [4]. Part 5, Ref. [5].

[2] Prof. Dr. H.G.O. Becker on the occasion of his 75th birthday.

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completely reverses the regioselectivity of some nucleophilic additions [13].

The aim of this study was to determine the effects of chlorine substituents on the regioselectivity of radical addition to chlorine-substituted fluoropropenes as represented by structures **1–4** (see below).

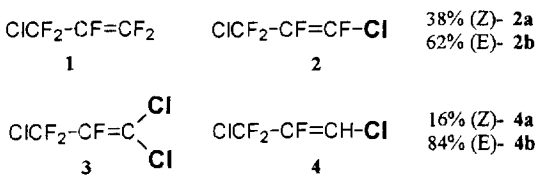
2. Results and discussion

2.1. Selection of reaction partners, type of initiation

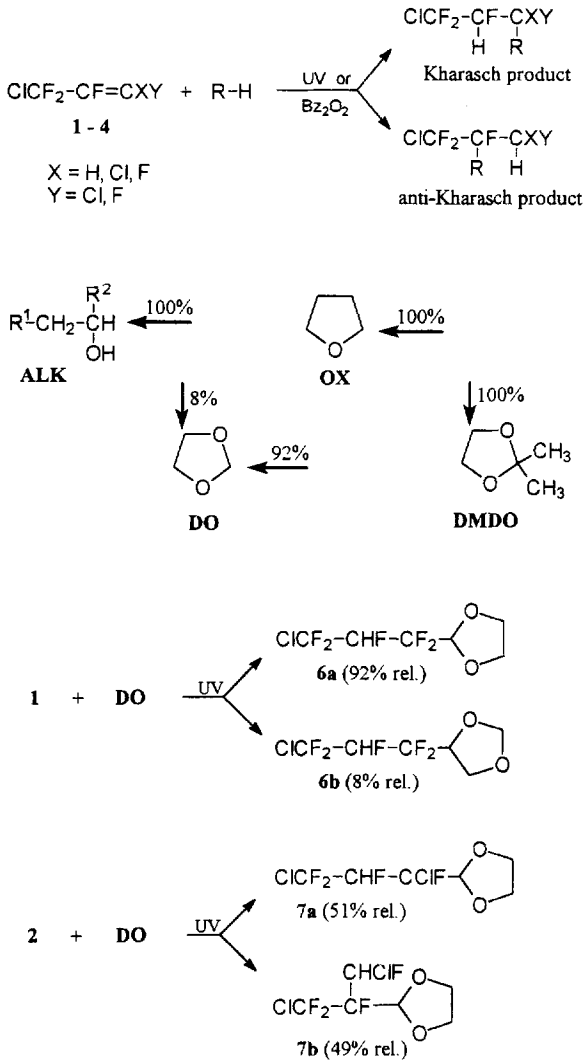
It is known from excellent reviews [10a,10b,12a,12b,14] on the addition reactions of halogenated species that interactions between radicals and olefins of opposite Lewis acid–base character are kinetically favoured. As highly fluorinated olefins, e.g. **1–4**, have electrophilic character, we employed nucleophilic radicals for the additions. 3-Chloropentafluoropropene (**1**, "perfluoroallyl chloride") was chosen as the basic olefinic structure modified at the terminal position with chlorine atoms (olefins **2** and **3**) or hydrogen (olefin **4**) (Scheme 1).

Nucleophilic radicals derived from alkanols and cyclic ethers (oxolane, 1,3-dioxolane, 2,2-dimethyl-1,3-dioxolane) were employed to test the regioselectivity of addition to chlorofluoropropenes **1–4**. It is known from the literature that they react easily with highly fluorinated aliphatic [15a–15d] and alicyclic [16a–16c] olefins, including 2,3,3-trifluoroacrylates using various initiators [17a,17b].

According to previous observations [4,15a–15d], a generalized scheme of the addition reactions of fluoropropenes **1–4** presupposes the formation of two regioisomeric adducts: a classical Kharasch product formed by the attack of radical R$^{\bullet}$ at the terminal position and an anti-Kharasch adduct (Scheme 2). The alkanols and cyclic ethers from which the radicals were generated in this study possess different kinds of cleavable C–H bond. In alkanols, oxolane (OX) and 2,2-dimethyl-1,3-dioxolane (DMDO), the homolytic cleavage of the C–H bonds takes place with complete regioselectivity (Scheme 2). An exception is 1,3-dioxolane (DO), with partial cleavage of the C–H bond at position 4. However, this incomplete selectivity was only observed in the reaction with olefin **1** (Scheme 2; products **6a** and **6b**, 92% and 8% respectively); a similar observation was reported [18] for addition to methyl-2,3,3-trifluoroacrylate with almost the same proportion of the minor adduct (9% rel.). In the addition of DO to sterically hindered olefin **2**, the cleavage of the C4–H bond is suppressed and only the C2–H bond is cleaved, but the addition is not completely regioselective on the double bond (Scheme 2; products **7a** and **7b**, see below).



Scheme 1.



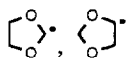
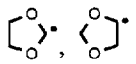
Scheme 2.

All reactions were carried out in the liquid phase and the radicals R$^{\bullet}$ were generated using dibenzoyl peroxide or by direct photochemical initiation. These different methods of initiation can result in different energies and concentrations of radicals R$^{\bullet}$ which, in turn, can influence the ratio of the regioisomeric adducts. Therefore we verified this ratio for olefin **2**, which is most sensitive to the nature of the attacking radical: the results in Table 2 confirm the lack of dependence of the adduct ratios on the type of initiation within experimental error ($\pm$ 1.5%).

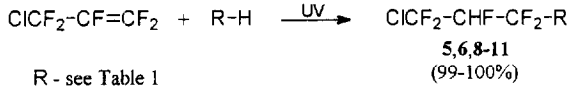
2.2. Regioselectivity of additions to 3-chloropentafluoropropene (1)

The additions of different nucleophilic radicals to olefin **1** (Scheme 3), listed in Table 1 (entries 1–6), reveal the complete regioselectivity from the point of view of the double bond, with a small exception for methanol (entry 1). These observations are in slight contrast with the additions to hexafluoropropene, which take place with a lower regioselectivity (Table 1, entries 7, 8, 11, 12).

Table 1
Regioselectivity of the addition of nucleophilic radicals R• to fluoroolefins R_F–CF=CF_2

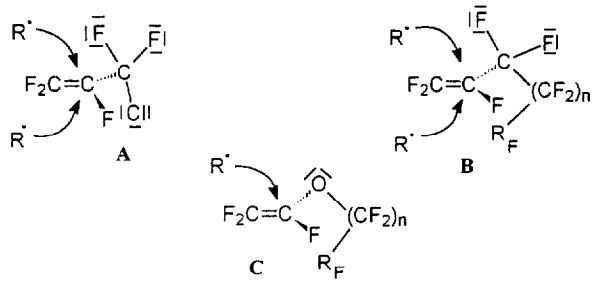
Entry	Fluoroolefin R_F	Radical R•	Attack to terminal C (%)	Product	Initiation	Reference
1	$ClCF_2$	$H_2\dot{C}(OH)$	99	**5**	UV	[a]
2	$ClCF_2$	$CH_3\dot{C}H(OH)$	100	**8**	UV	[a]
3	$ClCF_2$	$(CH_3)_2\dot{C}(OH)$	100	**9**	UV	[a]
4	$ClCF_2$		100	**10**	UV	[a]
5	$ClCF_2$		100 [b]	**6a, 6b**	UV	[a]
6	$ClCF_2$		100	**11**	UV	[a]
7	CF_3	$H_2\dot{C}(OH)$	96–97		UV	[19a]
8	CF_3	$H_2\dot{C}(OH)$	95.5–98		Peroxide	[15d]
9	CF_3	$CH_3\dot{C}H(OH)$	100		UV	[15d,19b]
10	CF_3	$(CH_3)_2\dot{C}(OH)$	100		UV	[15d,19b]
11	CF_3		99		UV	[4]
12	CF_3		99 [b]		UV	[20]
13	C_7F_{15}	$H_2\dot{C}(OH)$	100		UV	[20]
	C_7F_{15}	$H_2\dot{C}(OH)$	100		Peroxide	[20]
14	C_3F_7O	$H_2\dot{C}(OH)$	93		UV	[5]
15	C_3F_7O	$CH_3\dot{C}H(OH)$	96		UV	[5]
16	C_3F_7O	$(CH_3)_2\dot{C}(OH)$	99		UV	[5]
17	C_3F_7O		93		UV	[4]
					Peroxide	[4]
18	$C_3F_7OCF(CF_3)CF_2O$	$H_2\dot{C}(OH)$	95		UV	[4]
19	$C_3F_7OCF(CF_3)CF_2O$	$CH_3\dot{C}H(OH)$	>99		UV	[4]
20	$C_3F_7OCF(CF_3)CF_2O$	$(CH_3)_2\dot{C}(OH)$	100		UV	[5]
21	$C_3F_7OCF(CF_3)CF_2O$		94		UV	[4]
					Peroxide	[5]
22	$C_3F_7O[CF(CF_3)CF_2O]_2$		95		UV	[4]

[a] This paper.
[b] (92 + 8)% rel., see Scheme 2 and Table 2.



Scheme 3.

The exclusive attack of radicals on the terminal position in olefin **1** can be explained by the "tail effect" of the chlorine atom attached to C3. The situation is depicted in Scheme 4: the bulky Cl atom can protect the double bond from addition from one side and the CF_2 group from the other side (Scheme 4, **A**). The steric interactions between attacking radical and chlorine atom may include an electronic repulsion between the radical centre and the non-bonded electron pairs at the chlorine atom. A similar tail effect to that observed for the chlorine substituent in conformational state **A** can be caused by a long perfluorinated chain (Scheme 4, **B**), as



Scheme 4.

documented by the complete regioselectivity of methanol addition to perfluorinon-1-ene (Table 1, entry 13).

A generally lower regioselectivity of addition is found in reactions of perfluorovinyl ethers when compared with hexafluoropropene (Table 1, comparable entries: 7 and 14, 9 and 15, 10 and 16, 11 and 17). For these vinyl ethers, the regio-

Table 2
Regioselectivity of the addition to $ClCF_2$–CF=CF–Cl (**2**)

Entry	Radical R$^{\bullet}$	Terminal attack: $ClCF_2$–CHF–CFCl–R		Initiation
		(% rel.) [a]	Compound	
1	$CH_3\dot{C}H$–OH	73	**12a**	UV, Bz_2O_2
2	$(CH_3)_2\dot{C}$–OH	95	**13a**	UV, Bz_2O_2
3	$CH_3CH_2(CH_3)\dot{C}$–OH	95	**14a**	Bz_2O_2
4		52	**15a**	UV
5		51	**7a**	UV
6		51	**16a**	UV

[a] Calculated from the integral intensity of the signals in the ^{19}F NMR spectra; experimental error, ± 1.5%.

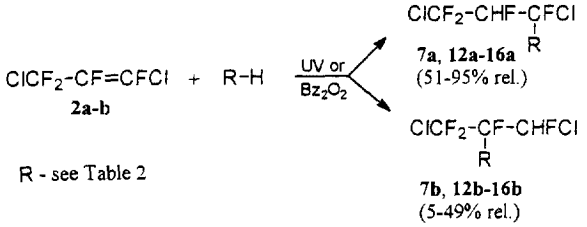
selectivity increases with increasing chain length (e.g. entries 14 and 18, 15 and 19 or 17 and 21). In the case of perfluorovinyl ethers, the lower regioselectivity is probably caused by the presence of an oxygen atom in the neighbourhood of the double bond instead of the CF_2 group (Scheme 4, **C**): one side of the double bond is less hindered by the oxygen atom than by the Cl or CF_2 group (Scheme 4, **A** and **B**).

