

Radical addition reactions of fluorinated species. Part 8. Regioselectivity of radical additions to perfluoroalkylethylenes and quantum chemical calculations. Highly selective two-step synthesis of 4-(perfluoroalkyl)butane-1,2-diols[☆]

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Dedicated to Professor Paul Tarrant on the occasion of his 85th birthday

Abstract

Perfluoroalkylethylenes $R_F\text{-CH=CH}_2$ ($R_F = C_4F_9, C_6F_{13}, C_8F_{17}$) added easily nucleophilic radicals generated from alkanols, oxolane and 2,2-dimethyl-1,3-dioxolane. The additions were initiated photochemically in the presence of acetone or by dibenzoyl peroxide and were completely regioselective and almost completely chemoselective with preparative yields up to 90%. 4-Fluoroalkylated dioxolanes obtained (**5a–5c**) were deprotected by methanolysis in acid media to afford 4-perfluoroalkyl-1,2 butanediols (**15a–15c**) that were converted to the corresponding bis-methacrylates (**16a–16c**). 2,2,4-Trimethyl-1,3-dioxolane (**17**) reacted at two centers to yield 84:16 regioisomeric mixture of fluoroalkylated dioxolanes with preferential attack of the adduct-radical to the more sterically hindered tertiary C–H bond in **17**. The complete regioselectivity of the additions to perfluoroalkylethylenes is discussed in relation to the “tail effect” of perfluoroalkylated chain and energies of intermediate adduct-radicals calculated using PM3 and ab initio quantum chemical methods.

Keywords: Regioselective radical addition; (Perfluoroalkyl)ethylenes; 2,2-Dimethyl-1,3-dioxolane; Photo-induced addition; Sensitized photoaddition; Peroxide-induced addition; Hydrolysis of substituted 1,3-dioxolanes; 4-(Perfluoroalkyl)butane-1,2-diols; Radical stability ¹H and ¹⁹F NMR spectroscopy; Ab initio method; Heats of formation of adduct-radicals; Total energies of adduct-radicals

1. Introduction

It has been mentioned in our preceding paper [1] that perfluoroolefins, including perfluoro(alkyl vinyl polyethers), can be transformed to fluoroalkylated ethane-1,2-diols by the application of radical addition of 1,3-dioxolane species. We have also found [1] that radical additions to perfluoroalk-1-enes on one side and to perfluoro(alkyl vinyl polyethers) on the other side differ slightly in regioselectivity, the additions to perfluoroolefins being more selective. Generally, perfluoroalkyl diols are versatile intermediate compounds in preparations of a variety of special monomers that can be applied in various technical fields (see

[2], and references therein). The presence of a perfluoroalkyl and a hydrophilic group in the monomers, as e.g. in monoesters of fluoroalkylated glycols, increases oxygen permeability and biocompatibility of the corresponding polymer. Typical medicinal applications of such materials are contact lenses [3–9] and also vein- and body-tissue prosthetics [10,11].

In this paper, the preparation of perfluoroalkylated 1,2-diols from perfluoroalkylethylenes using protected ethylene glycol (2,2-dimethyl-1,3-dioxolane, **13**) as a radical additive has been studied as well as the regioselectivity of additions of a series of nucleophilic radicals to the substrates.

The methods reported for the synthesis and preparation of (per)fluoroalkylated 1,2-diols bearing three or four-carbon in the initial non-fluorinated part in the chain (e.g. $R_F\text{-(CH}_2)_n\text{-CHOH-CH}_2\text{OH}$, $n = 0, 1, 2$) [12–21] have been generally reviewed in our preceding paper [1]; in addition, the diols with $R_F=C_2Cl_2F_3$ were prepared by acid hydrolysis

[☆]Part 1, Ref. [1].

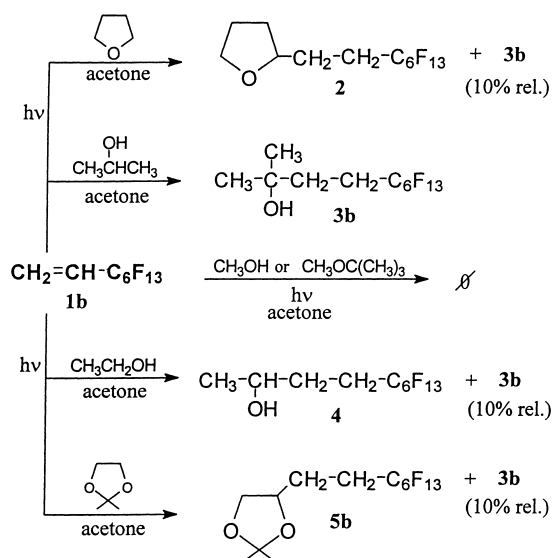
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of the starting epoxides [2]. Perfluoroalkyl- or perfluoroarylethylenes can be converted into the 1,2-diols by treatment with osmium tetroxide in the presence of primary oxidants as hydrogen peroxide or potassium hexacyanoferrate(III) in high yields [22]. An analogous procedure has been applied to carry out dihydroxylation of 4-(perfluoroalkyl)but-1-enes [23]. We would like to report here that perfluoroalkylethylenes can be transformed effectively to 4-(perfluoroalkyl)butane-1,2-diols (**15a–15c**) in high yields by a two-step synthesis using a highly selective radical addition of 2,2-dimethyl-1,3-dioxolane (**13**). We have applied [1] this strategy successfully to terminal perfluoroalkenes and perfluoro(alkyl vinyl (poly)ethers). Radical additions to perfluoroalkylethylenes are scarce in the literature: X-ray induced telomerization of 2-propanol with 3,3,3-trifluoropropene was carried out [24] and the preparation of fluorinated alcohols by a high temperature addition of alkanols to (perfluoroalkyl)ethylenes in an autoclave has been claimed [25]. Oxolane was added to 3,3,3-trifluoropropene to afford a mixture of four products after 112 h reaction at room temperature [26]. It is interesting that the reaction of refluxing oxolane with perfluorobutyl- (**1a**), -hexyl- (**1b**) and -octyl-ethylene (**1c**) for 7 days was completely chemoselective to give oxolan-2-yl radical adducts [27]. On the other hand, the addition of dioxolane **13** to oct-1-ene under peroxide initiation gave a mixture of products in only 3–25% yields [28,29].

