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Radical-induced reaction of monoiodo- and diiodo-perfluoroalkanes with allyl acetate: telomer and rearranged products, mass-spectral distinguishing of regioisomers

V. Církva [a], B. Améduri [b,*], B. Boutevin [b], J. Kvíčala [a], O. Paleta [a]

[a] *Department of Organic Chemistry, Prague Institute of Chemical Technology, Technicka 5, 16628 Prague 6, Czech Republic*

[b] *Ecole Nationale Supérieure de Chimie de Montpellier, URA (CNRS) 1193, 8, rue de l'Ecole Normale, 34053 Montpellier-Cedex, France*

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Abstract

The radical reaction of monoiodoperfluoroalkanes R_FI ($R_F = C_4F_9$, C_6F_{13}, C_8F_{17}) and diiodoperfluoroalkanes I–Q–I ($Q = C_4F_8$, C_6F_{12}) with allyl acetate initiated by peroxidic initiators is described. Under the reaction conditions employed, the conversion of both R_FI and IQI was complete in most cases. The reactions of R_FI also yielded some 2:1 telomers which are new compounds which have been characterized. In certain cases, the telomers were isolated in preparative yield up to 34%. Both 1:1 adducts [$R_FCH_2CHICH_2OCOCH_3$, (**2a–c**)] and 2:1 telomers (**5a–c**) underwent subsequent thermal rearrangement [formation of $R_FCH_2CH(OCOCH_3)CH_2I$, (**3a–c**), and telomers (**6a–c**), respectively] at elevated temperatures. In the reaction of diiodides IQI, monoadducts [$CH_3COOCH_2CHICH_2QI$, (**9a,b**)] and diadducts [$(CH_3COOCH_2CHICH_2)_2Q$ (**10a,b**)] were formed, but no telomeric and rearranged products were found under the reaction conditions employed. On the other hand, isolated mono- (**9**) and di-adducts (**10**) underwent a similar rearrangement to the compounds **2a–c** and **5a–c** at elevated temperatures. Regioisomeric primary and rearranged products could be distinguished by mass spectrometry in which characteristic signals for a series of compounds with different R_F groups were found.

Keywords: Telomerization; Allyl acetate; Radical initiation; Perfluoroalkyl iodides; Mass spectrometry; NMR spectroscopy

1. Introduction

The addition of perfluoroalkyl iodides (R_FI) to double bonds has been extensively investigated by many authors. Different methods of initiation or induction have been successfully employed leading to monoadduct compounds. Such initiation can be performed thermally [1], biochemically [2], electrochemically [3], from organic peroxides or azo derivatives [4–7] or by specific catalysts or complexes [8–18].

Of the olefins studied, functional ones and especially allyl acetate have been used frequently and it has been shown that the monoadduct was produced as the sole compound.

However, previous studies on the radical-induced telomerization of allyl acetate with methyl dichloroacetate [19] and chloroform [20] as telogens, initiated by peroxides or AIBN or both, produced not only monoadducts but also di- and tri-adducts in small amounts.

For this reason, it was of interest to investigate if, in the radical additions of R_FI to allyl acetate, telomeric product can also be formed. Furthermore, recent investigations [6] have shown that the primary monoadduct $R_FCH_2CHICH_2OAc$ (**2**) is rearranged to $R_FCH_2CH(OAc)CH_2I$ (**3**) on subsequent reaction at higher temperatures and from this point of view it seems of interest to perform the addition at lower temperatures. In the literature [4–6], only AIBN or dibenzoyl peroxide have been described as initiators.

The radical addition reaction of some diiodides, I–Q–I, with allyl acetate has been described previously [21] but the structures of products were assigned only on the basis of elemental analyses and refractive indices. In addition, the synthesis of fluorinated non-conjugated dienes from diiodo α,ω-diacetates produced from the radical addition of $I(CF_2)_nI$ ($n = 4$ or 6) to allyl acetate has been studied recently [22]. These diacetates were not purified but irrespective of their expected or thermally arranged structures, the fluorinated dienes were successfully produced in high yield.

In the light of recent knowledge regarding the behaviour of primary adducts at elevated temperatures [6], it seemed worthwhile verifying the former results.

* Corresponding author.

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The present work was focused on a more detailed study of the reaction of R_FI with allyl acetate from the viewpoint of the structure and relative amounts of telomers generated depending on the new initiators employed. In the case of diiodides, I–Q–I, an attempt has been made to establish a preparative route.