2.3. Regioselectivity of addition to 1,3-dichlorotetrafluoropropene (2)

The substitution of one fluorine atom for chlorine at the terminal position in olefin **1** substantially changes the regioselectivity of addition: in all additions performed (Scheme 5, Table 2), two regioisomeric adducts were formed. The starting olefin **2** consisted of a mixture of (*Z*)-**2a** and (*E*)-**2b** isomers (38% and 62% rel., Scheme 1). By ^{19}F nuclear magnetic resonance (NMR), it was verified that the relative amounts remained constant during addition with both peroxide and photochemical initiation.

The ratio of terminal to internal attack of the double bond in olefin **2** is strongly dependent on the effective bulk of the attacking radicals (Table 2), which are all of approximately similar nucleophilic nature: hydroxyalkyl radicals (entries 1–3) are more bulky than oxolanyl radicals (entries 4–6) with a conformationally more rigid skeleton; branching in hydroxyalkyl radicals (entries 1–3) causes increased terminal attack up to 95% rel.; in contrast, methyl groups attached to the 1,3-dioxolane skeleton at C2 have no influence on the regioselectivity ratio and all five-membered cyclic ethers employed react with the same regioselectivity.

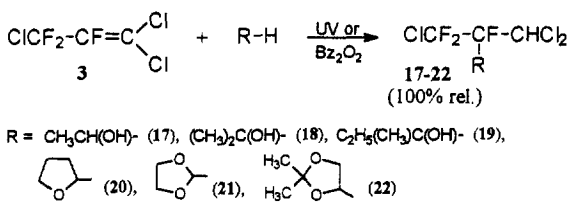
It can be concluded that the terminal chlorine atom exhibits a strong steric effect in the radical additions studied.



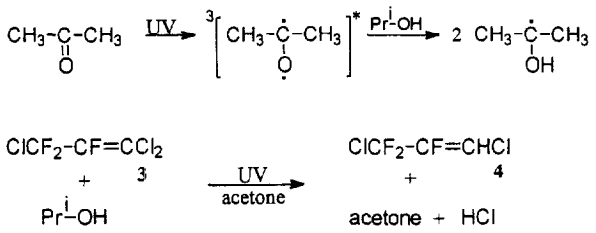
Scheme 5.

2.4. Regioselectivity of addition to 1,1,3-trichlorotrifluoropropene (3) and relative reaction rates

A dramatic change in regioselectivity is observed when two terminal chlorine atoms are attached to the double bond (olefin **3**): their effects completely reverse the regioselectivity of addition of the nucleophilic radicals and, in all reactions carried out (Scheme 6), only one anti-Kharasch regioisomer is formed. A similar effect of two terminal chlorine substituents was observed [13] in nucleophilic additions to $C_2F_5CF{=}CCl_2$, affording mainly or exclusively a Markovnikov adduct, while nucleophilic additions to $F(CF_2)_n$-$CF{=}CF_2$ were fully regioselective in terminal attack [21a,21b].



Scheme 6.



Scheme 7.

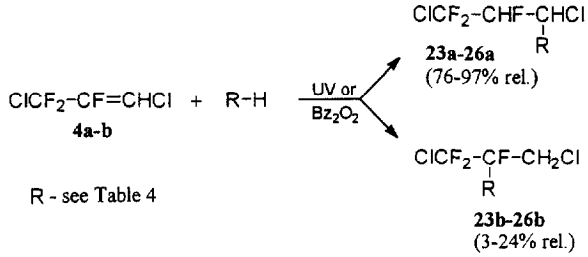
The inversion of regioselectivity when comparing olefin **3** with olefin **1** is combined with a dramatic decrease in the reaction rate. To obtain a quantitative comparison of the olefin reactivity, we carried out kinetic measurements at photostationary conditions in the same manner as described previously [1a,1]: 2-propanol was chosen as the additive as it is easily transformed into a pair of dimethylketyl radicals (2-hydroxy-2-propanyl) by reaction with triplet-excited acetone (Scheme 7); in this arrangement, the light was absorbed by acetone acting as a photosensitizer and the initiation process was independent of the olefins present. In the experiments, we also observed the reduction of a C–Cl bond to a C–H bond (Scheme 7). A similar photoreduction of a vinylic carbon–halogen bond has been reported previously [22a–22d].

The relative rates of addition were measured as parallel reactions in the initial period of addition until the rates obeyed a pseudo-zero-order kinetic dependence (gas chromatography (GC) calibrated measurement of the concentrations of the products). The results are presented in Table 3. They reveal that, in the olefin series **1–3**, the rate of addition decreases with increasing number of chlorine atoms at the terminal position. A dramatic decrease in the reaction rate of fluoroolefin **3** can be attributed to the steric hindrance of the terminal chlorine substituents.

We also compared the reactivity of olefin **2** with its hydrogenated analogue, olefin **4** (see Section 4; concentrations were followed by NMR). It is expected that the terminal =CHCl group in olefin **4** will be more easily attacked than =CFCl in olefin **2** from the steric or electronic repulsion point of view. However, olefin **4** appears to be less reactive. This surprising result can be explained in terms of the polar interactions between the attacking radical and olefinic carbon: at C1 of the =CFCl group of olefin **2**, the electron density is decreased relative to that at C2 to a greater degree than in the case of the =CHCl group of olefin **4** (Table 5, see below), thus enabling an easier interaction with the nucleophilic radical [10a,10b]. Similar observations have been reported for additions to halogenoethylenes [10a,10b,11a–11c].

Table 3
Relative reaction rates of the photosensitized addition of 2-propanol to halogenopropenes **1–3**

Fluoroolefin $ClCF_2$–CF=CXY			Relative rate
No.	X	Y	
1	F	F	355
2	F	Cl	50
3	Cl	Cl	1–4



Scheme 8.

2.5. Regioselectivity of addition to 1,3-dichloro-2,3,3-trifluoropropene (4)

The change of fluorine for hydrogen at the terminal position in olefin **2**, i.e. change to structure **4**, produces a better regioselectivity in all the addition reactions tested (Table 4) (Scheme 8): the apparently higher regioselectivity of addition of cyclic ethers to olefin **4**, when compared with that to halogenopropene **2**, is surprising in view of its lower reactivity (see above). Several factors can be considered to control the regioselectivity:

1. H and F have van der Waals' radii (120 and 135 pm respectively), and therefore steric hindrance can be excluded as an explanation for the better regioselectivity of **4**;
2. fluorine attached to a double bond usually develops a positive charge at the carbon to which it is attached (Table 5), and hence causes an easier attack of a nucleophilic radical; however, an opposite effect is observed;
3. a fluorine substituent differs from a hydrogen atom in that non-bonded electron pairs are present that may cause electronic repulsion of an attacking radical; this factor is in accord with the observations.

A similar effect has been observed in the addition of methyl radicals to 1,1-difluoroethene [10a,10]. Thus electronic repulsion by the fluorine substituent seems to be one factor responsible for the decreased regioselectivity of radical addition to halogenopropene **2** when compared with that to olefin **4**.

2.6. Electronic structure and regioselectivity of addition

Frontier orbital theory can be a useful tool in the rationalization and prediction of the experimental behaviour of addition reactions. The nature of the interaction between radicals and olefins is given by the corresponding interaction of the frontier orbitals of both reaction partners. According to the analysis of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, all the radicals studied seem to be nucleophiles in comparison with the studied olefins, regardless of whether PM3 or ab initio quantum-chemical methods are used [23,24] (Table 5). The interaction of the SOMO of a radical and the

Table 4
Regioselectivity of the additions to $ClCF_2$–CF=CH–Cl (**4**)

Radical R$^{\bullet}$	Products (% rel.)			Initiation
	No.	Cl-CF_2-CHF-CHCl (R)	Cl-CF_2-CF-CH_2Cl (R)	
$CH_3\dot{C}H$(OH)	**23a, 23b**	86	14	Bz_2O_2
$(CH_3)_2\dot{C}$(OH)	**24a, 24b**	97	3	UV, Bz_2O_2
	**25a, 25b**	76	24	UV
	**26a, 26b**	76	24	UV

Table 5
Energies of frontier orbitals for olefins and radicals and total charges on the double bond (charges in 10^{-3} units of electron charge)

Fluoroolefin	PM3 [a]			3-21G [b]			6-311+G [b]		
	HOMO (eV)	LUMO (eV)	Charge	HOMO (a.u.)	LUMO (a.u.)	Charge	HOMO (a.u.)	LUMO (a.u.)	Charge
1 $ClCF_2$–CF=**CF_2**	−11.39	−1.16	C1 0.21 C2 −0.13	−0.431	0.132	C1 0.85 C2 0.27	−0.423	0.150	C1 0.74 C2 0.14
2 $ClCF_2$–CF=**CClF**	−10.66	−1.05	C1 −0.01 C2 −0.10				−0.411	0.128	C1 0.30 C2 0.31
3 $ClCF_2$–CF=**CCl_2**	−10.24	−0.95	C1 −0.24 C2 −0.07	−0.413	0.096	C1 −0.73 C2 0.54	−0.402	0.107	C1 −0.23 C2 0.48
4 $ClCF_2$–CF=**CHCl**	−10.36	−0.68	C1 −0.18 C2 −0.08				−0.404	0.068	C1 −0.242 C2 0.383
Radical R$^{\bullet}$	SOMO (eV)			SOMO (a.u.)			SOMO (a.u.)		
$CH_3\dot{C}H$(OH)	−3.46			−0.042			−0.051		
$(CH_3)_2\dot{C}$(OH)	−3.58			−0.043					
	−3.40			−0.044					
	−3.76			−0.057					

[a] Ref. 23.
[b] Ref. 24.

LUMO of an olefin is thus responsible for product formation. In the case of olefins **1** and **3**, the preferred radical attack, i.e. favourable overlap of both orbitals (SOMO and LUMO), is in complete agreement with the experimental results (Fig. 1, Table 5). However, the regioselectivity predicted by frontier orbital interactions does not take into account the different steric requirements of the reacting radicals.

An analogous analysis for olefins **2** and **4** leads to less satisfactory conclusions: both types of radical attack, i.e. "inner" and "end", have the same probability. These results reflect the experimental results discussed above (Tables 2 and 4), showing a strong regioselectivity dependence on the effective bulkiness of the radical. On the basis of qualitative frontier orbital theory, a more detailed analysis of the different and changing regioselectivities for these two olefins is not possible. The effects of solvation, for example, probably have an important influence on the reaction course, but they cannot be analysed by this relatively simple quantum-chemical interpretation. The thermodynamic stabilities of the possible "inner" and "end" adducts of olefins **2** and **4** also

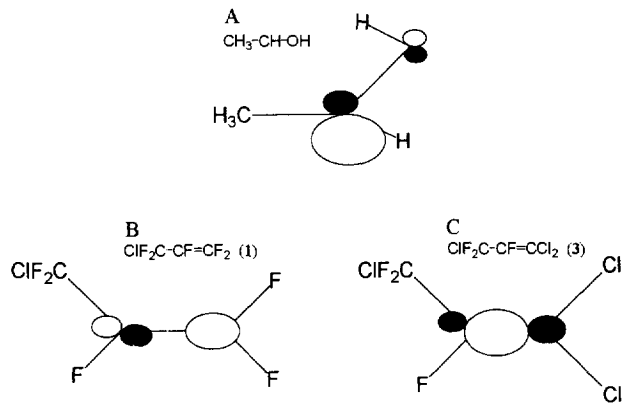


Fig. 1. Natural frontier orbitals:A SOMO, B LUMO, C LUMO.

do not provide clear results: both adduct radicals display comparable thermodynamic stabilities (practically equal heats of formation) strongly influenced by conformation. The thermodynamic calculations thus support the incomplete regioselectivity of the addition reactions for olefins **2** and **4** as observed experimentally.