2. Results

We have found here that perfluoroalkylethylenes reacted easily with nucleophilic radicals generated from alkanols, oxolane and 2,2-dimethyl-1,3-dioxolane (Scheme 1). The additions were initiated photochemically



Scheme 1. Photo-sensitized addition of alkanols and cyclic ethers.



or by dibenzoyl peroxide and were completely regioselective under both the types of initiation. The conditions and results are summarized in Table 1. Almost complete conversions were achieved in 3–4 h reaction (in contrast to the previously reported 7-day reaction with oxolane [27]). The best preparative yields up to 92% and complete chemoselectivity were obtained under the initiation with dibenzoyl (Table 1).

The direct photochemical initiation of additions of alcohols, aliphatic and cyclic ethers, which was successful in the case of perfluoroolefins [30–32], chlorofluoropropenes [33], polyfluoro(alkyl vinyl(poly)ethers) [1,30–32,34], and methyl trifluoroacrylate [35–37], completely failed in the case of perfluoroalkylethylenes. Therefore, acetone was used as a triplet sensitizer. Under these conditions, the additions of a series of nucleophilic additives, ethanol, 2-propanol, oxolane, 2,2-dimethyl-1,3-dioxolane (**13**), and 2,2,4-trimethyl-1,3-dioxolane (**17**) proceeded easily with the exception of methanol, which did not react (Table 1). Elementary processes in this type of initiation are depicted in Scheme 2. However, with this initiation, the reactions were not completely chemoselective as byproducts, **3a–3c**, of the additions of the ketyl radical **8** (Scheme 1), having its origin in triplet-excited acetone (**6**), to the starting (perfluoroalkyl)ethylenes (**1a–1c**) were formed. The relative amount of byproducts was practically constant (ca. 10% rel., Scheme 1) for all the reactions carried out.

A different photochemical behavior of perfluoroalkylethylenes when compared with perfluoroolefins or chlorofluoropropenes [30–34] can be explained by absorption quantities. The absorption data in Table 2 show a great difference in absorbance and absorption coefficient ϵ between perfluoroalkenes [38,39] and perfluoroalkylethylenes, which is very low for the latter. As a consequence, the UV light is mostly absorbed by a solvent under irradiation of the reaction mixture and thus the excitation of perfluoroalkylethylene is insufficient in the region 205–250 nm. The excitation energy can be transferred to the olefin through acetone whose absorption maximum is about 270 nm.

Fluoroalkylated oxolanes (**5a–c**) were transformed to the corresponding diols (**15a–c**) in yields 90–92% by a deprotection procedure using a mixture of hydrochloric acid and methanol [1] (Scheme 3, Table 3). Acetone dimethyl acetal was formed as a volatile compound in the deprotection, which is a reacetalization. No fluorinated by-products were detected in the reaction mixture. A completely chemoselective transformation of 1-(perfluoroalkyl)ethane-1,2-diols to the corresponding mono-methacrylates has been reported [27]. In this study, we were not successful in the preparation of mono-methacrylates of the diols (**15a–c**) according to procedure [27]; therefore, the diols were in turn converted to bis-methacrylates (**16a–c**) by their reaction with methacryloyl chloride as reported previously [1] (Scheme 3). These type of compounds can be used as special cross-linking agents or for novel hydrophobic coatings [2].

Table 1
Radical additions to perfluoroalkylethylenes (**1a–c**)

Olefins ^a	Additive ^a	Initiation ^b	Time (h)	Conversion ^c (%)	Products							
					No.	Yield (g)	Yield (%)	Purity (%)	B.p. (m.p.) (°C/mm Hg)			
1b		Heating ^d	7 days		2	76		93/20				
1b		<i>hν</i>	3	0	2		0					
1b		<i>hν</i> + acetone	3	97	2	7.61	91	98	100–102/10			
1a	<i>i</i> -PrOH	<i>hν</i> + acetone	3	97	3a	5.51	90	99	70–72/40			
1b					3b	7.31	90	99	73–75/20 (31–33)			
1c					3c	9.21	91	99	70–72/8 (42–44)			
1b	EtOH	<i>hν</i> + acetone	3	97	4	7.06	90	98	71–73/20			
1b^c	MeOH	<i>hν</i> + acetone	4	0			0					
1b	MTBE ^f	<i>hν</i> + acetone	4	0			0					
1a–c		<i>hν</i>	3	0	5a–c		0					
1a					hv + acetone	3	97	5a	4.94	71	95 ^g	89–91/30
1b								5b	6.54	73	95 ^g	109–111/30
1c								5c	8.33	76	95 ^g	128–130/30
1a	Bz ₂ O ₂		4	96	5a	6.41	92	98	115–117/40			
1b					5b	8.16	91	98	117–119/25			
1c					5c	9.87	90	98	116–118/10 (115–117)			
1c					17	18, 19	9.90	88	98	105–108/5		

^a Olefin 0.02 mol, additive 0.10 mol.

^b Acetone or dibenzoyl peroxide 2 mmol.