2. Results and discussion

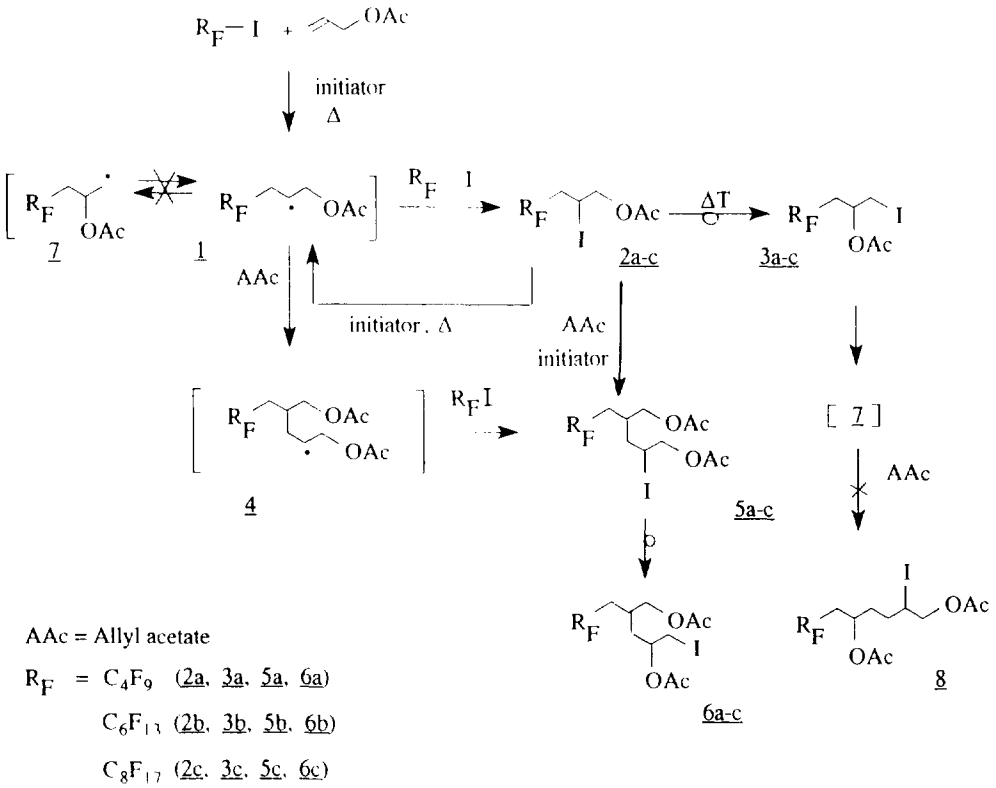
2.1. Reactions of perfluoroalkyl iodides

The reaction of R_FI with allyl acetate in the presence of organic peroxide as an initiator undoubtedly occurs via a free-radical chain reaction [4–6] as demonstrated by the formation of telomers. The reaction mixture also contained rearranged products which were formed subsequently from primary adducts [6]. Probable mechanistic routes for the formation of the products **2**, **3**, **5** and **6** are depicted in Scheme 1. The initially formed adduct-radical **1** does not rearrange to radical **7** because of the high stability of radical **1** [23] and from the fact that no rearranged product was formed at lower temperatures (Table 1, runs 5, 8–16). On the other hand, the primary adducts **2a–c** undergo thermal rearrangement, resulting in the formation of regioisomers **3a–c**, respectively. This is clearly shown by the ^{1}H NMR spectra of **3a–c** which exhibit a doublet of quadruplets centred at δ 5.2 ppm characteristic of the proton linked to the tertiary carbon atom adjacent to the lateral acetoxy function.

The initially formed radical **1** can react with a second molecule of monomer to yield the telomer-radical **4** which as a result of the transfer of R_FI forms the 2:1 telomer **5**. This is also demonstrated by the production of monoadducts **2a–c** which also provide interesting telogens for the further addition of allyl acetate in the presence of dibenzoyl peroxide. The reactivity of these monoadducts is intermediate between that of $R_FC_2H_4I$, which is very unreactive for such an olefin, and R_FCH_2I, which leads to $R_FC_2H_4CHICH_2OAc$ in 30% yield [24]. In fact, compound **2** gave the unrearranged 2:1 telomer **5**. This observation supports the idea that 2:1 telomers can also be formed in a subsequent reaction of the corresponding monoadducts **2**. Thus both a stepwise and a propagation mechanism may occur.

The chemical shifts in the ^{1}H NMR spectra of these 2:1 telomers are in good agreement with those observed for the diadduct $Cl_3CCH_2CH(CH_2OAc)CH_2CH_2CH_2OAc$ obtained by the radical telomerization of allyl acetate with chloroform [20], but also indicate that the CHI group is located in the β position relative to the terminal acetoxy group.

Most probably the 2:1 telomers **5a–c** are rearranged thermally to the corresponding regioisomers **6a–c** in a similar manner to the rearrangement of monoadducts **2a–c** to the regioisomers **3a–c**. This is verified by ^{1}H NMR spectrum of the mixture of normal **5b**/rearranged **6b** monoadducts which



Scheme 1. Reaction mechanism for the radical telomerization of allyl acetate with perfluoroalkyl iodides.