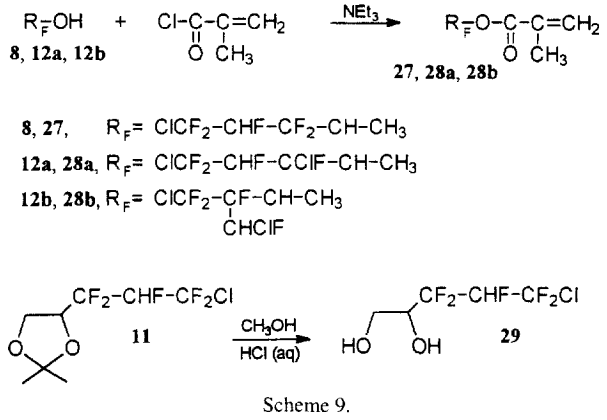
The regioselectivity of kinetically controlled reactions can be interpreted on the basis of electron charge distributions. On the other hand, a correlation of the charge distribution with regioselectivity can be understood as theoretical support for kinetic control. In the case of olefins **1** and **3**, the nucleophilic nature of the radicals must lead to preferred interactions with more positively charged carbon atoms (Table 5), in agreement with the experimental findings. It is interesting that the polarity of the double bond is reversed when terminal fluorines are substituted by chlorine atoms (Table 5). In the case of olefins **2** and **4**, analogous predictions of the regioselectivity of addition are not possible because the differences in the total charges of C1 and C2 for olefins **2** and **4** are very small (Table 5), with the exception of the 6-311 + G** calculation for olefin **4** (Table 5). In contrast with the experimental results (Table 2 and Table 4), however, all values predict a better terminal attack by a nucleophilic radical for olefin **2**.

The results obtained allow us to formulate the following conclusions:

1. both treatments, i.e. frontier orbital interactions and charge distributions, give qualitatively similar results;
2. the reactions studied are probably kinetically controlled;
3. the experimental data on radical addition regioselectivity can be explained on the basis of the quantum-chemical calculations used;
4. the total charge distributions on the double-bonded carbons and the shapes of the frontier orbitals reveal that the polar effects of the chlorine substituents contribute substantially to the observed regioselectivity changes.

2.7. *Transformations of addition products: methacrylates of alkanols and hydrolysis of dioxolane adduct*

Chlorofluoroalkanols are more acidic than alkanols owing to the electronegativity of the fluoro and chloro substituents.



Scheme 9.

Their transformation to esters by esterification is not possible; instead, acylation was used [9a] (Scheme 9). The conversions of fluoroalkanols **8**, **12a** and **12b** were above 95%. Asymmetric centres in the starting fluoroalkanols were transferred into the corresponding fluoroalkyl methacrylates **27**, **28a** and **28b** without any change: according to the NMR spectra, methacrylate **27** consisted of two diastereoisomers in a ratio of 47% and 53% rel., i.e. the same ratio as in the starting fluoroalkanol **8**; regioisomeric methacrylate **28a**, with three asymmetric carbons, consisted of four pairs of enantiomers in the ratio of 23%, 23%, 24% and 30% rel. as in alkanol **12a**; similarly, the diastereoisomeric composition of regioisomeric methacrylate **28b** corresponded to starting alkanol **12b** as documented by values of 14%, 22%, 28% and 36% rel.

2.8. *Structural elucidation*

The structures of products **5–26** were confirmed on the basis of elemental analyses (Table 6) and ^{1}H and ^{19}F NMR spectra. Regioisomeric adducts, when formed, were not separated, and elemental analyses are given for their mixtures.

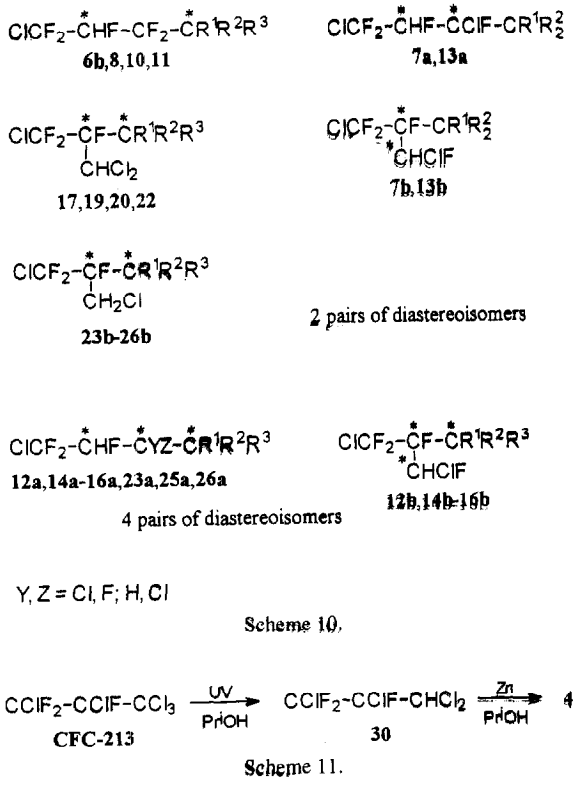
Each addition product consisted of several configurational isomers. In the additions to olefins **1** and **3**, two new chiral centres were created and two pairs of diastereoisomers were formed (**6b**, **7a**, **7b**, **8**, **10**, **11**, **13a**, **13b**, **17**, **19**, **20**, **22**, **23b–26b**; Scheme 10). In the case of fluoroolefin **2**, three chiral centres were sometimes created and four pairs of diastereoisomers for each of the two regioisomers were formed (**12a**, **14a–16a**, **23a**, **25a**, **26a** and **12b**, **14b–16b**; Scheme 10), i.e. the NMR spectrum of such a compound contained complex signals of eight regioisomers and diastereoisomers.

Simpler NMR spectra were obtained in the case of the products of addition to olefin **4** because they contained signals of only six regioisomers and stereoisomers (**23a** + **23b**, **25a** + **25b**, **26a** + **26b**). We were successful in assigning the signals of the ^{1}H and ^{19}F NMR spectra to individual diastereoisomers (see Table 7) by means of their integral intensity, signal multiplicity and coupling constants.

Table 6
Reaction and analytical data for products **6–26**

Olefin	Additive [a] (g)		Time (h)	Conversion of olefin (%)	Product obtained						Found (%) (required)			
					No.	Yield [c]		B.p. (°C) [mmHg]	Formula	M.W.	C	H	Cl	F
						(g)	(%)							
1	MeOH	16.02	3	98	**5**	8.24	83	77–79 [60]	$C_4H_4ClF_5O$	198.5	24.3 (24.2)	2.10 (2.03)	17.75 (17.9)	47.9 (47.85)
1	DO	37.04	2	99	**6**	10.22	85	91–93 [40]	$C_6H_6ClF_5O_2$	240.6	30.3 (30.0)	2.87 (2.51)	14.55 (14.7)	39.7 (39.5)
2	DO	11.11	6	90	**7**	6.17	80	90–92 [20]	$C_6H_6Cl_2F_4O_2$	257.1	28.5 (28.4)	2.57 (2.35)	27.1 (27.5)	29.9 (29.6)
1	EtOH	23.04	2.5	99	**8**	8.18	77	70–72 [50]	$C_5H_6ClF_5O$	212.6	28.5 (28.25)	2.86 (2.85)	16.4 (16.7)	44.7 (44.7)
1	Pr^{i}OH	30.05	2	99	**9**	10.00	88	77–79 [50]	$C_6H_8ClF_5O$	226.6	32.3 (31.81)	3.93 (3.56)	15.0 (15.65)	41.1 (41.9)
1	OX	36.06	2	99	**10**	10.10	85	80–82 [40]	$C_7H_8ClF_5O$	238.6	35.6 (35.2)	3.40 (3.38)	15.13 (14.9)	39.6 (39.8)
1	DMDO	51.07	2	99	**11**	11.68	87	95–97 [40]	$C_8H_{10}ClF_5O_2$	268.6	35.9 (35.8)	3.81 (3.75)	12.95 (13.2)	35.1 (35.4)
2	EtOH	6.91	5	80	**12**	4.12	60	92–94 [40]	$C_5H_6Cl_2F_4O$	229.0	26.6 (26.2)	2.72 (2.64)	30.2 (30.9)	33.9 (33.2)
2	EtOH	6.90	6 [b]	77	**12**	3.98	58 [d]	81–83 [20]						
2	Pr^{i}OH	9.02	3	87	**13**	5.61	77	95–97 [35]	$C_6H_8Cl_2F_4O$	243.0	29.6 (29.65)	3.66 (3.32)	29.8 (29.2)	32.0 (31.27)
2	Pr^{i}OH	9.00	6 [b]	80	**13**	4.37	60 [d]	85–87 [20]						
2	Bu^{s}OH	11.12	6 [b]	70	**14**	4.24	55 [d]	80–82 [8]	$C_7H_{10}Cl_2F_4O$	257.1	32.9 (32.7)	4.24 (3.92)	27.4 (27.6)	29.9 (29.6)
2	OX	10.82	5	88	**15**	5.28	69	93–95 [30]	$C_7H_8Cl_2F_4O$	255.0	33.2 (33.0)	2.80 (3.16)	26.9 (27.8)	30.2 (29.8)
2	DMDO	15.32	5	90	**16**	6.84	80	94–96 [20]	$C_8H_{10}Cl_2F_4O_2$	285.1	33.6 (33.7)	3.61 (3.54)	24.7 (24.9)	27.35 (26.7)
3	EtOH	6.91	9	73	**17**	4.57	62 [d]	81–83 [10]	$C_5H_6Cl_3F_3O$	245.5	24.7 (24.5)	2.89 (2.46)	42.95 (43.3)	24.0 (23.22)
3	Pr^{i}OH	9.02	7	75	**18**	5.22	67 [d]	80–82 [5]	$C_6H_8Cl_3F_3O$	259.5	28.0 (27.8)	3.52 (3.11)	40.2 (41.0)	21.25 (22.0)
3	Bu^{s}OH	11.12	9	71	**19**	5.09	62 [d]	96–98 [3]	$C_7H_{10}Cl_3F_3O$	273.5	30.6 (30.7)	3.84 (3.69)	38.6 (38.9)	20.2 (20.8)
3	OX	10.82	7	75	**20**	5.38	66 [d]	75–77 [3]	$C_7H_8Cl_3F_3O$	271.5	31.4 (31.0)	3.23 (2.97)	38.9 (39.2)	21.2 (21.0)
3	DO	11.11	8	74	**21**	5.25	64 [d]	82–84 [3]	$C_6H_6Cl_3F_3O_2$	273.5	26.8 (26.35)	2.44 (2.21)	38.2 (38.9)	21.0 (20.8)
3	DMDO	15.32	7	74	**22**	5.88	65 [d]	87–89 [3]	$C_8H_{10}Cl_3F_3O_2$	301.5	31.7 (31.9)	3.21 (3.34)	34.9 (35.3)	18.7 (18.9)
4	EtOH	6.91	15	70	**23**	3.36	53 [d]	96–98 [40]	$C_5H_7Cl_2F_3O$	211.0	28.3 (28.5)	3.40 (3.34)	33.4 (33.6)	27.4 (27.0)
4	Pr^{i}OH	9.02	12	78	**24**	4.39	65 [d]	97–99 [30]	$C_6H_9Cl_2F_3O$	225.0	32.1 (32.0)	4.12 (4.03)	31.4 (31.5)	25.55 (25.3)
4	OX	10.82	14	73	**25**	4.41	62 [d]	90–92 [20]	$C_7H_9Cl_2F_3O$	237.1	35.3 (35.5)	3.89 (3.83)	30.2 (29.9)	24.3 (24.0)
4	DMDO	15.32	13	70	**26**	5.05	63 [d]	91–93 [15]	$C_8H_{11}Cl_2F_3O_2$	267.1	35.9 (36.0)	4.21 (4.15)	26.4 (26.55)	21.45 (21.3)

[a] OX, oxolane; DO, 1,3-dioxolane; DMDO, 2,2-dimethyl-1,3-dioxolane.
[b] Initiation by dibenzoyl peroxide.
[c] Purity 99%.
[d] Purity 98%.