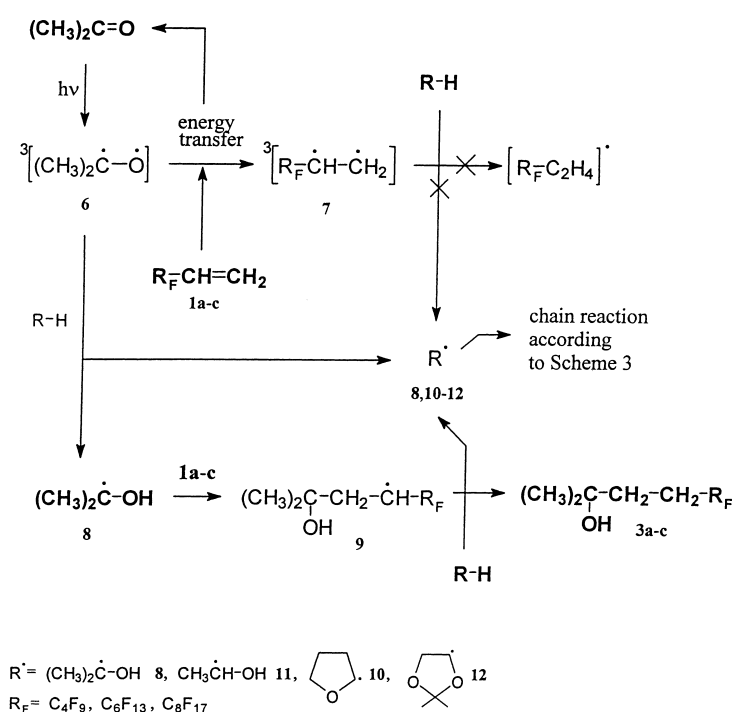
^c Conversion of olefins (checked by GC).

^d Reflux [27].

^e Olefin 0.04 mol, MeOH 0.20 mol.

^f *tert*-Butyl methyl ether (MTBE).

^g Azeotropic mixture containing ca. 5% of **3a–c**.



Scheme 2. Photo-sensitized initiation processes.

Table 2
Absorption coefficients ϵ of fluoroolefins

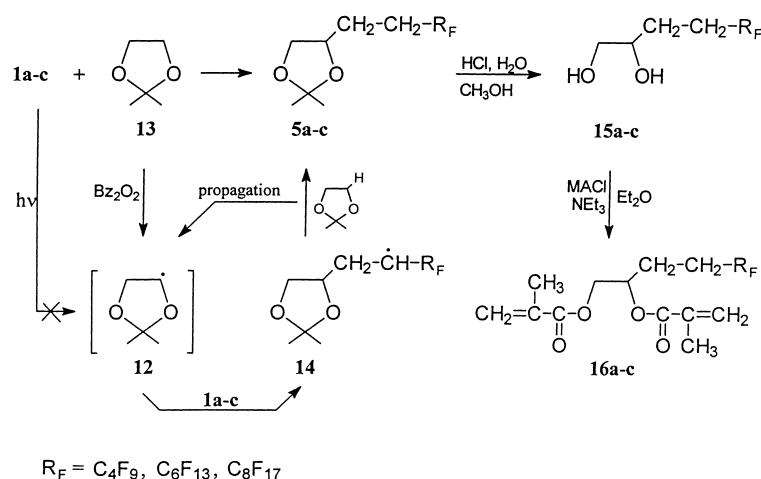
Olefins	Concentration ^a (10^3 mol l^{-1})	Absorbance ^b (A_{max})	ϵ^b ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)
$\text{C}_9\text{F}_{19}\text{CF}=\text{CF}_2$	1.16	0.3802	327.0
$\text{CF}_3(\text{OCF}_2\text{CF}_2)_4\text{OCF}=\text{CF}_2$	2.29	0.1608	70.4
$\text{C}_3\text{F}_7\text{OCF}=\text{CF}_2$	7.82	0.2212	28.3
$\text{C}_8\text{F}_{17}\text{CH}=\text{CH}_2$	46.76	0.1621	3.5

^a In methanol.

^b Absorbance at $\lambda_{\text{max}} = 204 \text{ nm}$.

Table 3
Yields of diols (**15a–c**) and the corresponding bis-methacrylates

No.	Yield		Purity (%)	B.p. (m.p.) ($^{\circ}\text{C}/\text{mm Hg}$)
	(g)	(%)		
15a	5.55	90	99	74–76/0.1
15b	7.51	92	99	87–89/0.08 (47–49)
15c	9.25	91	99	90–92/0.01 (82–84)
16a	3.73	84	98	90–93/0.01
16b	4.57	84	98	96–98/0.008
16c	5.54	86	98	92–94/0.006 (31–33)



Scheme 3. Preparation of fluoroalkylated dioxolanes (**5a–c**) and their transformation to bis-methacrylates (**16a–c**).

3. Discussion

3.1. Polar effects in radical additions

We have emphasized in the preceding papers [1,33] easy radical addition between reaction partners of opposite Lewis acid–base character, e.g. between perfluoroolefins and nucleophilic radicals. High conversions and preparative yields of the reactions of perfluoroalkylethylenes with nucleophilic radicals in this paper (Table 1) have revealed that perfluoroalkylethylenes behave as electron-deficient olefins and display a similar reactivity as perfluoroolefins discussed recently [1]. Electrophilic perfluoroalkyl radicals add with decreased rate to perfluoroalkylethylenes [40].

3.2. Regioselectivity of additions to perfluoroalkylethylenes

We have found recently [1] that the regioselectivity of radical additions to fluoroalkylated ethylenes is influenced by the structure of perfluoroalkylated chain (e.g. perfluoroalkyl or perfluorinated (poly)ether chain) and by the chain length. The regioselectivity is also strongly influenced by the Lewis acid–base character and bulkiness

of a carbon-centered radical additive. Some selected examples demonstrating the mentioned factors are collected in Table 4 (entries 1–9). The regioselectivity data for (perfluoroalkyl)ethylenes in Table 4 (entries 10–15) have revealed a similar regioselectivity as that for perfluoroalk-1-enes (entries 1–6); nucleophilic and non-bulky methyl radical adds partly to the inner carbon atom connected with electron-withdrawing trifluoromethyl group (entry 10). In contrast, electrophilic trifluoromethyl radical adds almost exclusively to the terminal carbon (entry 11) than can be caused both by electronic and field effects (i.e. repulsion between the radical and trifluoromethyl group).