Table 1
Radical additions of R_FI to allyl acetate in the presence of various initiators: experimental conditions employed

Run No.	Initiator	R_F	$R_0 = m_{RI}/m_{AA}$	Reaction time (min)	Temperature (°C) [a]		Conversion of R_FI (%) [b]	Product yield (%)			
					T_i	T_m		1:1 Adducts		2:1 Telomers	
								Preparative yield [c] (**2a–c**)	Rearranged product [d] (**3a–c**)	Preparative yield [e] (**5a–c**)	Rearranged product [d] (**6a–c**)
1	DBP	C_4F_9	1.00	45	80	120	95	90	0	5	50
2		C_6F_{13}	1.00	1	95	170	96	92	6	5	71
3		C_8F_{17}	1.00	1	95	170	90	88	15	3	77
4		C_8F_{17}	0.80	1	95	170	97	90	15	8	77
5	T-25	C_4F_9	1.00	15	77	120	90	87	0	5	0
6		C_6F_{13}	1.00	1	80	160	94	90	4	3	–
7		C_8F_{17}	1.00	1	80	160	88	86	8	2	–
8	P-16	C_4F_9	1.00	5	65	120	82	84	0	5	0
9		C_6F_{13}	1.00	5	65	120	90	88	0	2	0
10		C_8F_{17}	1.00	5	65	120	85	84	0	2	0
11	P-16	C_4F_9	0.50	8	65	110	96	72	0	25	0
12		C_6F_{13}	0.50	8	65	110	94	74	0	21	0
13		C_8F_{17}	0.50	8	65	110	92	78	0	15	0
14	P-16	C_4F_9	0.25	10	65	110	98	64	0	34	0
15		C_6F_{13}	0.25	10	65	110	99	68	0	32	0
16		C_8F_{17}	0.25	10	65	110	99	70	0	29	0

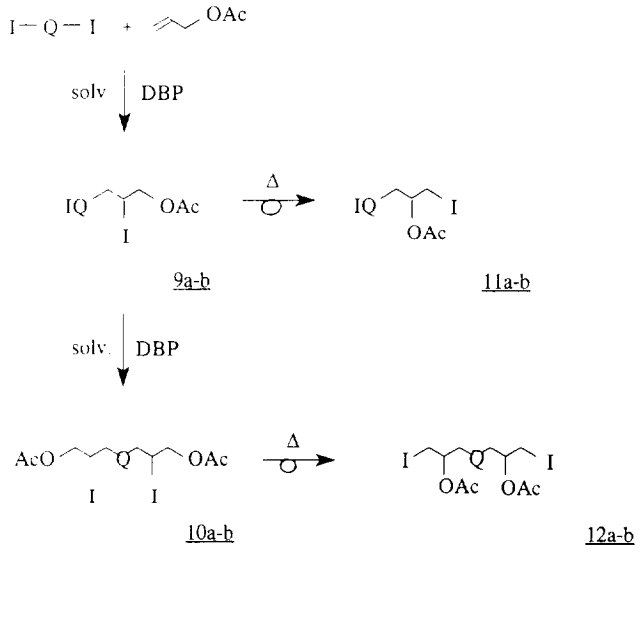
[a] T_i = temperature at which initiator was introduced; T_m = maximum reaction temperature.
[b] Calculated for GC analysis of the total product.
[c] Obtained by distillation.
[d] Obtained from ^1H NMR analysis after distillation.
[e] Mol% relative to 1:1 adduct (100%).

exhibits five separate characteristic signals which may be assigned to the various groups present.

Compounds with structure **8**, i.e. products of a subsequent reaction between the rearranged monoadduct **3** and one molecule of allyl acetate, were not observed in the reaction mixture. Two general reasons may be advanced to explain this: first, the intermediate radical **7** may rearrange rapidly to the more stable radical **1**; secondly, no cleavage of the C–I bond takes place under the reaction conditions because of the presence of weak electron-withdrawing groups and hence radical **7** is not formed. The first reason seems to be more significant [23].

2.2. From $I(CF_2)_nI$

The reaction of diiodides I–Q–I ($Q = C_4F_8$, C_6F_{12}) with allyl acetate was initiated by dibenzoyl peroxide. The reaction is a stepwise process in which monoadduct **9** is formed initially and subsequently reacts with another molecule of allyl acetate to form the diadduct **10**. The reactions are depicted in Scheme 2. The reaction mechanism obviously follows pathways analogous to the reactions of R_FI and will not be discussed further here. In contrast to the reactions of R_FI, neither the rearranged nor the telomeric products were detected in the reaction mixture because of the lower reaction tempera-



DBP = Dibenzoyl peroxide

Q = C_4F_8 (9a, 10a, 11a, 12a), C_6F_{12} (9b, 10b, 11b, 12b)

Scheme 2. Reaction mechanism for the radical addition of α,ω-diiodoperfluoroalkanes to allyl acetate.

ture employed. On the other hand, heating the isolated individual products **9a**, **10a** and **10b** up to 180 °C led to the same rearrangement as observed in the case of the monoiodides **2** and **5**, with the corresponding regioisomers **11a** and **12a,b** being obtained.

Similar results have been described in a previous paper [21] in which, however, the structures of products were only confirmed by elemental analyses and refractive indexes. The products were isolated by distillation (b.p. above 160 °C), and, in the light of present knowledge [6], under such temperatures rearrangement must have proceeded and a mixture of regioisomers resulted.