Scheme 10.

Scheme 11.

2.9. Synthesis of 1,3-dichloro-2,3,3-trifluoropropene (4)

Compound **4** was prepared by a new two-step synthesis (Scheme 11). In the first step, the starting 1,2,3,3,3-pentachloro-1,1,2-trifluoropropane [25] (CFC-213) was transformed selectively to monohydrogenated alkane **30** by photochemical reduction [26a,26b]. In the second step, we used modified conditions for the dehalogenation [27a,27b] of compound **30** to olefin **4**.

3. Conclusions

The strong effect of the terminal chlorine atom in highly fluorinated propenes on the regioselectivity of addition of nucleophilic radicals was confirmed. The effect of two chlorine atoms (instead of fluorine atoms) at the terminal position (olefin **3** vs. **1**) appeared to be sufficiently strong to reverse completely the regioselectivity of the addition from the Kharasch to the anti-Kharasch mode. In the case of one terminal chlorine (olefin **2**), the regioselectivity ratio of the Kharasch and anti-Kharasch adducts was strongly dependent on the effective bulkiness of the radicals. The influence of chlorine on the regioselectivity can be explained by a steric (repulsive) effect, combined with a dramatic decrease in the reaction rate, and by polar effects, as expressed by frontier orbitals and total electron densities. Some evidence of a steric repulsive effect of the fluorine atom relative to the hydrogen atom was obtained. The regioselectivity of addition is also influenced by the character of the fluorinated chain attached to trifluorovinyl in terminal fluoroolefins: longer perfluoroalkyls, as well as a chlorine atom in the CF_2Cl group, improve the regioselectivity, whereas in perfluorovinyl ethers the regioselectivity is relatively decreased. It has been verified that the allylic chlorine in **1** mimics a longer perfluoroalkylated chain, which enables the prediction of a similar regioselectivity for the addition reactions of long-chain perfluoroalkyl analogues of olefins **1–4**.

4. Experimental details

4.1. General comments

The temperature data were not corrected. Distillations of high boiling compounds were carried out on a Vacuubrand RC5 high vacuum oil pump. GC analyses were performed on a Chrom 5 instrument (see Ref. [27b]; silicon elastomer E-301 (GCa), poly(butane diol succinate) (GCb), nitrogen). NMR spectra were recorded on Bruker 400 AM (FT, ^{19}F at 376.5 MHz) and Bruker WP 80 SY (FT, ^{19}F at 75 MHz) instruments; tetramethylsilane (TMS) and $CFCl_3$ were used as the internal standards; chemical shifts were given in parts per million (s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quadruplet; qi, quintuplet; sex, sextuplet; sep, septuplet; m, multiplet) and coupling constants *J* in hertz.

The chemicals used were as follows; chlorofluoropropenes **1–3** [27b], 1,3-dioxolane (Fluka) and 2,2-dimethyl-1,3-dioxolane [28] (yield, 83%; 1,1,2-trichlorotrifluoroethane (CFC-113) was used as azeotropic solvent) were prepared according to the literature procedures; silica gel L40/100 (Merck); 2,2-diphenyl-1-picrylhydrazyl (Aldrich); methacryloyl chloride (Fluka) was distilled before use; oxolane (Fluka); ethanol, 2-propanol, 2-butanol and acetone were dried and purified according to standard procedures [29].

Quantum chemistry calculations were performed: PM3 (program MOPAC6) [23]; ab initio bases 3-21G and 6-311+G** (program GAUSSIAN94) [24].

4.2. Photoinduced additions to 3-chloro-1,1,2,3,3-pentafluoropropene (1) (products 5, 6 and 8–11)

Reactions were carried out in an immersion-well photoreactor (75 ml) cooled from outside to −15 to −5 °C; a medium-pressure UV lamp (Tesla, RVK 125) in a water-cooled double jacket (quartz and Simax® glass, gas inlet) was used as light source; a dry-ice-cooled spiral reflux condenser was connected to a dry-ice-cooled trap which was connected to atmosphere through a hydraulic seal with sulphuric acid. The reactor was charged with additive (0.5 mol) and the apparatus was flushed with argon for 2 h with cooling. Gaseous olefin **1** (8.32 g, 50 mmol) was then introduced into the photoreactor on irradiation and the conversion of olefin **1** was monitored by GC. The surplus additive was distilled off using a distillation column (15 cm, Berle saddles) and the pure product was obtained by distillation under vacuum (for

Table 7
NMR spectral data for products **6–29** (^{1}H NMR: 400 MHz, $CDCl_3$, Me_4Si; ^{19}F NMR: 376 MHz, $CDCl_3$, CCl_3F)