The regioselectivity of the additions of nucleophilic radicals to perfluoroalkylethylenes (entries 12–15) appeared to be complete, no regioisomers have been found in the reaction mixture.

^{19}F NMR spectra enable us to detect the amount of ca. 0.5 mol% of a regioisomer [31]. It is the same regioselectivity as observed for longer-chain perfluoroalk-1-enes (entries 5 and 6). This observation has been reported and discussed as a repulsive field (or stereoelectronic) effect of a longer perfluorinated chain, so-called “tail effect” [1,31,33]. This effect is represented graphically in Scheme 4.

Table 4
Regioselectivity of additions of some radicals to fluoroolefins

Entry	Olefin	X	Radical R [•]	Initiation	Regioisomeric adduct-radicals (% rel.)		References
					R _F -C [•] X-CX ₂ R	R _F -CX-C [•] X ₂ R	
1	CF ₃ -CF=CF ₂	F	(OH)H ₂ C [•]	UV, peroxide	95.5–98	2–4.5	[41,42]
2	CF ₃ -CF=CF ₂	F	OH(CH ₃) ₂ C [•]	UV, peroxide	100	0	[41,42]
3	CF ₃ -CF=CF ₂	F		UV	98	2	[32]
4	CF ₃ -CF=CF ₂	F		UV	99	1	[1]
5	C ₇ F ₁₅ -CF=CF ₂	F	(OH)H ₂ C [•]	UV, peroxide	100	0	[1,43]
6	C ₉ F ₁₉ -CF=CF ₂	F		UV	100	0	[1]
7	C ₃ F ₇ OCF(CF ₃)CF ₂ OCF=CF ₂	F	(OH)H ₂ C [•]	UV	95	5	[32]
8	C ₃ F ₇ OCF(CF ₃)CF ₂ OCF=CF ₂	F		UV	94	6	[32]
9	C ₃ F ₇ OCF(CF ₃)CF ₂ OCF=CF ₂	F		UV, peroxide	94	6	[1]
10	CF ₃ -CH=CH ₂	H	CH ₃ [•]	^a	77	23	[44]
11	CF ₃ -CH=CH ₂	H	CF ₃ [•]	^a	98	2	[44–46]
12	(1b) C ₆ F ₁₃ -CH=CH ₂	H	OH(CH ₃)HC [•]	Sens. ^b	100	0	^c
13	(1b) C ₆ F ₁₃ -CH=CH ₂	H		Sens. ^b	100	0	^c
14	(1) R _F -CH=CH ₂	H ^d	OH(CH ₃) ₂ C [•]	Sens. ^b	100	0	^c
15	(1) R _F -CH=CH ₂	H ^d		Sens. ^b , peroxide	100	0	^c

^a Gas phase reaction.

^b UV + acetone.

^c This paper.

^d R_F = C₄F₉ (1a), C₆F₁₃ (1b), C₈F₁₇ (1c).



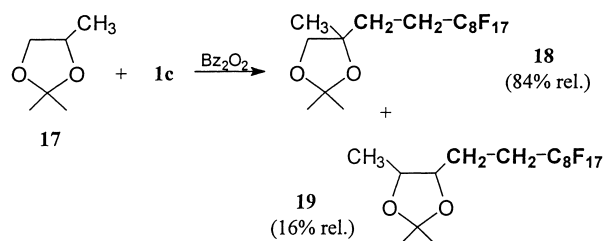
C-C Bond formation between trivalent carbon radical and inner C atom of the double bond, **low stereoelectronic shielding** of the reaction site.

C-C Bond formation between trivalent carbon radical and inner C atom of the double bond, **high stereoelectronic shielding** of the reaction site.

Scheme 4. Representation of stereoelectronic shielding of the reaction site in 3,3,3-trifluoropropene (A) and in 1-(perfluoroalkyl)ethylenes (B).



3.3. Regioselectivity on 1,3-dioxolane ring

The addition of 2,2,4-trimethyl-1,3-dioxolane (**17**) to 1-(perfluoroalkyl)ethylene (**1c**, Scheme 5) was completely regioselective from the point of view of the olefin, but both C–H bonds at C4 and C5 in the dioxolane (**17**) were cleaved to give a mixture of two products (**18** and **19**). The ratio of these regioisomeric adducts 84:16 revealed a much greater reactivity of the tertiary C–H bond at C4. Almost the same result was obtained (Table 5) in the addition reaction of **17** with perfluorohept-1-ene [1]. We have reported previously [1] (see also Table 5) that the ratio of regioisomeric adducts



Scheme 5. Regioselectivity of the addition to 2,2,4-trimethyl-1,3-dioxolane (**17**).

Table 5
Products and regioselectivity of radical addition reactions of dioxolane (**17**) with fluoroolefins (Scheme 5)

Olefin	Initiation	Temperature (°C)	Regioisomeric adducts ^a (% rel.)		R _F	Ref.
						
C ₈ F ₁₇ -CH=CH ₂ (1e)	Bz ₂ O ₂	Reflux	84 (18)	16 (19)	a	b
CF ₃ -CF=CF ₂	UV	-15 to -5	87	13	c	[1]
CF ₃ (CF ₂) ₄ -CF=CF ₂	UV	-15 to -5	87	13	d	[1]
CF ₃ (CF ₂) ₄ -CF=CF ₂	Bz ₂ O ₂	Reflux	80	20	d	[1]
CF ₃ F ₇ O-CF=CF ₂	UV	-15 to -5	87	13	e	[1]

^a C₈F₁₇-CH₂CH₂.

^b This paper.

^c CF₃-CHF₂.