2.3. Composition of the reaction mixtures

The influence of the reaction conditions and initiators on the composition of the resulting product mixture is listed in Table 1. All the reactions were exothermal and an increase in temperature of the system was observed (Table 1). The conversion of R_FI was generally virtually complete, a slight decrease in reactivity being detected for the perfluoroalkyl iodide with the longest chain (viz. Table 1, runs 7, 10 and 13). The initial reaction temperature was chosen in such a manner as to correspond to an initiator half-life of ca. 1 h [1]. In fact, all the exothermicity of the reactions led to a temperature jump that caused a drastic reduction in the reaction time: thus, in runs 2–4 and 6 and 7, the reaction was complete in ca. 1 min and in most cases did not exceed 10 min.

The relative amounts of monoadduct and the 2:1 telomer present in the reaction products was strongly dependent on the R_0 value, i.e. the $[R_FI]_0/[\text{allyl acetate}]_0$ ratio: the greater the excess amount of allyl acetate present in the initial mixture, the higher proportion of telomers formed; the latter reached a maximum value of ca. 34% of the total preparative yield in run 14.

The three different initiators used, dibenzoyl peroxide, t-butyl peroxypivalate (Trigonox 25) and bis(4-t-butylcyclohexyl)peroxydicarbonate (Perkadox 16), allowed the reaction temperature to be modified. Subsequent rearrangement of the primary adducts was connected with this particular reaction factor. Such 1,2-migration has recently been described for the monoadducts **2** [6]. In addition, we have confirmed that rearrangement takes place with the 2:1 telomers **5** leading to formation of the regioisomers **6**. As can be seen from Table 1, the use of initiators with a lower working temperature (runs 8–16) resulted in no rearranged product being formed. However, when the reaction (and distillation) temperatures were greater than 140 °C [6], rearranged products were obtained (runs 6 and 7). Above 160 °C, the amounts of regioisomers **3** were greater (runs 3 and 4) and, during distillation of the 2:1 telomer **5**, isomerization to the regioisomer **6** proceeded to a considerable degree (runs 1–4). Thus the general features of the isomerization have been confirmed.

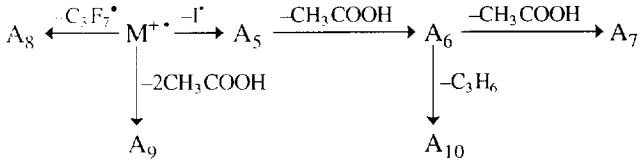
[1] Half-life of initiator taken from *Technical Data Akzo*, 1989.

2.4. Mass spectra

Elemental analyses of samples of the highly fluorinated products which was usually coloured with free iodine gave unsatisfactory results despite their 99% yield and higher percentage purity. This was the principal reason for the use of mass spectrometry. In addition, some regularities appeared in the splitting of molecules within a series, as discussed below. Generally, the molecular ion $M^{+\bullet}$ was either not registered or its signal exhibited only a very weak intensity. In contrast, the fragments $(M-I)^{+\bullet}$ and $(M-CH_3CO_2H)^{+\bullet}$ were quite intense allowing confirmation of the molecular weight.

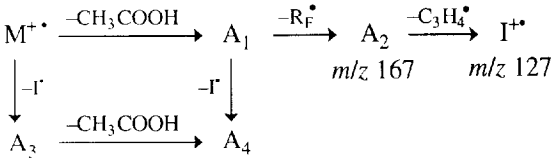
The regularities found are also interesting: (a) the MS spectra were very similar for the same structural type, e.g. for the group of compounds **3a–c**, or **5a–c**; and (b) in contrast, the spectra were different for the corresponding regioisomers, i.e. group **2a–c** differs in MS splitting from group **3a–c**.

The scheme applies for the MS splitting of the regioisomeric compounds **2** and **3**:



However, a remarkable difference in the relative intensity of the fragments A_2 and $I^{+\bullet}$ was observed. Whereas for compounds **2a–c** the A_2 fragment with $m/z = 167$ was less intense than that of the radical-ion $I^{+\bullet}$ with $m/z = 127$ (approximate ratio 15:48), for the corresponding regioisomers **3a–c**, the relative intensities were reversed in the approximate ratio 40:13.

For the 2:1 telomers **5a–c** and their corresponding regioisomers **6a–c**, two apparent differences were found in the MS spectra:



First, the ion A_9 $(M-2CH_3CO_2H)^{+\bullet}$ was not detected in the MS spectra of telomers **5** in contrast to the situation with compounds **6**. Secondly, in the MS spectra of telomers **5**, the most intense ion A_5 $(M-I)^{+\bullet}$ was observed together with the less intense ion A_7 $(M-I-2CH_3CO_2H)^{+\bullet}$ in 30%–40% relative intensity, while for regioisomers **6** the relative intensities were in the reverse ratio, i.e. $A_5:A_7 = 50:100$.