Compd.	Structure[a]	Diastereo-isomers (% rel.)	^{1}H NMR	^{19}F NMR
5a	$CClF_2CHFCF_2CH_2OH$		3.10 (1 H, bs, OH), 3.95 (2 H, t, $^3J_{HF}$ = 12, CH_2O), 5.04 (1 H, ddq, $^2J_{HF}$ = 43, $^3J_{HF}$ = 6, 12(q), CHF)	-62.13 (1 F(a), dddt, $^2J_{FF}$ = 179, $^3J_{FF}$ = 16, $^4J_{FF}$ = 12(t), $^3J_{HF}$ = 6, $CClF_2$), -64.13 (1 F(b), ddq, $^2J_{FF}$ = 179, $^3J_{FF}$ = 16, $^3J_{HF}$ = $^4J_{FF}$ = 12(q), $CClF_2$), -117.42 (1 F(a), ddsex, $^2J_{FF}$ = 274, $^3J_{HF}$ = 12(sex), $^3J_{FF}$ = 7, CF_2), -121.66 (1 F(b), dsep, $^2J_{FF}$ = 274, $^3J_{HF}$ = $^3J_{FF}$ = $^4J_{FF}$ = 12(sep), CF_2), -203.74 (1 F, dddt, $^2J_{HF}$ = 43, $^3J_{FF}$ = 16(t), 12, 7, CHF)
5b	$CClF_2CF(CH_2OH)CHF_2$		3.10 (1 H, bs, OH), 4.00 (2 H, d, $^3J_{HF}$ = 5, CH_2), 6.18 (1 H, dt, $^2J_{HF}$ = 53(t), $^3J_{HF}$ = 5, CHF_2)	-62.21, -64.23 (2 F, 2 x ddt, $^2J_{FF}$ = 179, $^3J_{FF}$ = 12, $^4J_{FF}$ = 9(t), $CClF_2$), -133.81 (2 F, ddt, $^2J_{HF}$ = 53, $^3J_{FF}$ = 7, $^4J_{FF}$ = 9(t), CHF_2), -184.38 (1 F, ttq, $^3J_{FF}$ = 12, 7, $^3J_{HF}$ = 5(q), CF)
6a	$CClF_2CHFCF_2$-Do		4.08-4.12 (4 H, m,CH_2O), 5.03 (1 H, dddt, $^2J_{HF}$ = 42, $^3J_{HF}$ = 9, 6(t) and 2, CHF), 5.30 (1 H, ddd, $^3J_{HF}$ = 10 and 5, $^4J_{HF}$ = 2, CHO)	-61.94, -64.06 (2 F, 2 x dddt, $^2J_{FF}$ = 178, $^3J_{FF}$ = 17, $^4J_{FF}$ = 12(t), $^3J_{HF}$ = 9 or 6, $CClF_2$), -128.45 (2 F, dddt, $^4J_{FF}$ = 12(t), $^3J_{FF}$ = 9, $^3J_{HF}$ = 10 or 5, 6 or 2, CF_2), -205.65 (1 F, ddtt, $^2J_{HF}$ = 42, $^3J_{FF}$ = 17(t) and 9(t), $^4J_{HF}$ = 2, CHF)
6b	$CClF_2CHFCF_2$-Dox	A(55) B(45)	4.20 (2 H, m, CH_2O), 4.42 (2 H, s, CH_2O), 4.55 (1 H, m, CHO), 5.04 (1 H, m, CHF)	-61.16, -61.71 (1 F(a), 2 x m, $CClF_2$), -63.75, -64.32 (1 F(b), 2 x m, $CClF_2$), -118.46, -121.57, -125.06 and -127.37 (2 F, 4 x dm, $^2J_{FF}$ = 271, CF_2), -202.76, -207.10 (1 F(A,B), 2 x dm, $^2J_{HF}$ = 43, CHF)
7a	$CClF_2CHFCClF$-Do	A(55) B(45)	4.11 (4 H, m, 2 CH_2O), 5.13 (1 H(B), ddt, $^2J_{HF}$ = 43, $^3J_{HF}$ = 16, 12(t), CHF), 5.14 (1 H (A), dt, $^2J_{HF}$ = 43, $^3J_{HF}$ = 4 (t), CHF), 5.41 (1 H(B), d, $^3J_{HF}$ = 4, CH), 5.42 (1 H(A), d, $^3J_{HF}$ = 23, CH)	-57.90, -58.08 (1 F(F(a), A,B), 2 x ddt, $^2J_{FF}$ = 177, $^3J_{FF}$ = $^4J_{FF}$ = 15, 16(t), $^3J_{HF}$ = 12, 4, $CClF_2$), -62.68 (1 F(F(b), B), ddt, $^2J_{FF}$ = 177, $^3J_{FF}$ = $^4J_{FF}$ = 16(t), $^3J_{HF}$ = 12, $CClF_2$), -62.81 (1 F(F(b), A), dddd, $^2J_{FF}$ = 177, $^3J_{FF}$ = 15, $^4J_{FF}$ = 6, $^3J_{HF}$ = 4, $CClF_2$), -137.21 (1 F(A), ddt, $^3J_{HF}$ = 23, $^3J_{FF}$ = 15, $^4J_{FF}$ = 15, 6, CClF), -140.05 (1 F(B), dqi, $^4J_{FF}$ = = $^3J_{FF}$ = 16(q), $^3J_{HF}$ = 16, 4, CClF), -194.0, -196.0 (1 F(A,B), 2 x dq, $^2J_{HF}$ = 43, $^3J_{FF}$ = = 15, 16(q), CHF)
7b	$CClF_2CF(Do)CHClF$	A(57) B(43)	4.11 (4 H, m, 2 CH_2O), 5.57, 5.59 (1 H (A,B), 2 x d, $^3J_{HF}$ = 15, 13, CH), 6.51, 6.57 (1 H(A,B), 2 x dd, $^2J_{HF}$ = 48, $^3J_{HF}$ = 6, CHClF)	-57.61 (1 F(F(a), B), dt, $^2J_{FF}$ = 177, $^3J_{FF}$ = $^4J_{FF}$ = 11(t), $CClF_2$), -57.70 (1 F (F(a), A), ddd, $^2J_{FF}$ = 177, $^4J_{FF}$ = 15, $^3J_{FF}$ = 8, $CClF_2$), -60.10, -62.52 (1 F(F(b), B,A), 2 x ddd, $^2J_{FF}$ = 177, $^4J_{FF}$ = 16, 15, $^3J_{FF}$ = 11, 8, $CClF_2$), -151.22 (1 F(B), ddt, $^2J_{HF}$ = 48, $^4J_{FF}$ = 16, 11, $^3J_{FF}$ = 11, CHClF), -153.31 (1 F (A), dq, $^2J_{HF}$ = 48, $^4J_{FF}$ = $^3J_{FF}$ = 15(q), CHClF), -178.42 (1 F(A), dtt, $^3J_{FF}$ = 15, 8(t), $^3J_{HF}$ = 15, 6, CF), -179.43 (1 F(B), ddq, $^3J_{FF}$ = 11(q), $^3J_{HF}$ = 13, 6, CF)
8	$CClF_2CHFCF_2CH(CH_3)OH$	A(53) B(47)	1.41 (3 H, d, $^3J_{HH}$ = 6, CH_3), 2.50, 2.72 (1 H (A,B), 2 x bs, OH), 4.18 (1 H, m, CH), 5.13 (1 H(A), ddddd, $^2J_{HF}$ = 42, $^3J_{HF}$ = 14, 11, 5, 3, CHF), 5.15 (1 H(B), ddddd, $^2J_{HF}$ = 44, $^3J_{HF}$ = 14, 11, 10, 5, CHF)	-61.41 (1 F(F(a), B), dtt, $^2J_{FF}$ = 177, $^3J_{FF}$ = $^3J_{HF}$ = 14(t), $^4J_{FF}$ = 11(t), $CClF_2$), -61.83 (1 F(F(a), A), ddq, $^2J_{FF}$ = 177, $^3J_{FF}$ = $^3J_{HF}$ = $^4J_{FF}$ = 14(q), $^4J_{FF}$ = 11, $CClF_2$), -63.84 (1 F (F(b), A), $^2J_{FF}$ = 177, $^3J_{FF}$ = $^4J_{FF}$ = 14(q), $^3J_{HF}$ = 11, $CClF_2$), -64.40 (1 F(F(b), B), dddt, $^2J_{FF}$ = 177, $^3J_{FF}$ = 14, $^4J_{FF}$ = 11(t), $^3J_{HF}$ = 5, $CClF_2$), -120.71, -124.72 (2 F(B), 2 x ddq, $^2J_{FF}$ = 270, $^3J_{FF}$ = 14, $^3J_{HF}$ = $^4J_{FF}$ = 11(q), CF_2), -125.02 (1 F(F(a), A), ddq, $^2J_{FF}$ = 270, $^3J_{FF}$ = $^4J_{FF}$ = 14(q), $^3J_{HF}$ = 5, CF_2), -130.64 (1 F(F(b), A), dddt, $^2J_{FF}$ = 270, $^4J_{FF}$ = 14, 11, $^3J_{FF}$ = $^3J_{HF}$ = 3, CF_2), -203.04 (1 F(A), ddq, $^2J_{HF}$ = 42, $^3J_{FF}$ = 14(q), 3, CHF), -204.82 (1 F(B), dqi, $^2J_{HF}$ = 44, $^3J_{FF}$ = 14(qi), CHF)
9	$CClF_2CHFCF_2C(CH_3)_2OH$		1.36, 1.40 (6 H, 2 x s, 2 CH_3), 2.58 (1 H, bs, OH), 5.23 (1 H, ddddd, $^2J_{HF}$ = 43, $^3J_{HF}$ = 17, 11, 6, 1, CHF)	-60.24, -63.97 (2 F, 2 x dddt, $^2J_{FF}$ = 177, $^4J_{FF}$ = 20, $^3J_{FF}$ = 15, $^3J_{HF}$ = $^4J_{FF}$ = 11(t) or 6(t), $CClF_2$), -123.19 (1 F(a), dddt, $^2J_{FF}$ = 274, $^4J_{FF}$ = 20(t), $^3J_{FF}$ = 4, $^3J_{HF}$ = 1, CF_2), -126.47 (1F(b), dddt, $^2J_{FF}$ = 274, $^4J_{FF}$ = 11, 6, $^3J_{FF}$ = 11, $^3J_{HF}$ = 17, CF_2), -196.70 (1 F, dddt, $^2J_{HF}$ = 43, $^3J_{FF}$ = 15(t), 11, 4, CHF)

[a] Dmdo - 2,2-dimethyl-1,3-dioxolan-4-yl, Ox - oxolan-2-yl.

(*continued*)

Table 7 (*continued*)

Compd.	Structure[a]	Diastereo-isomers (% rel.)	^{1}H NMR	^{19}F NMR	J(Hz)
10	$CClF_2CHFCF_2$-Ox	A(55) B(45)	2.14 (4 H, m, CH_2), 3.90 (2 H, m, CH_2O), 4.30 (1 H, m, CHO), 5.08, 5.10 (1 H(B,A), 2 x ddddd, CHF)	-60.95 (1 F(F(a), B), dddt, $CClF_2$), -61.57 (1 F(F(a), A), dddd, $CClF_2$), -63.75 (1 F(F(b), A), ddq, $CClF_2$), -64.39 (1 F(F(b), B), ddt, $CClF_2$), -119.50, -122.50 (2 F(B), 2 x ddq, CF_2), -124.51 (1 F(F(a), A), dddd, CF_2), -129.12 (1 F(F(b), A), ddt, CF_2), -202.94 (1 F(A), dq, CHF), -208.02 (1 F(B), ddt, CHF)	F(a) $CClF_2$ A/B 178 F(b) 15/8 15/0 CHF 6 11/10 43 CHF 24/15 15 0/15 0.5/19 F(a) CF_2 0/15 15 15 20/0.5 269 F(b)
11	$CClF_2CHFCF_2$-Dmdo	A(55) B(45)	1.38, 1.39, 1.47, 1.48 (6 H, 4 x s, 2 CH_3), 4.17, 4.28 (2 H, 2 x m, CH_2O), 4.43 (1 H, m, $^3J_{HF}$ = 9, 6 and 5, CHO), 5.05 (1 H(B), dddt, CHF), 5.06 (1 H(A), dtt, CHF)	-61.16, -61.71 (1 F(F(a), B,A), 2 x ddddd, $CClF_2$), -63.75, -64.32 (1 F(F(b), A,B), 2 x dddt, $CClF_2$), -118.66, -121.65 (1 F(F(a), B, A), 2 x dtq, CF_2), -122.68 (1 F(F(b), B), dddq, CF_2), -125.81 (1 F (F(b), A), ddtt, CF_2), -202.75, -207.12 (1 F(A,B), 2 x dddt, CHF)	F(a) $CClF_2$ A/B 178 F(b) 16/17 16/17 CHF 7 7 43 CHF 14/11 14/9 6/11 15/9 F(a) CF_2 11/9 14/9 11/9 15 271 F(b)
12a	$CClF_2CHFCClFCH(CH_3)OH$	A(28) B(27) C(24) D(21)	1.40 (3 H, m, CH_3), 2.41 (1 H, bs, OH), 4.51 (1 H, m, CHO), 5.14, 5.15, 5.18, 5.35 (1 H(A,D,C,B), 4 x dddd, CHF)	-56.27, -59.12, -59.36, -61.27 (1 F(F(a), D,B,C,A), 4 x ddt, $CClF_2$), -62.08, -62.32, -63.18, -63.73 (1 F (F(b), D,A,B,C), 4 x ddt, $CClF_2$), -129.04, -129.18, -134.66, -141.04 (1 F(C,A,D,B), 4 x dq, CClF), -190.15, -192.89 (1 F(D,C), 2 x dq, CHF), -193.87, -194.28 (1 F(A,B), 2 x ddt, CHF)	F(a) $CClF_2$ A B 177 F(b) C D 20 16 14 16 15 14 15 14 CHF 3 3 25 16 43 3 3 11 20 CHF 20 19 14 19 14 19 14 16 CClF 15 14 15 14 15 14 13 11
12b	$CClF_2CF(CHClF)CH(CH_3)OH$	A(31) B(25) C(22) D(22)	1.48 (3 H, m, CH_3), 2.41 (1 H, bs, OH), 4.51 (1 H, m, CHO), 6.61, 6.65, 6.66, 6.67 (1 H(B,A,D,C), 4 x dd, CHClF)	-57.37, -58.39, -58.40, -59.71 (1 F(F(a), A,B,D,C), 4 x dt, $CClF_2$), -57.89, -59.09, -59.10, -60.20 (1 F (F(b), A,B,D,C), 4 x dt, $CClF_2$), -148.49, -149.90, -149.97, -151.67 (1 F(D,B,C,A), 4 x ddt, CHClF), -166.62, -171.14, -174.21, -175.49 (1 F(C,B,A,D), 4 x ddt, CF)	F(a) $CClF_2$ A B 177 F(b) C D 11 11 CF 11 11 14 16 13 11 CHClF 0 0 8 5 48 CHClF 6 9
13a	$CClF_2CHFCClFC(CH_3)_2OH$	A(82) B(18)	1.38, 1.51 (6 H, 2 x s, 2 CH_3), 2.38 (1 H, bs, OH), 5.20 (1 H(B), dddd, CHF), 5.42 (1 H(A), ddd, CHF)	-59.44 (1 F(F(a), B,A), dddd, $CClF_2$), -63.20 (1 F(F(b), B,A), ddt, $CClF_2$), -133.61 (1 F(A), ddd, CClF), -135.25 (1 F(B), ddt, CClF), -181.56, -183.14 (1 F(A,B), 2 x ddt, CHF)	F(a) $CClF_2$ A/B 175 F(b) 16 16 CHF 6 11 44/43 CHF 26 16 20/13 0/16 CClF
13b	$CClF_2CF(CHClF)C(CH_3)_2OH$	A(60) B(40)	1.40, 1.47 (6 H, 2 x s, CH_3), 2.38 (1 H, bs, OH), 6.67, 6.81 (1 H(A,B), 2 x dd, CHClF)	-54.20 (1 F(F(a), A,B), dt, $CClF_2$), -54.89 (1 F (F(b), A,B), ddd, $CClF_2$), -146.75, -148.75 (1 F (A,B), 2 x ddt, CHClF), -159.92, -162.50 (1 F (A,B), 2 x ddt, CF)	F(a) $CClF_2$ A/B 176 F(b) 11 9 CF 11 15 10/11 CHClF 10/3 45 CHClF

[a] Dmdo - 2,2-dimethyl-1,3-dioxolan-4-yl, Ox - oxolan-2-yl.