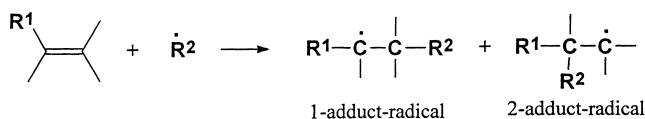
^d CF₃(CF₂)₄-CHF₂.

^e C₃F₇O-CHF₂.

of dioxolane (**17**) is not dependent on the olefin character and the olefin-chain length, which is in sharp contrast with the perfluorinated-chain length effect (the “tail effect” [1]). It has been shown that the ratio of products is given by the relative reactivity of the C–H bonds in the hydrogen-abstraction in the propagation step. A slightly higher relative amount of the minor adduct (e.g. **19**) in peroxide-initiated reaction has been explained [1] by much higher reaction temperature.

3.4. Quantum chemical calculations and the radical additions

The complete regioselectivity of the additions of nucleophilic radicals to (perfluoroalkyl)ethylenes (**1a–c**), which is the same as for perfluoroalk-1-enes, as summarized in Table 4, has led us to compare these observations with quantum chemical calculations. The free radical addition to double bond was studied on the basis of spin density surface examination and comparison of energies of both possible radical intermediates (e.g. 1- and 2-adduct-radical). Fluorinated propenes CF₃-CH=CH₂, CF₃-CF=CF₂, CH₃-CH=CH₂ and CH₃-CH=CF₂ as olefin models and CF₃, CH₃ and CH₂OH as models of electrophilic and nucleophilic radicals [40] were chosen for the calculations. For a comparison of reliability of the calculations, two quantum chemical methods have been employed, i.e. ab initio B3LYP/6-31G** [47] and the PM3 methods. The geometries of all radical intermediates (adduct-radicals, Scheme 6) were fully optimized on the same level of theory — thus PM3 for semiempirical and B3LYP/6-31G** for ab initio calculations. The results of both calculation procedures (adduct-radical energies) are summarized in Table 6.



Scheme 6. Regioisomeric adduct-radicals.

The energies of two regioisomeric adduct-radicals are compared for both methods in Table 6: 1-adduct-radical stands for the intermediate formed by the terminal carbon attack. A direct relation of the adduct-radical energy to the activation energy of its formation has been supposed: lower energy of an adduct-radical is combined with lower activation energy and therefore with its more rapid formation and preferential amount in the reaction mixture. Further discussion is based on this concept.

For 3,3,3-trifluoropropene (CF₃-CH=CH₂), which is a model structure of (perfluoroalkyl)-ethylenes (**1a–c**), and all the model radical partners (CF₃, CH₃ and CH₂OH), both theoretical models (PM3 and ab initio) prefer 1-adduct-radical in accord with experimental findings (Table 4) [44–46]. Analogous theoretical prediction was obtained for CH₃-CH=CH₂, which corresponds to the regioselectivity of the homolytic addition of trifluoromethyl iodide [44,46]. Inconsistent are theoretical predictions for addition preferences to CF₃-CF=CF₂: ab initio calculations predict preferential formation of 1-adduct-radical that is in accord with experimental observation for the additions of both trifluoromethyl [44,46,48,49] and hydroxymethyl radicals (Table 4) [41,42], while semiempirical PM3 predicts the opposite regioselectivity (Table 6). In the case of CH₃-CH=CF₂ molecule, the calculations give different predictions for the additions of electrophilic (CF₃) on one side, and for nucleophilic radicals (CH₃ and CH₂OH) on the other side (Table 6). Both methods predict preferential attack to the internal position with CF₃ radical, which completely corresponds to the experimental observation [50]. For the additions of nucleophilic radicals the predictions of the two calculation methods are inconsistent, however, the validity of them could not be verified as no data have been found in the literature.

The energy differences of both possible adduct-radicals are significantly high for reliability of predictions in the above discussion. It can be concluded on correlation of the above theoretical and experimental data that the more accurate level of ab initio calculations together with the

Table 6

Energy quantities for intermediate adduct radicals (ΔH_f — heat of formation, E_{rel} — energy preference, E_{TOT} — total energy)

Entry	Additive	PM3				B3LYP/6-31G**			
		1-Adduct		2-Adduct		1-Adduct		2-Adduct	
		ΔH_f^a	E_{rel}^a	ΔH_f^a	E_{rel}^a	E_{TOT}^b	E_{rel}^a	E_{TOT}^b	E_{rel}^a
<i>CF₃-CH=CH₂</i>									
1	CF ₃	-299.13	0.0	-293.63	5.5	-753.2385189	0.0	-753.2294398	5.7
2	CH ₃	-148.68	0.0	-145.52	3.2	-455.5217341	0.0	-455.5192785	1.5
3	CH ₂ OH	-186.72	0.0	-182.33	4.4	-530.7316250	0.0	-530.7255223	3.8
<i>CF₃-CF=CF₂</i>									
4	CF ₃	-427.97	1.7	-429.69	0.0	-1050.9124883	0.0	-1050.9077761	3.0
5	CH ₃	-284.01	2.2	-286.19	0.0	-753.2147835	0.0	-753.2121119	1.7
6	CH ₂ OH	-320.01	3.9	-323.88	0.0	-828.4198744	0.0	-828.4163266	2.2
<i>CH₃-CH=CH₂</i>									
7	CF ₃	-153.10	0.0	-145.51	7.6	-455.5248698	0.0	-455.5192785	3.5
8	CH ₃	0.20	0.0	6.73	6.5	-157.8045211	0.0	-157.7985721	3.7
9	CH ₂ OH	-40.15	0.0	-33.56	6.6	-233.0125231	0.0	-233.0070320	3.4
<i>CH₃-CH=CF₂</i>									
10	CF ₃	-240.72	5.3	-246.00	0.0	-653.9867522	1.1	-653.9885364	0.0
11	CH ₃	-91.88	4.0	-95.87	0.0	-356.2822319	0.0	-356.2745959	4.8
12	CH ₂ OH	-131.78	4.0	-135.76	0.0	-431.4890376	0.0	-431.4835825	3.4

^a kcal/mol.^b a.u. (atom units).

inclusion of correlation energy substantiate a greater reliability for the predictions based on this method.