Some regularities were also found in MS spectral splitting of products of the reactions of diiodides: thus, in the monoadducts **9a,b**, a signal corresponding to A_{14} $(M-CH_3CO_2H-H)^{+\bullet}$ with a relative intensity of ca. 30% together with a signal corresponding to A_{13}

$(M-CH_3CO_2H-21)^{+\bullet}$ of a low intensity (below 10%) was observed.

$$A_{14} \xleftarrow[H]{-CH_3COOH} M^{+\bullet} \xrightarrow{I^{\bullet}} \underset{(\mathbf{9a,b})}{} \qquad A_{11} \xrightarrow{CH_3COOH} A_{12} \xrightarrow{I^{\bullet}} A_{13}$$

Similarly, in the rearranged product **11a** (which is a regioisomer of the primary adduct **9a**), a signal corresponding to A_{16} $(M-CH_3CO_2H)^{+\bullet}$ (100% rel. intensity) was observed in the mass spectrum together with a more intense signal (ca. 30% rel. intensity) corresponding to A_{13}.

$$\begin{array}{ccccc} & & M^{+\bullet} & \xrightarrow{-I^{\bullet}} & A_{15} \\ & & (\mathbf{11a}) & & \\ & & \downarrow -CH_3COOH & & \downarrow -CH_3COOH \\ & & A_{16} & \xrightarrow{-I^{\bullet}} & A_{17} \xrightarrow{-I^{\bullet}} A_{13} \end{array}$$

The primary diadducts **10** can be distinguished from the regioisomeric products of their rearrangement (**12**) by the fact that the splitting is little different:

$$M^{+\bullet} \xrightarrow{-HI} A_{18} \xrightarrow{-CH_3COOH} A_{19}$$
(**10a,b**)

$$M^{+\bullet} \xrightarrow{I^{\bullet}} A_{20} \xrightarrow{-CH_3COOH} A_{21}$$
(**12a,b**)

The mass spectra of compounds **10a,b** contain signals corresponding to A_{18} $(M-HI)^{+\bullet}$ and A_{19} $(M-HI-CH_3CO_2H)^{+\bullet}$, while in the regioisomers **12a,b** the corresponding ions A_{20} $(M-I)^{+\bullet}$ and A_{21} $(M-I-CH_3CO_2H)^{+\bullet}$ differ by a value of 1.

3. Experimental details

3.1. General comments

Perfluoroalkyl iodides were kindly supplied by Elf Atochem whereas allyl acetate, dibenzoyl peroxide, Trigonox 25 and Perkadox 16 were purchased from Aldrich, Merck and Akzo, and did not require any purification prior to use with the exception of dibenzoyl peroxide which was used in the anhydrous form. 1,4-Diiodoperfluorobutane and 1,6-diiodoperfluorohexane were obtained from Mihama Corp., Japan and were worked-up with alkaline thiosulphate solution.

After reaction, the products were worked-up and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with a SE30 column, 1 m × 1/8 in. (i.d.). (The nitrogen pressure was maintained at 0.6 bar, and the detector and injector temperatures were 260 °C and 255 °C, respectively. The temperature program covered the range 50–250 °C at 15 °C min^{-1}.) The GC apparatus was connected to a Hewlett Packard integrator (model 3390) which automatically calculated the area of each peak on the chromatogram.

Mass spectra were scanned on a GLC–mass spectrometer tandem JEOL DX-303 (JMA 5000, single focus, 70 eV, helium, GLC inlet via a capillary column 100 cm, coated with silicone elastomer).

The products were characterized by ^1H, ^{19}F and ^{13}C NMR spectroscopy, all undertaken at room temperature and recorded in $CDCl_3$ on a Bruker AC-200 or -250 apparatus or a Bruker WM-360 instrument, with hexamethyldisiloxane and trichlorofluoromethane as the internal references. The letters s, d, t, q, kv and m designate singlet, doublet, triplet, quadruplet, quintuplet and multiplet, respectively.

3.2. Radical addition of perfluoroalkyl iodides to allyl acetate

3.2.1. From perfluoro-n-butyl iodide

Into a 250 ml three-necked round-bottom flask equipped with a condenser and a thermometer were introduced perfluorobutyl iodide (22.3 g, 0.05 mol) and allyl acetate (5.0 g, 0.05 mol). The mixture was heated up to 60, 75 or 80–95 °C, depending upon the nature of the initiator: bis(4-t-butylcyclohexyl)peroxydicarbonate (Perkadox 16), t-butyl peroxypivalate (Trigonox 25) or dibenzoyl peroxide, respectively. At the corresponding temperature, a quarter of the required initiator (0.001/4 mol) was introduced into the stirred solution every 15 min and the temperature of the medium carefully checked. After a fixed time (see Table 1), the amber mixture became clear within a few seconds and an exotherm up to 100–120 °C (Table 1) occurred leading to an instantaneous change of colour to violet brown. This indicated completion of the reaction. The monoadduct (20.1 g) was distilled as a reddish liquid.