(*continued*)

Table 7 (*continued*)

Compd.	Structure[a]	Diastereo-isomers (% rel.)	^{1}H NMR	^{19}F NMR	J(Hz)
14a	$CClF_2CHFCClFC(CH_3)$-$(C_2H_5)OH$	A(49) B(42) C (5) D (4)	1.01, 1.04 (3 H(A,B), 2 x t, $^3J_{HH}$ = 7, CH_3CH_2), 0.98 (3 H(C,D), m, CH_3CH_2), 1.35 (3 H, m, CH_3), 1.66, 1.75 (2 H(A,B), 2 x q, $^3J_{HH}$ = 7, CH_2), 1.71(2 H(C,D), m, CH_2), 2.08 (1 H, bs, OH), 5.27, 5.31 (1 H(C,D), 2 x dm, CHF), 5.39, 5.45 (1 H(A,B), 2 x ddd, CHF)	-59.21, -59.30 (1 F(F(a), A,B), 2 x dddd, $CClF_2$), -63.19, -63.28 (1 F(F(b), A,B), 2 x dddd, $CClF_2$), -132.30 (1 F(A,B), dt, CClF), -134.61 (1 F(C,D), ddd, CClF), -180.34, -180.42 (1 F(A,B), 2 x ddt, CHF), -182.75, -183.26 (1 F(C,D), 2 x dq, CHF)	F(a) $CClF_2$ A B 175 F(b) C D 15 15 15 15 13 13 13 13 *CHF* 6 11 44 *CHF* 26 19 19 19 0 CClF 13 13
14b	$CClF_2CF(CHClF)C(CH_3)$-$(C_2H_5)OH$	A(31) B(28) C(24) D(17)	0.98 (3 H, m, CH_3CH_2), 1.35 (3 H, 4 x s, CH_3), 1.71 (2 H, m, CH_2), 2.08 (1 H, bs, OH), 6.67, 6.69, 6.83, 6.87 (1 H(D,B,A,C), 4 x dm, CHClF)	-54.95, -60.85 (2 F, 2 x ddd, $CClF_2$), -143.72, -145.61, -146.42, -148.50 (1 F(A,C,D,B), 4 x ddt, CHClF), -158.55, -160.15, -162.51, -163.72 (1 F(B,C,D,A), 4 x dt, CF)	F(a) $CClF_2$ A B 177 F(b) C D 12 8 CF 20 20 8 CHClF 0 0 0 48 *CH*ClF
15a	$CClF_2CHFCClF$-Ox	A(32) B(24) C(23) D(21)	2.12 (4 H, m, CH_2), 3.90 (2 H, m, CH_2O), 4.42 (1 H, m, CHO), 5.07, 5.33 (1 H(D,B), 2 x dddd, CHF), 5.12, 5.26 (1 H(A,C), 2 x ddd, CHF)	-55.77, -58.92, -60.03, -61.31 (1 F(F(a), B,C,A,D), 4 x dddd, $CClF_2$), -61.82, -62.35 (1 F(F(b), B,D), 2 x ddt, $CClF_2$), -63.53, -64.08 (1 F(F(b), C,A), 2 x ddd, $CClF_2$), -127.42, -128.35, -134.58, -141.25 (1 F(B,D,A,C), 4 x ddt, CClF), -189.93, -194.28, -194.81, -199.60 (1 F(B,C,D,A), 4 x dq, CHF)	F(a) $CClF_2$ A B 177 F(b) C D 16 14 16 14 15 16 15 16 CHF 4 11 0 6 44 42 8 11 0 6 44 42 *CHF* 8 6 12 14 16 14 8 1.5 CClF 13 5 12 16 15 16 4 1.5
15b	$CClF_2CF(Ox)CHClF$	A(42) B(20) C(19) D(19)	2.12 (4 H, m, CH_2), 3.90 (2 H, m, CH_2O), 4.42 (1 H, m, CHO), 6.48, 6.52 (1 H(D,B), 2 x dd, CHClF), 6.63, 6.69 (1 H(C,A), 2 x ddt, CHClF)	-57.02, -57.03, -58.32, -59.05 (1 F(F(a), A,B,C, D), 4 x ddd, $CClF_2$), -57.59 (1 F(F(b), A), ddd, $CClF_2$), -58.88, -59.62, -60.21 (1 F(F(b), D,B,C), 3 x dt, $CClF_2$), -147.83, -150.20 (1 F(D,B), 2 x ddt, CHClF), -148.97, -154.48 (1 F(C,A), 2 x dq, CHClF), -170.74, -172.87, -178.20, -179.33 (1 F(D,C,A,B), 4 x ddt, CF)	F(a) $CClF_2$ A B 177 F(b) C D 7 7 7 9 13 10 13 5 CF 15 15 15 9 15 8 13 10 13 5 13 5 CHClF 1 0 1 0 6 7 49 48 *CH*ClF 1 0 1 0 6 7 49 48
16a	$CClF_2CHFCClF$-Dmdo	A(32) B(24) C(23) D(21)	1.36-1.45 (6 H, 4 x s, 2 CH_3), 4.23 (2 H, m, CH_2O), 4.63 (1 H, m, CHO), 5.21-5.24 (1 H(A,D), 2 x dddd, CHF), 5.22-5.25 (1 H (B,C), 2 x dd, CHF)	-57.48, -57.90, -60.05, -61.42 (1 F(F(a), B,C,A,D), 4 x dddd, $CClF_2$), -61.73, -62.52, -63.41, -64.10 (1 F(F(b), B,D,C,A), 4 x dddd, $CClF_2$), -127.93, -129.82, -136.68, -141.35 (1 F(C,A,B,D), 4 x ddt, $^3J_{HF}$ = 20(B) and 8(C), CClF), -189.68, -194.01, -194.40, -199.45 (1 F(B,D,C,A), 4 x dq, CHF)	F(a) $CClF_2$ A B 172 F(b) C D 17 14 17 14 15 14 15 14 CHF 10 4 44 42 42 44 *CH*F 6 6 6 21 17 14 8 0 CClF 12 17 12 17 15 14 0 6

[a] Dmdo - 2,2-dimethyl-1,3-dioxolan-4-yl, Ox - oxolan-2-yl.

(*continued*)

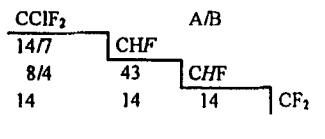
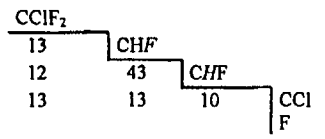
Table 7 (*continued*)

Compd.	Structure[a]	Diastereo-isomers (% rel.)	^{1}H NMR	^{19}F NMR	J(Hz)
16b	$CClF_2CF(Dmdo)CHClF$	A(42) B(22) C(18) D(18)	1.36-1.45 (6 H, 4 x s, 2 CH_3), 4.23 (2 H, m, CH_2O), 4.63 (1 H, m, CHO), 6.45, 6.51 (1 H(B,C), 2 x dd, CHClF), 6.53, 6.57 (1 H(A,D), 2 x d, CHClF)	-57.82, -58.04, -58.63, -59.01 (1 F(F(a), A,B,D,C), 4 x ddd, $CClF_2$), -57.55, -58.90, -59.70, -60.25 (1 F(F(b), A,D,B,C), 4 x ddd, $CClF_2$), -146.85, -151.40 (1 F(D,B), 2 x ddt, CHClF), -148.55, -154.45 (1 F(C,A), 2 x dq, CHClF), -174.45, -174.55, -177.68, -179.10 (1 F(C,B,A,D), 4 x ddt, $^3J_{HF}$ = 16(A) and 23(D), CF)	F(a) $CClF_2$ A B 175 F(b) C D 8 13 8 13 12 14 11 14 CF 14 6 14 17 14 6 12 9 12 9 12 14 CHClF 0 0 0 7 49 48 CHClF 7 0 49 48
17	$CClF_2CF(CHCl_2)CH(CH_3)OH$	A(51) B(49)	1.51, 1.52 (3 H, 2 x d, $^3J_{HH}$ = 7, CH_3), 2.42 (1 H, bs, OH), 4.53, 4.72 (1 H(A,B), 2 x dq, $^3J_{HF}$ = 18(A) and 10(B), $^3J_{HH}$ = 7(q), CH), 6.24, 6.41 (1 H(A,B), 2 x d, $^3J_{HF}$ = 6(A) and 4(B), $CHCl_2$)	-55.05, -56.37 (2 F(B), 2 x dd, $^2J_{FF}$ = 175, $^3J_{FF}$ = 9, $CClF_2$), -55.56, -56.90 (2 F(A), 2 x dd, $^2J_{FF}$ = 175, $^3J_{FF}$ = 9, $CClF_2$), -156.08, -164.27 (1 F(A,B), 2 x ddt, $^3J_{FF}$ = 9(t), $^3J_{HF}$ = 18, 10, 6, 4, CF)	
18	$CClF_2CF(CHCl_2)C(CH_3)_2OH$		1.53, 1.54 (6 H, 2 x s, 2 CH_3), 2.50 (1 H, bs, OH), 6.51 (1 H, d, $^4J_{HF(a)}$ = 2, $CHCl_2$)	-52.45 (1 F(a), ddd, $^2J_{FF}$ = 180, $^3J_{FF}$ = 9, $^4J_{HF}$ = 2, $CClF_2$), -53.93 (1 F(b), dd, $^2J_{FF}$ = 180, $^3J_{FF}$ = 5, $CClF_2$), -147.96 (1 F, dd, $^3J_{FF(a)}$ = 9, $^3J_{FF(b)}$ = 5, CF)	
19	$CClF_2CF(CHCl_2)C(CH_3)$-$(C_2H_5)OH$	A(50) B(50)	0.98 (3 H, t, $^3J_{HH}$ = 8, CH_3CH_2), 1.33, 1.35 (3 H, 2 x s, CH_3), 1.73 (2 H, q, $^3J_{HH}$ = 8, CH_2), 2.50 (1 H, bs, OH), 6.52, 6.58 (1 H, 2 x d, $^3J_{HF}$ = 2, $CHCl_2$)	-51.61, -53.02 (2 F(A), 2 x dd, $^2J_{FF}$ = 179, $^3J_{FF}$ = 9, $CClF_2$), -53.65, -54.27 (2 F(B), 2 x dd, $^2J_{FF}$ = 179, $^3J_{FF}$ = 5, $CClF_2$), -147.00, -148.83 (1 F(A,B), 2 x dt, $^3J_{FF}$ = 9(A) and 5(B), $^3J_{HF}$ = 2, CF)	
20	$CClF_2CF(Ox)CHCl_2$	A(60) B(40)	2.13 (4 H, m, 2 CH_2), 3.88 (2 H, m, CH_2O), 4.55, 4.72 (1 H (A, B), 2 x dt, $^3J_{HF}$ = 25(A) and 21(B), $^3J_{HH}$ = 7.5(t), CHO), 6.16, 6.41 (1 H(B,A), 2 x d, $^3J_{HF}$ = 4(B) and 3(A), $CHCl_2$)	-54.80, -55.84 (2 F(A), 2 x dd, $^2J_{FF}$ = 177, $^3J_{FF}$ = 9, $CClF_2$), -56.63, -56.92 (2 F(B), 2 x dd, $^2J_{FF}$ = 175, $^3J_{FF}$ = 9, $CClF_2$), -160.16, -166.33 (1 F(B,A), 2 x ddt, $^3J_{FF}$ = 9(t), $^3J_{HF}$ = 25, 21, 4 and 3, CF)	
21	$CClF_2CF(Do)CHCl_2$		4.10 (4 H, m, 2 CH_2), 5.70 (1 H, d, $^3J_{HF}$ = 16, CH), 6.21 (1 H, d, $^3J_{HF}$ = 4, $CHCl_2$)	-55.80, -56.56 (2 F, 2 x dd, $^2J_{FF}$ = 178, $^3J_{FF}$ = 6, $CClF_2$), -166.78 (1 F, ddt, $^3J_{FF}$ = 6(t), $^3J_{HF}$ = 16 and 4, CF)	
22	$CClF_2CF(Dmdo)CHCl_2$	A(60) B(40)	1.43 (6 H, s, 2 CH_3), 4.20, 4.33 (2 H(A,B), 2 x d, $^3J_{HH}$ = 7, CH_2O), 4.72, 4.87 (1 H(A,B), 2 x dt, $^3J_{HF}$ = 23, $^3J_{HH}$ = 7(t), CHO), 6.16, 6.30 (1 H(B,A), 2 x d, $^3J_{HF}$ = 5(B), 3(A), $CHCl_2$)	-55.36, -56.42 (2 F(A), 2 x dd, $^2J_{FF}$ = 178, $^3J_{FF}$ = 9, $CClF_2$), -56.21, -57.20 (2 F(B), 2 x dd, $^2J_{FF}$ = 178, $^3J_{FF}$ = 7, $CClF_2$), -162.97, -166.57 (1 F(B,A), 2 x ddt, $^3J_{FF}$ = 9(A), 7(B), $^3J_{HF}$ = 23, 5, 3,CF)	
23a	$CClF_2CHFCHClCH(CH_3)OH$	A(50) B(25) C(15) D(10)	1.40 (3 H, m, CH_3), 2.40 (1 H, bs, OH), 4.13 (1 H, m, CHCl), 4.30 (1 H, m, CHO), 4.97 (1 H(B,C,D), dm, $^2J_{HF}$ = 44, CHF), 5.28 (1 H(A), dt, $^2J_{HF}$ = 44, $^3J_{HF}$ = 8.5(t), CHF)	-62.25, -62.28, -62.33, -62.64 (1 F(F(a), D,C,B,A), 4 x ddd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 16, $^3J_{HF}$ = 8.5, $CClF_2$), -64.52, -65.20, -65.23, -65.29 (1 F(F(b), A,B,C,D), 4 x ddd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 16, $^3J_{HF}$ = 8.5, $CClF_2$), -194.52, -198.20, -203.30, -203.33 (1 F(B,C,D,A), 4 x ddt, $^2J_{HF}$ = 44, $^3J_{FF}$ = 16(t), $^3J_{HF}$ = 26 and 20, CHF)	
23b	$CClF_2CF(CH_2Cl)CH(CH_3)OH$	A(64) B(36)	1.47 (3 H, m, CH_3), 2.40 (1 H, bs, OH), 3.82 (2 H, m, CH_2Cl), 4.30 (1 H, m, CHO)	-60.05, -64.32 (1 F(F(a), B,A), 2 x dd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 10, $CClF_2$), -60.58, -64.81 (1 F(F(b), B,A), 2 x dd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 10, $CClF_2$), -169.44 (1 F(A), ddt, $^3J_{FF}$ = 10(t), $^3J_{HF}$ = 30 and 12, CF), -172.91 (1 F(B), ddq, $^3J_{FF}$ = 10, $^3J_{HF}$ = 30, 10 and 2, CF)	