4. Experimental

4.1. General comments

The temperature data were uncorrected. 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 (Laboratorní přístroje, Prague; FID, 380 × 0.3 cm packed column, silicone elastomer E-301 on Chromaton N-AW-DMCS (Lachema, Brno, 240/190°C, nitrogen) and on Micromat HRGC 412 (Nordion Analytical; FID, 25 m glass capillary column, SE-30, 240/190°C). NMR spectra were recorded on a Bruker 400 AM (FT, ¹⁹F at 376.5 MHz) and a Bruker WP 80 SY (FT, ¹⁹F at 75 MHz) instruments: TMS and CFCl₃ as the internal standards, chemical shifts in ppm (s singlet, bs broad singlet, d doublet, t triplet, q quadruplet, qi quintuplet, sx sextuplet, sep septuplet, m multiplet), coupling constants *J* in Hz, solvents CDCl₃, acetone-*d*₆, and DMSO-*d*₆. UV spectra were measured on a Hewlett-Packard 8452A (diode array) apparatus.

Quantum chemistry calculations: ab initio bases 3-21G and 6-311+G** — program Gaussian 94 [44]; PM3 — program MOPAC6 [51].

The chemicals used were as follows: 2,2-dimethyl-1,3-dioxolane (**13**, b.p. 91–93°C) and 2,2,4-trimethyl-1,3-dioxolane (**17**, b.p. 105–107°C, yield 83–85%; 1,1,2-trichloro-

trifluoroethane (CFC-113) was used as an azeotropic solvent) were prepared according to the literature procedures [52]. Acetone (for UV, Merck), perfluoroalkylethylenes (**1a–c**) (Elf Atochem) and methacryloyl chloride (Fluka) was distilled before use. Oxolane (Fluka), ethanol, 2-propanol and *tert*-butyl methyl ether (Kaučuk, Kralupy) were dried and purified according to the standard procedures: silica gel L40/100 (Merck), 2,2-diphenyl-1-picrylhydrazyl (Aldrich). Dibenzoyl peroxide (Merck) as precipitated from its chloroform solution by methanol and dried in vacuo.

4.2. General procedures

4.2.1. Photochemical initiation with UV light in the presence of acetone (products **2**, **3a–c**, **4**, **5a–c**)

Apparatus. The reactions were 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 externally by a medium pressure UV lamp (Tesla, RVK 400 W), placed in a reflecting-metal cylindrical housing, with a round window (diameter 5 cm) made of a quartz lens.

Reaction. The reaction mixture consisted of an additive (Table 1; 0.1 mol), the perfluoroalkylethylene (**1a–c**; 0.02 mol) and acetone (was deaerated for 1 h at ca. –40°C with a stream of argon (inlet–outlet by needles through septa). The mixture was then irradiated at r.t. for 3–4 h (ca. 97% conversion of the olefin, monitoring by GC) while stirring (magnetic spinbar). Excess additive was then distilled off (5 cm column packed with Berle saddles) and

the crude product was distilled to afford pure colorless product (for reaction amounts, conversion, yields, product purity and b.p. (m.p.), see Table 1).

2-(3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluorooctyl)oxolane (2). Analysis: Found: C, 34.69; H, 2.74; F, 58.14%. $C_{12}H_{11}F_{13}O_1$ requires: C, 34.46; H, 2.65; F, 59.06%. M, 418.20. 1H NMR ($CDCl_3$) δ : 1.51 (ddt, 1H(a), $CH_2CH_2CF_2$, $^2J_{HH} = 11$, $^3J_{HH} = 9$ and 7(t)); 1.79 (ddt, 1H(b), $CH_2CH_2CF_2$, $^2J_{HH} = 11$, $^3J_{HH} = 7$ and 4(t)); 1.91 (m, 2H, CH_2CH_2O); 2.03 (m, 2H, CH_2CHO); 2.31 (m, 2H, CH_2CF_2); 3.75, 3.85 (2 \times m, 2H, CH_2O); 3.87 (m, 1H, CHO) ppm. ^{19}F NMR ($CDCl_3$) δ : -81.38 (t, 3F, CF_3 , $^3J_{FF} = 10$); -115.02 (m, 2F, CF_2CH_2); -122.48 (m, 2F, $CF_2CF_2CH_2$); -123.41 (m, 2F, $CF_2(CF_2)_2CH_2$); -124.02 (m, 2F, $CF_2(CF_2)_3CH_2$); -126.71 (m, 2F, CF_2CF_3) ppm.

5,5,6,6,7,7,8,8,8-Nonafluoro-2-methyloctan-2-ol (3a). Analysis: Found: C, 35.47; H, 3.66; F, 56.66%. $C_9H_{11}F_9O$ requires: C, 35.31; H, 3.62; F, 55.85%. M, 306.17. Summarized NMR spectra of **3a-c**: 1H NMR ($CDCl_3$) δ : 1.28 (s, 6H, 2 CH_3); 1.38 (bs, 1H, OH); 1.74 (m, 2H, CH_2); 2.21 (m, 2H, CH_2CF_2) ppm. ^{19}F NMR ($CDCl_3$) δ : -81.37 to -81.60 (t, 3F, CF_3 , $^3J_{FF} = 10$); -114.74 to -115.15 (m, 2F, CF_2CH_2); -122.20 to -124.87 (m, 2-10 F, 1-5 CF_2); 126.48 to -126.75 (m, 2F, CF_2CF_3) ppm.

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluoro-2-methyldecan-2-ol (3b). Analysis: Found: C, 32.60; H, 2.74; F, 60.67%. $C_{11}H_{11}F_{13}O$ requires: C, 32.53; H, 2.73; F, 60.80%. M, 406.19.