2-Iodo-4,4,5,5,6,6,7,7,7-nonafluoroheptyl acetate (C_4F_9-$CH_2CHICH_2OCOCH_3$) (**2a**): b.p. 48 °C/0.5 mmHg (lit. value [10]: 107–113 °C/30 Torr). Analysis: Found: C, 24.7; H, 1.8; F, 38.1%. $C_9H_8F_9IO_2$ requires: C, 24.2; H, 1.8; F, 38.3%; M, 446.0. ^1H NMR ($CDCl_3$) δ: 2.05 (s, 3H, CH_3); 2.82 (dt, 2H, CH_2CF_2); 4.28 (2dd, 2H, CH_2–O); 4.38 (m, 1H, CHI) ppm. ^{13}C NMR ($CDCl_3$) δ: 169.64 (s, 1C, C=O); 108–125 (m, C_4F_9); 68.19 (s, 1 C, CH_2–O); 37.79 (t, 1C, CH_2CF_2, $^2J_{CF}=21$ Hz); 20.06 (s, 1C, CH_3); 11.55 (s, 1C, CHI) ppm. ^{19}F NMR ($CDCl_3$) δ: −81.92 (t, 3F, CF_3); −113.40 (F_a), −115.30 (F_b) (ddm, 2F, CF_2–CH_2); −125.21 (m, 2F, CF_2); −126.63 (m, 2F, CF_2CF_3) ppm. MS *m/z* (% rel. int.): 446 [(1.2, M)$^{+\bullet}$]; 387 [31, $M-CH_3CO_2)^{+\bullet}$]; 386 [80, $(M-CH_3CO_2H)^{+\bullet}$]; 367 [12, $(C_7H_4F_8I^{+\bullet})$]; 320 (24); 319 [100, $(M-I)^{+\bullet}$]; 259 [27, $(C_7H_4F_9)^{+\bullet}$]; 240 [23, $(C_7H_4F_8)^{+\bullet}$]; 213 [21, $(C_5HF_8)^{+\bullet}$]; 195 [22, $(C_5H_2F_7)^{+\bullet}$]; 189 [17, $(C_6H_3F_6)^{+\bullet}$]; 167 [10, $(C_3H_4I)^{+\bullet}$]; 141 [11, $(CH_2I)^{+\bullet}$]; 127 (37, $I^{+\bullet}$); 121(11); 91(27); 90(15); 77(16); 69 [35, $(CF_3)^{+\bullet}$]; 58 [42, $(C_2H_2O_2)^{+\bullet}$]; 53(11).

On heating this compound up to 170–190 °C, the rearranged product **3a** was obtained.

1-Iodomethyl-3,3,4,4,5,5,6,6,6-nonafluorohexyl acetate ($C_4F_9CH_2CH(OCOCH_3)CH_2I$) (**3a**): b.p. 89–90 °C/10 mmHg. Analysis: Found: C, 23.8; H, 1.8; F, 37.9%. $C_9H_8F_9IO_2$ requires: C, 24.2; H, 1.8; F, 38.3%; M, 446.0. ^{1}H NMR ($CDCl_3$) δ: 2.03 (s, 3H, CH_3); 2.82 (m, 2H, CH_2CF_2); 3.36 (m, 2H, CH_2I); 5.10 (m, 1H, CH–O) ppm. MS *m/z* (% rel. int.): 446 (0.7, $M^{+\bullet}$); 387 [25, $(M-CH_3CO_2)^{+\bullet}$]; 386 [99, $(M-CH_3CO_2H)^{+\bullet}$]; 366 [9, $(C_7H_3F_8I)^{+\bullet}$]; 320 (14); 319 [100, $(M-I)^{+\bullet}$]; 259 [8, $(C_7H_4F_9)^{+\bullet}$]; 240 [12, $(C_7H_4F_8)^{+\bullet}$]; 213 [20, $(C_5HF_8)^{+\bullet}$]; 195 [17, $(C_5H_2F_7)^{+\bullet}$]; 189 [13, $(C_6H_3F_6)^{+\bullet}$]; 167 [38, $(C_3H_4I)^{+\bullet}$]; 141 [11, $(CH_2I)^{+\bullet}$]; 127 (16, $I^{+\bullet}$); 91 (11); 69 [12, $(CF_3)^{+\bullet}$]; 58 (19).

The 2:1 telomer **5a** was also produced in higher yield when excess of allyl acetate was present (Table 1).