[a] Dmdo - 2,2-dimethyl-1,3-dioxolan-4-yl, Do - 1,3-dioxolan-2-yl, Ox - oxolan-2-yl

(*continued*)

Table 7 (*continued*)

Compd.	Structure[a]	Diastereo-isomers (% rel.)	^{1}H NMR	^{19}F NMR	J(Hz)
24a	$CClF_2CHFCHClC(CH_3)_2OH$	A(93) B (7)	1.37, 1.50 (6 H, 2 x s, 2 CH_3), 2.40 (1 H, bs, OH), 4.10 (1 H, m, CHCl), 4.92 (1 H(B), dm, $^2J_{HF}$ = 43, CHF), 5.25 (1 H(A), dt, $^2J_{HF}$ = 43, $^3J_{HF}$ = 6, CHF)		-63.77, -65.46 (2 F, 2 x ddd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 16, $^3J_{HF}$ = 6, $CClF_2$), -187.88, -198.25 (1 F(B,A), 2 x ddt, $^2J_{HF}$ = 43, $^3J_{HF}$ = 27 and 24, $^3J_{FF}$ = 16(t), CHF)
24b	$CClF_2CF(CH_2Cl)C(CH_3)_2OH$		1.40, 1.49 (6 H, 2 x s, 2 CH_3), 2.40 (1 H, bs, OH), 3.81 (2 H, m, CH_2Cl)		-64.21, -64.87 (2 F(a,b), 2 x dd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 11 and 8.5, CClF), -165.02 (1 F, dd, $^3J_{FF(a)}$ = 11, $^3J_{FF(b)}$ = 8.5, CF)
25a	$CClF_2CHFCHCl$-Ox	A(51) B(23) C(13) D(13)	2.05 (4 H, m, 2 CH_2), 3.90 (2 H, m, CH_2O), 4.13 (1 H, m, CHCl), 4.35 (1 H, m, CHO), 4.95 (1 H(B,C,D), dm, $^2J_{HF}$ = 44, CHF), 5.27 (1 H(A), dt, $^2J_{HF}$ = 44, $^3J_{HF}$ = 9, CHF)		-61.65, -61.79, -61.80, -62.20 (1 F(F(a), B,D,A,C), 4 x ddd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 16, $^3J_{HF}$ = 9, $CClF_2$), -62.75, -64.08, -64.11, -65.03 (1 F(F(b), D,B,A,C), 4 x ddd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 16, $^3J_{HF}$ = 9, $CClF_2$), -192.42, -194.29, -198.22, -206.20 (1 F(D,B,C,A), 4 x ddt, $^2J_{HF}$ = 44, $^3J_{FF}$ = 16(t), $^3J_{HF}$ = 26, CHF)
25b	$CClF_2CF(Ox)CH_2Cl$	A(64) B(36)	2.05 (4 H, m, 2 CH_2), 3.83 (2 H, m, CH_2Cl), 3.90 (2 H, m, CH_2O), 4.35 (1 H, m, CHO)		-60.02, -64.37 (1 F(F(a), B,A), 2 x dd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 10, $CClF_2$), -60.62, -64.87 (1 F(F(b), B,A), 2 x dd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 10, $CClF_2$), -169.00 (1 F(A), ddt, $^3J_{FF}$ = 10(t), $^3J_{HF}$ = 30, 12, CF), -174.74 (1 F(B), ddq, $^3J_{FF}$ = 10, $^3J_{HF}$ = 30, 10 and 2, CF)
26a	$CClF_2CHFCHCl$-Dmdo	A(51) B(23) C(13) D(13)	1.35-1.45 (6 H, 4 x s, 2 CH_3), 4.13 (1 H, m, CHCl), 4.23 (2 H, m, CH_2O), 4.61 (1 H, m, CHO), 5.22 (1 H(B,C,D), 3 x dm, $^2J_{HF}$ = 44, CHF), 5.25 (1 H(A), dt, $^2J_{HF}$ = 44, $^3J_{HF}$ = 8, CHF)		-61.64, -61.75, -61.80, -62.21 (1 F(F(a), B,D,A,C), 4 x ddd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 15, $^3J_{HF}$ = 8, $CClF_2$), -62.77, -64.10, -64.16, -65.05 (1 F(F(b), D,B,A,C), 4 x ddd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 15, $^3J_{HF}$ = 8, $CClF_2$), -194.46, -195.83, -198.20, -206.58 (1 F(D,B,C,A), 4 x ddt, $^2J_{HF}$ = 44, $^3J_{FF}$ = 15(t), $^3J_{HF}$ = 26, CHF)
26b	$CClF_2CF(Dmdo)CH_2Cl$	A(64) B(36)	1.40 (6 H, 2 x s, 2 CH_3), 3.83 (2 H, m, CH_2Cl), 4.22 (2 H, m, CH_2O), 4.61 (1 H, m, CHO)		-60.03, -64.35 (1 F(F(a), B,A), 2 x dd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 10, $CClF_2$), -60.62, -64.88 (1 F(F(b), B,A), 2 x dd, $^2J_{FF}$ = 168, $^3J_{FF}$ = 10, $CClF_2$), -169.56 (1 F(A), ddt, $^3J_{FF}$ = 10(t), $^3J_{HF}$ = 30 and 20, CF), -173.47 (1 F(B), ddq, $^3J_{FF}$ = 10, $^3J_{HF}$ = 30, 10 and 2, CF)
27	$CClF_2CHFCF_2CH(CH_3)O$- $-COC(CH_3)=CH_2$	A(53) B(47)	1.44 (3 H, d, $^3J_{HH}$ = 6, CH_3), 1.97 (3 H, m, CH_3-C=), 4.94 (1 H, dm, CHF), 5.36 (1 H, m, CH), 5.68, 6.18 (2 H, 2 x m, CH_2=)	-61.82, -64.51 (2 F(B), 2 x dddt, $^2J_{FF}$ = 178, $CClF_2$), -62.13, -63.93 (2 F(A), 2 x ddq, $CClF_2$) -117.75, -122.21, -122.70, -123.52 (2 F(B,A), 4 x dsex, $^2J_{FF}$ = 275, $^3J_{HF}$ = 14, CF_2), -202.42 (1 F(A), dqi, CHF), -203.72 (1 F(B), dtt, CHF)	
28a	$CClF_2CHFCClFCH(CH_3)O$- $-COC(CH_3)=CH_2$	A(28) B(27) C(24) D(21)	1.52 (3 H, d, $^3J_{HH}$ = 7, CH_3), 1.96 (3 H, m, CH_3-C=), 5.06 (1 H, dm, CHF), 5.43 (1 H, m, CH), 5.68, 6.17 (2 H, 2 x m, CH_2=)	-57.0(C), -59.8(D), -60.0(B), -61.4(A), -62.3(A), -62.4(C), -63.2(D), -63.7(B) (2 F, 8 x ddt, $^2J_{FF}$ = 174, $CClF_2$), -127.1, -128.2, -133.0, -133.9 (1 F(B,C,D,A), 4 x dq, CClF), -189.3, -191.9, -192.3, -194.2 (1 F(D,C,B,A), 4 x dq, CHF)	

[a] Dmdo - 2,2-dimethyl-1,3-dioxolan-4-yl, Ox - oxolan-2-yl

(*continued*)

Table 7 (*continued*)