5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluoro-2-methyldodecan-2-ol (3c). Analysis: Found: C, 30.78; H, 2.23; F, 63.87%. $C_{13}H_{11}F_{17}O$ requires: C, 30.85; H, 2.19; F, 63.80%. M, 506.20.

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecan-2-ol (4). Analysis: Found: C, 30.81; H, 2.34; F, 62.42%. $C_{10}H_9F_{13}O_1$ requires: C, 30.63; H, 2.31; F, 62.98%. M, 392.16. 1H NMR ($CDCl_3$) δ : 1.26 (d, 3H, CH_3 , $^3J_{HH} = 6.2$); 1.67 (bs, 1H, OH); 1.72 (m, 2H, CH_2); 2.22 (m, 2H, CH_2CF_2); 3.87 (ddq, 1H, CH, $^3J_{HH} = 8$, 6.2(q) and 4) ppm. ^{19}F NMR ($CDCl_3$) see **2**.

4.2.2. Thermal initiation with dibenzoyl peroxide (products **5a-c**, **18**, **19**)

A homogenous mixture of perfluoroalkylethylene (**1a-c**, 0.02 mol), dioxolane (**17**, 0.1 mol) and dibenzoyl peroxide (0.48 g, 2 mmol) was deaerated for 0.5 h at ca. $-20^\circ C$ with a stream of argon (inlet-outlet by two needles through the septa) in a flask (25 ml) equipped with a dry-ice cooled spiral reflux condenser with a hydraulic seal (sulfuric acid). The reaction mixture was refluxed for 4 h while stirring (96–97% conversion of olefins, monitoring by GC) and passing through a slight stream of nitrogen. The reaction mixture was passed through a short column of silica gel (1 \times 1 cm), excess of dioxolane was distilled off (column 5 cm packed with Berle saddles), and the crude product was distilled in vacuo to afford pure colorless product (for reaction

amounts, conversion, yields, product purity and b.p. (m.p.), see Table 1).

2,2-Dimethyl-4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)-1,3-dioxolane (5a). Analysis: Found: C, 37.91; H, 3.86; F, 49.27%. $C_{11}H_{13}F_9O_2$ requires: C, 37.94; H, 3.76; F, 49.10%. M, 348.21. Summarized NMR spectra of **5a-c**: 1H NMR ($CDCl_3$) δ : 1.36, 1.43 (2 \times s, 6H, 2 CH_3); 1.83 (m, 2H, CH_2CHO); 2.23 (m, 2H, CH_2CF_2); 3.60 (dd, 1H(a), CH_2O , $^2J_{HH} = 6$, $^3J_{HH} = 8$); 4.09 (t, 1H(b), CH_2O , $^2J_{HH} = ^3J_{HH} = 6$); 4.13 (ddt, 1H, CHO, $^3J_{HH} = 12$, 8 and 6(t)) ppm. ^{19}F NMR ($CDCl_3$) see (**3a-c**).

2,2-Dimethyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-1,3-dioxolane (5b). Analysis: Found: C, 34.94; H, 3.06; F, 55.29%. $C_{13}H_{13}F_{13}O_2$ requires: C, 34.84; H, 2.92; F, 55.10%. M, 448.22.

2,2-Dimethyl-4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)-1,3-dioxolane (5c). Analysis: Found: C, 33.07; H, 2.46; F, 59.34%. $C_{15}H_{13}F_{17}O_2$ requires: C, 32.86; H, 2.39; F, 58.91%. M, 548.24.

4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-2,2,4-trimethyl-1,3-dioxolane (18) and **4-(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluorodecyl)-2,2,5-trimethyl-1,3-dioxolane (19).** Analysis (**18 + 19**): Found: C, 34.12; H, 2.84; F, 57.95%. $C_{16}H_{15}F_{17}O_2$ requires: C, 34.18; H, 2.69; F, 57.44%. M, 562.27. 1H NMR (**18**, 84% rel., $CDCl_3$) δ : 1.31, 1.39 (2 \times s, 9H, 3 CH_3); 1.74, 1.89 (2 \times dt, 2H, $CH_2CH(CH_3)$, $^2J_{HH} = 12$, $^3J_{HH} = 12$ and 5); 2.22 (m, 2H, CH_2CF_2); 3.78, 3.82 (2 \times d, 2H, CH_2O , $^2J_{HH} = 9$) ppm. 1H NMR (**19**, 16% rel., $CDCl_3$) δ : 1.27, 1.29, 1.34, 1.44 (4 \times s, 9H, 3 CH_3); 1.70–1.90 (m, 2H, CH_2); 2.22 (m, 2H, CH_2CF_2); 2.76, 2.92 (2 \times m, 1H, CH_3CHO); 3.53 (dt, 1H, CH_2CHO , $^3J_{HH} = 8$ (t) and 3) ppm. ^{19}F NMR ($CDCl_3$): see **3a-c**.

4.2.3. General procedure for hydrolysis of fluoroalkylated dioxolanes (**5a-c**) to the corresponding diols (**15a-c**)

Apparatus. The reactions were carried out in a round-bottomed flask (25 ml) equipped with Dimroth reflux condenser, a drying tube (potassium hydroxide) and with a magnetic spinbar.

Reaction. A mixture of fluoroalkylated dioxolane (**5a-c**, 0.02 mol), methanol (12.8 g, 0.40 mol) and concentrated hydrochloric acid (0.5 g) was refluxed for 3 h while stirring (the complete conversion of the dioxolane was checked by ^{19}F NMR or TLC). Methanol was removed on a rotary evaporator and toluene (ca. 50 ml) was then added to the residue and the mixture was fractionated on a packed column (15 cm, Berle saddles, heated jacket). After distilling toluene off under atmospheric pressure, the residue was then distilled in vacuo and the product (**15a-c**) was taken as the last fraction (for yields, purity, b.p. and m.p., see Table 3).