2-Iodo-4-acetoxymethyl-6,6,7,7,8,8,9,9,9-nonafluorononyl acetate ($C_4F_9CH_2CH(CH_2CHICH_2OCOCH_3)CH_2OCOCH_3$) (**5a**) (two pairs of diastereoisomers): b.p. 120 °C/2 mmHg. Analysis: Found: C, 29.8; H, 2.8; F, 29.7; I, 19.9%. $C_{14}H_{16}F_9O_4I$ requires: C, 30.8; H, 2.9; F, 31.3; I, 23.2%; M, 546.2. ^{1}H NMR ($CDCl_3$) δ: 1.92 (m, 2H, CH_2–CHI); 2.04, 2.05 (2s, 6H, CH_3); 2.12 (m, 1H, CH); 2.40 (m, 2H, CH_2CF_2); 4.07, 4.20 (2 × m, 4H, CH_2–O); 4.36 (m, 1H, CHI) ppm. ^{13}C NMR ($CDCl_3$) δ: 169.95; 170.49 (2s, 2C, C=O); 108–125 (m, 4C, C_4F_9); 69.18 and 68.88 (2s, 1C, $-CH_2$–O); 65.78, 63.93 (2s, 1C, CH_2–O); 39.13, 38.22 (CH, 2s, 1C); 31.64, 31.75 (2s, 1C, CH_2); 32.18, 30.67 (2t, 1C, CH_2–CF_2, $^2J_{CF}$ = 21 Hz); 25.71, 26.20 (2s, 1C, CHI); 20.49, 20.48, 20.44, 20.43 (4s, 2C, CH_3) ppm. ^{19}F NMR ($CDCl_3$) δ: −81.56 (t, 3F, CF_3); −113.27 (m, 2F, CF_2–CH_2); −124.88 (m, 2F, CF_2); −126.32 (m, 2F, CF_2—CF_3) ppm. MS *m/z* (% rel. int.) 419 [100, $(M-I)^{+\bullet}$]; 377 [19, $(M-C_3F_7)^{+\bullet}$]; 359 [8, $(C_{12}H_{12}F_9O_2)^{+\bullet}$]; 317 [59, $(C_9H_6F_9O_2)^{+\bullet}$]; 299 [66, $(C_{10}H_8F_9)^{+\bullet}$]; 169 [10, $(C_3F_7)^{+\bullet}$]; 81 (74); 73 (58); 66 (40); 58 (66).

When this product underwent thermal rearrangement, isomer **6a** was produced.

1-Iodomethyl-3-acetoxymethyl-5,5,6,6,7,7,8,8,8-nonafluoro-octyl acetate ($C_4F_9CH_2CH[CH_2CH(OCOCH_3)CH_2I]CH_2OCOCH_3$) (**6a**): b.p. 120 °C/2 mmHg. Analysis: Found: C, 32.0; H, 3.0; F, 33.8%. $C_{14}H_{16}F_9O_4I$ requires: C, 30.8; H, 2.9; F, 31.3%; M, 546.2. ^{1}H NMR ($CDCl_3$) δ: 1.95 (m, 2H, CH_2–CH–O); 2.03, 2.04 (2s, 6H, CH_3); 2.12 (m, 1H, CH); 2.40 (dt, 2H, CH_2CF_2); 3.28 (2dd, 2H, CH_2I); 4.05 (2dd, 2H, CH_2–O); 4.75 (m, 1H, CH–O) ppm. ^{13}C NMR ($CDCl_3$) δ: 7.16, 7.23 (2s, 1C, CH_2I); 20.36, 20.37, 20.40, 20.41 (4s, 2C, CH_3); 27.96, 28.13 (2s, 1C, CH); 31.11, 31.63 (2t, 1C, CH_2CF_2); 36.17, 36.26 (2s, 1C, CH_2CHO); 65.29, 65.95 (2s, 1C, CHO); 69.82, 69.92 (2s, 1C, CH_2O); 108–125 (m, 4C, C_4F_9); 170.15, 170.55 (2s, 2C, CO) ppm. ^{19}F NMR ($CDCl_3$) δ: −81.56 (t, 3F, CF_3); −113.27 (m, 2F, CF_2CH_2); −124.88 (m, 2F, CF_2); −126.34 (m, 2F, CF_2CF_3) ppm. MS *m/z* (% rel. int.): 486 [3, $(M-CH_3CO_2H)^{+\bullet}$]; 426 [26, $(M-2CH_3CO_2H)^{+\bullet}$]; 419 [40, $(M-I)^{+\bullet}$]; 377 [20, $(M-C_3F_7)^{+\bullet}$]; 359 [14, $(C_{12}H_{12}F_9O_2)^{+\bullet}$]; 371[62, $(C_9H_6F_9O_2)^{+\bullet}$]; 299 [100, $(C_{10}H_8F_9)^{+\bullet}$]; 127 [16, $(I)^{+\bullet}$]; 69 [42, $(CF_3)^{+\bullet}$]; 58 (34).

3.2.2. From perfluorohexyl iodide

A similar reaction as above was carried out in the presence of $C_6F_{13}I$ (25.1 g, 0.046 mol) of allyl acetate (0.046 mol, 4.6 g) and 0.001 mol of initiator at the corresponding temperature. The monoadduct **2b** was distilled, b.p. 51–53 °C/0.04 mmHg (lit. value [6]: 62–65 °C/0.05 Torr).