Compd.	Sinicture	Diastereo-isomers (% rel.)	^{1}H NMR	^{19}F NMR	J(Hz)
28b	$ClF_2CF(CHClF)CH(CH_3)O$- $-COC(CH_3)=CH_2$	A(31)	1.52 (3 H, d, $^3J_{HH}$ = 7, CH_3), 1.96	-58.0(D), -58.5(D), -58.9(C,A), -59.8(C,A), -60.5(B),	$CClF_2$ 13; CHClF 48; CHClF 7; CF
		B(25)	(3 H, m, CH_3-C=), 5.43 (1 H, m,	-61.0(B) (1 F, 6 x dt, $^2J_{FF}$ = 174, $CClF_2$), -148.1, -149.9,	
		C(22)	CH), 5.68, 6.17 (2 H, 2 x m, CH_2=),	-149.4, -150.4 (1 F(C,A,B,D), 4 x dq, CHClF), -166.8,	0
		D(22)	6.58 (1 H, dd, $^3J_{HF}$ = 7, CHClF)	-169.6, -173.0, -173.3 (1F(C,A,B,D), 4 x dq, CF)	13
29	$ClF_2CHFCF_2CH(OH)$- $-CH_2OH$	A(55)	3.60 (2 H, m, CH_2O), 3.88 (1 H, m,	-60.11, -60.54 (1 F(F(a), B,A), 2 x ddddd, $CClF_2$),	F(a) 177; $CClF_2$ F(b) 16/17; CHF 42; CHF 4; F(a) 268
		B(45)	CHO), 5.03, 5.12 (1 H, 2 x t, $^3J_{HH}$ =	-62.55, -63.23 (1 F(F(b), A,B), 2 x dddt, $CClF_2$),	A/B
			6, CH_2OH), 5.78, 5.81 (1 H, 2 x	-119.69, -120.44 (1 F(F(a), B,A), 2 x dddt, CF_2),	16/17
			dddt, CHF), 6.18, 6.21 (1 H, 2 x d,	-120.53 (1 F(F(b), B), ddddd, CF_2), -123.28 (1 F	9
			$^3J_{HH}$ = 6, CHOH)	(F(b), A), dddt, CF_2), -202.53, -204.26 (1 F(A,B),	14/11
				2 x dddt, CHF)	11/7

reaction amounts, yields, boiling points and elemental analyses, see Table 6).

4.3. Photoinduced additions to 1,3-dichloro-1,2,3,3-tetrafluoropropene (2), 1,1,3-trichloro-2,3,3-trifluoropropene (3) and 1,3-dichloro-2,3,3-trifluoropropene (4) (products 7, 12–16; 17–22; 23–26)

The reactions were carried out in round-shaped, two-necked (sealed with septa) quartz cells with volumes of approximately 10 or 20 ml (diameter, 5 cm; plane-parallel sites); these were irradiated from outside by a medium-pressure UV lamp (Tesla, RVK 400 W), placed in a reflecting metal cylindrical housing, through a round window (diameter, 5 cm) with a quartz lens; magnetic follower. The cell was charged with olefin (**2**–**4**, 0.03 mol; (*Z*)-**2** 38%, (*E*)-**2** 62%; (*Z*)-**4** 16%, (*E*)-**4** 84%) and additive (0.15 mol) and the mixture was deaerated at −10 °C for 1 h with argon. The site of the cell was then irradiated at room temperature for 3–15 h with stirring and the progress of the reaction was checked by GC (the conversions of olefins achieved were 70%–90%). Unreacted additive was distilled off (column, 5 cm; Berle saddles), and the pure product was obtained by distillation under vacuum (for reaction amounts, yields, boiling points and elemental analyses, see Table 6). The ratio of the (*Z*) and (*E*) isomers of both olefins **2** and **4** remained constant during the reaction (checked by ^{19}F NMR).

4.4. Peroxide-induced additions to 1,3-dichloro-1,2,3,3-tetrafluoropropene (2) (products 12–14)

In the apparatus described above, the cell (25 ml) was charged with olefin **2** (5.49 g, 0.03 mol), alkanol (0.15 mol) and dibenzoyl peroxide (0.182 g, 0.75 mmol) and deaerated with cooling to −20 °C for 1 h. The cell was then irradiated at room temperature for 3–15 h with stirring and the progress of the reaction was checked by GC (the conversion of olefin was 70%–80%). Unreacted additive was then distilled off as above (product **7**) and the pure product was obtained by distillation under vacuum (for reaction amounts, yields, boiling points and elemental analyses, see Table 6). The ratio of the (*Z*) and (*E*) isomers of olefin **2** remained constant during the reaction.

4.5. Relative rates of addition to fluoroolefins

4.5.1. Method A

An immersion-well photoreactor, as described for products **8**–**12**, was charged with 2-propanol (30.3 g, 0.5 mol) and deaerated with nitrogen for 3 h. The reactor was then cooled to −15 to −25 °C and charged with gaseous fluoroolefin **1** (2.83 g, 17 mmol); fluoroolefins **2** (3.0 g, 17 mmol) and **3** (3.33 g, 17 mmol), together with acetone (1.2 ml), were then added by syringe. The reaction was carried out at −15 to −20 °C and samples of the reaction mixture were taken at

Table 8
Competiive photoreaction of olefins **2** and **4**

	Time (min)				
	0	20	60	90	120
Content of **2** (% rel.)	45.2	43.7	41.5	40.0	38.4
Content of **4** (% rel.)	54.8	56.3	58.5	60.0	61.6
Ratio **4** : **2**	1.21	1.29	1.41	1.50	1.60

intervals of 10 min (GC analysis using calibration graphs relative to trichloroolefin **3** which gave an unmeasurable amount of product over 50 min). The relative reactivities were obtained from the linear part of the product–time plot (pseudo-zero-order kinetics; experimental error, ±10%). The amount of addition product of olefin **3** after 4 h of reaction was calculated by GC analysis, using an external standard [1a] (bromobenzene), with calibration for the product of olefin **2**; therefore the calculated yield of product **18** is only approximate.

4.5.2. Method B

In the apparatus described for products **12–14**, the cell was charged with halogenoolefins (**2** and **4**, 2.5 mmol), 2-propanol (9.02 g, 0.15 mol) and acetone (0.29 g, 5 mmol) and the mixture was deaerated as above for 1 h. The site of the cell was then irradiated at room temperature for 2 h with stirring, and samples for ^{19}F NMR determination of the olefin **2** and **4** contents were withdrawn through septa (argon atmosphere, 0.2 ml of the sample was mixed with 0.3 ml of $CDCl_3$; Table 8). The ratio of the (*Z*) and (*E*) isomers of olefins **2** and **4** remained constant during the reaction.

4.6. Methacrylates of chlorofluoroalkanols 8 and 12 (products 27 and 28)

A three-necked flask was charged with methacryloyl chloride (3.14 g, 30 mmol), CFC-113 (1,1,2-trichlorotrifluoroethane, 12 ml) and halogenoalkanol (30 mmol; **8**, 6.38 g; **12**, 6.89 g) in a dry atmosphere with stirring and cooling with ice. A solution of triethylamine (3.19 g, 32 mmol) in CFC-113 (6 ml) was added dropwise into the flask with cooling with ice, at such a rate that the reaction temperature did not exceed 20 °C, and the mixture was then stirred for 3 h at room temperature. Water (20 ml) was then added to the flask and the oily layer was washed with an aqueous solution of $NaHCO_3$ and water and then dried ($MgSO_4$). CFC-113 was distilled off and the distillation of the residue gave the product. Methacrylate **27** (5.27 g, 71%, purity (GCb) 98%), b.p. 65–68 °C/4 mmHg (0.53 kPa). Analysis: found: C, 39.3%; H, 3.81%; Cl, 12.3%; F, 34.15%. $C_9H_{10}ClF_5O_2$ requires: C, 38.5%; H, 3.59%; Cl, 12.6%; F, 33.9%. *M*, 280.6; two diastereoisomers in the ratio 53% : 43% rel. Methacrylate **28** (4.32 g, 51%, purity (GCb) 98%), b.p. 72–74 °C/2 mmHg (0.27 kPa). Analysis: found: C, 36.7%; H, 3.19%; Cl, 23.65%; F, 25.6%. $C_9H_{10}Cl_2F_4O_2$ requires: C, 36.4%; H, 3.39%; Cl, 23.9%; F, 25.6%. *M*, 297.1; two groups of diastereoisomers belonging to two regioisomers: **28a**, four regioisomers in the ratio 30 : 24 : 23 : 23; **28b**, four regioisomers in the ratio 36 : 28 : 22 : 14 (see Table 7).

4.7. Hydrolysis of 4-(3-chloro-1,1,2,3,3-pentafluoropropyl)-2,2-dimethyl-1,3-dioxolane (11) (product 29)

A mixture of dioxolane **11** (1.34 g, 5 mmol), methanol (6.4 g, 200 mmol) and concentrated hydrochloric acid (0.25 g) was heated to reflux for 3 h with stirring (complete conversion checked by GCa). Methanol was removed under reduced pressure, toluene (15 ml) was added to remove water by azeotropic distillation and the residue was distilled in vacuo to afford diol **29** (1.01 g, 88%, purity (GCb) 98%), b.p. 93–95 °C/10 mmHg. Analysis: found: C, 26.4%; H, 2.72%; Cl, 15.65%; F, 41.4%. $C_5H_6ClF_5O_2$ requires: C, 28.3%; H, 2.65%; Cl, 15.5%; F, 41.6%. *M*, 228.6.

4.8. Preparation of 1,3-dichloro-2,3,3-trifluoropropene (4)

4.8.1. 1,1,2,3-Tetrachloro-2,3,3-trifluoropropane (HCFC-223)

In the apparatus described for products **12–14**, the cell was charged with a mixture of 1,1,1,2,3-pentachloro-2,3,3-trifluoropropane [25] (CFC-213, 10.81 g, 40 mmol) and 2-propanol (30.05 g, 500 mmol) and deaerated at −10 to −15 °C (argon, 0.5 h). The site of the cell was then irradiated at room temperature for 6 h with stirring and the progress of the reaction was checked by ^{19}F NMR (time (h)/conversion of CFC-213 (%): 1/71, 2/92, 3/95, 4/96, 5/97, 6/98). The unreacted 2-propanol was removed by distillation (column, 15 cm; Berle saddles), residual 2-propanol was removed by treating with water (2 × 5 ml), the residue was dried ($CaCl_2$) and the product, HCFC-223, was obtained by distillation (8.21 g, 87%, purity (GCa) 98%), b.p. 65–67 °C/90 mmHg (reported: 129.8 °C [30]; 40–44 °C/2.6 mmHg [27b]). For the transformation of the product to halogenopropene **4**, a raw reaction mixture can be used directly.

4.8.2. 1,3-Dichloro-2,3,3-trifluoropropene (4)

A two-necked flask equipped with a distillation column (30 cm, Berle saddles), low-temperature head and hydraulic seal (concentrated H_2SO_4) was charged with zinc powder (70 g, 1.07 mol), activated with a glacial acetic acid–acetic anhydride mixture (0.5 ml, 1 : 1), and with 2-propanol (100 ml, 78.5 g, 1.31 mol). The mixture was then refluxed, and HCFC-223 (30.9 g, 0.131 mol) was added over 2 h, while a distillate of b.p. 50–65 °C was collected (a mixture of 2-propanol and product **4**). 2-Propanol was removed from the distillate by a distillation column (15 cm, stainless spirals), residual 2-propanol was removed by treating with a concentrated water solution of $CaCl_2$ and the raw product **4** was dried with $CaCl_2$. The product **4** was obtained by distillation

(13.4 g, 62%, purity (GCa) 98%), b.p. 60–62 °C (reported: 56–57 °C [27b]), 16% (*Z*) and 84% (*E*).

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