5,5,6,6,7,7,8,8,8-Nonafluorooctane-1,2-diol (15a). Analysis: Found: C, 31.44; H, 3.02; F, 55.49%. $C_8H_9F_9O_2$ requires: C, 31.18; H, 2.94; F, 55.49%. M, 308.14. Summarized NMR spectra of **15a-c**: 1H NMR ($DMSO-d_6$) δ :

1.49 (ddt, 1H(a), CH_2CH , $^2J_{\text{HH}} = 12$, $^3J_{\text{HH}} = 12$, 9 and 5); 1.77 (ddt, 1H(b), CH_2CH , $^2J_{\text{HH}} = 12$, $^3J_{\text{HH}} = 12$, 5 and 3.5); 2.29 (m, 2H, CH_2CF_2); 3.26, 3.38 ($2 \times$ dt, 2H, CH_2O , $^2J_{\text{HH}} = 11$, $^3J_{\text{HH}} = 5$); 3.49 (ddq, 1H, CHO, $^3J_{\text{HH}} = 9$, 5(q) and 3.5); 4.65 (t, 1H, CH_2OH , $^3J_{\text{HH}} = 5$); 4.77 (d, 1H, CHO, $^3J_{\text{HH}} = 5$) ppm. ^{19}F NMR ($\text{DMSO}-d_6$) δ : -80.47 to -80.51 (t, 3F, CF_3 , $^3J_{\text{FF}} = 10$); -113.34 to -113.46 (m, 2F, CF_2CH_2); -121.55 to -123.87 (m, 2–10 F, 1–5 CF_2); 125.63 to -125.79 (m, 2F, CF_2CF_3) ppm.

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecane-1,2-diol (15b). Analysis: Found: C, 29.81; H, 2.30; F, 59.60%. $\text{C}_{10}\text{H}_9\text{F}_{13}\text{O}_2$ requires: C, 29.43; H, 2.22; F, 60.51%. M, 408.16.

5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecane-1,2-diol (15c). Analysis: Found: C, 28.35; H, 1.79; F, 63.85%. $\text{C}_{12}\text{H}_9\text{F}_{17}\text{O}_2$ requires: C, 28.36; H, 1.79; F, 63.56%. M, 508.18.

4.2.4. General procedure for the preparation of bis-methacrylates (**16a–c**)

The reaction was carried out in a round-bottomed flask (25 ml) equipped with a Dimroth reflux condenser connected to the atmosphere through a drying tube (potassium hydroxide) and with a magentic spinbar (for apparatus see Section 4.2.3, flask 100 ml).

Reaction. A mixture of methacryloyl chloride (6.28 g, 60 mmol), fluoroalkylated diol (**15a–c**, 10 mmol), triethylamine (7.1 g, 70 mmol), diethyl ether (60 ml) and a stabilizer (2,2-diphenyl-picrylhydrazyl, 0.1 mmol) was stirred at r.t. for 2 h (the complete conversion of a diol was checked by ^{19}F NMR). Methanol (1.3 g, 40 mmol) was then added and the mixture was stirred for an additional hour. Water (2×100 ml) was then added slowly to the mixture, the ethereal layer was separated, the water layer was extracted with ether (40 ml), ethereal solutions were combined and dried with magnesium sulfate. After evaporation of diethyl ether (rotary evaporator), triethylamine and methyl methacrylate were removed in vacuo (water pump) and the residue was distilled under high vacuum to give pure product (for yields, purity of products **16a–c**, b.p. and m.p., see Table 3).

5,5,6,6,7,7,8,8,8-Nonafluorooctane-1,2-diyl bis-methacrylate (16a). Analysis: Found: C, 43.12; H, 3.95; F, 38.82%. $\text{C}_{16}\text{H}_{17}\text{F}_9\text{O}_4$ requires: C, 43.25; H, 3.86; F, 38.48%. M, 444.29. Summarized NMR spectra of **16a–c**: ^1H NMR (CDCl_3) δ : 1.50 (ddt, 1H(a), CH_2CH , $^2J_{\text{HH}} = 12$, $^3J_{\text{HH}} = 12$, 8 and 4); 1.80 (ddt, 1H(b), CH_2CH , $^2J_{\text{HH}} = 12$, $^3J_{\text{HH}} = 12$, 5 and 3); 1.94, 1.95 ($2 \times$ s, 6H, 2 CH_3); 2.48 and 2.58 ($2 \times$ dm, 2H, CH_2CF_2 , $^2J_{\text{HH}} = 19$); 4.27–4.32 (dd, 1H(a), CH_2O , $^2J_{\text{HH}} = 12$, $^3J_{\text{HH}} = 5$); 4.43–4.48 (dd, 1H(b), CH_2O , $^2J_{\text{HH}} = 12$, $^3J_{\text{HH}} = 4$); 5.58–5.62 (s, 2H(E), 2 $\text{CH}_2=$); 5.63–5.65 (m, 1H, CHO); 6.12, 6.13 ($2 \times$ m, 2H(Z), 2 $\text{CH}_2=$) ppm. ^{19}F NMR (CDCl_3) see (**3a–c**).

5,5,6,6,7,7,8,8,9,9,10,10,10-Tridecafluorodecane-1,2-diyl bis-methacrylate (16b). Analysis: Found: C, 39.81; H, 3.19; F, 45.42%. $\text{C}_{18}\text{H}_{17}\text{F}_{13}\text{O}_4$ requires: C, 39.72; H, 3.15; F, 45.37%. M, 544.31.

5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluorododecane-1,2-diyl bis-methacrylate (16c). Analysis: Found: C, 37.35; H, 2.72; F, 50.44%. $\text{C}_{20}\text{H}_{17}\text{F}_{17}\text{O}_4$ requires: C, 37.28; H, 2.66; F, 50.13%. M, 644.33.

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