2-Iodo-4,4,5,5,6,6,7,7,8,8,9,9,9-tridecafluorononyl acetate (**2b**). Analysis: Found: C, 24.0; H, 1.5; F, 45.3%. $C_{11}H_8F_{13}IO_2$ requires: C, 24.2; H, 1.5; F, 45.2%; M, 546.1. ^{1}H NMR ($CDCl_3$) δ: 2.06 (s, 3H, CH_3); 2.84 (dt, 2H, CH_2CF_2, $^2J_{HH}$ = 5 Hz, $^3J_{HF}$ = 20 Hz); 4.28 (2dd, 2H, CH_2O); 4.38 (m, 1H, CHI) ppm. ^{13}C NMR ($CDCl_3$) δ: 11.64 (s, 1C, CHI); 20.33 (s, 1C, CH_3); 38.01 (t, 1C, CH_2CF_2, $^2J_{CF}$ = 21 Hz); 68.28 (s, 1C, CH_2O); 105–125 (m, 6C, C_6F_{13}); 169.82 (s, 1C, CO) ppm. ^{19}F NMR ($CDCl_3$) δ: -81.55 (t, 3F, CF_3); −113.10, −114.90 (2m, 2F, CF_2CH_2); −122.34 (m, 2F, $CF_2CF_2CH_2$); −123.41 (m, 2F, CF_2); −124.14 (m, 2F, $CF_2CF_2CF_3$); −126.72 (m, 2F, CF_2CF_3) ppm. MS *m/z* (% rel. int.): 546 (0.7, $M^{+\bullet}$); 527 [0.7, $(C_{11}H_8F_{12}IO_2)^{+\bullet}$]; 487 [33, $(M-CH_3CO_2)^{+\bullet}$]; 486 [78, $(M-CH_3CO_2H)^{+\bullet}$]; 467 [12, $(C_9H_4F_{12}I)^{+\bullet}$]; 420 (25); 419 [100, $(M-I)^{+\bullet}$]; 359 [16, $(C_9H_4F_{13})^{+\bullet}$]; 340 [10 $(C_9H_4F_{12})^{+\bullet}$]; 313 [17, $(C_7HF_{12})^{+\bullet}$]; 295 [9, $(C_7H_2F_{11})^{+\bullet}$]; 167 [11, $(C_3H_4I)^{+\bullet}$]; 141 [8, $(CH_2I)^{+\bullet}$]; 127 (17, $I^{+\bullet}$); 91 (27); 77 (13); 69 [38, $(CF_3)^{+\bullet}$]; 58 (25).

On increasing the temperature to 170 °C (Table 1), particularly for an equimolar ratio of $C_6F_{13}I$ and olefin, the rearranged **3b** monoadduct was obtained.

1-Iodomethyl-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyl acetate (**3b**): b.p. 90 °C/1 mmHg. Analysis: Found: C, 24.0; H, 1.4; F, 45.3%. $C_{11}H_8F_{13}IO_2$, requires: C, 24.2; H, 1.5; F, 45.2%; M, 546.1. ^{1}H NMR ($CDCl_3$) δ: 2.04 (s, 3H, CH_3); 2.50 (dt, 2H, CH_2CF_2); 3.38 (2dd, 2H, CH_2I); 5.11 (m, 1H, CHO) ppm. MS *m/z* (% rel. int.): 546 (0.4, $M^{+\bullet}$) 487 [18, $(M-CH_3CO_2)^{+\bullet}$]; 486 [100, $(M-CH_3CO_2H)^{+\bullet}$]; 467 [7, $(C_9H_4F_{12}I)^{+\bullet}$]; 420 (12); 419 [100, $(M-I)^{+\bullet}$]; 359 [4, $(C_9H_4F_{13})^{+\bullet}$]; 340 [6, $(C_9H_4F_{12})^{+\bullet}$]; 313 [14, $(C_7HF_{12})^{+\bullet}$]; 295 [7, $(C_7H_2F_{11})^{+\bullet}$]; 167 [37, $(C_3H_4I)^{+\bullet}$]; 141 [8, $(CH_2I)^{+\bullet}$]; 127 (11, $I^{+\bullet}$); 91 (15); 69 [23, $(CF_3)^{+\bullet}$]; 58 (23).

Both the 2:1 telomers **5b** and **6b** were also isolated.

1,5-Diacetoxy-4-iodo-2(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluoroheptyl)pentane (**5b**): b.p. 118–122 °C/0.2 mmHg. Analysis: Found: C, 29.5; H, 2.4; F, 36.8; I, 17.3%. $C_{16}H_{16}F_{13}IO_4$ requires: C, 29.7; H, 2.5; F, 38.2; I, 19.6%; M, 646.2. ^{1}H NMR ($CDCl_3$) δ: 1.90 (m, 2H, CH_2CHI); 2.05 (2s, 6H, CH_3); 2.15 (m, 1H, CH); 2.38 (dt, 2H, CH_2CF_2); 4.10 (2dd, 2H, $CHCH_2O$); 4.20 (2dd, 2H, $CHICH_2O$); 4.35 (m, 1H, CHI) ppm. MS *m/z* (% rel. int.): 519 [100, $(M-I)^{+\bullet}$]; 477 [17, $(M-C_3F_7)^{+\bullet}$]; 459 [12, $(C_{14}H_{12}F_{13}O_2)^{+\bullet}$]; 417 [31, $(C_{11}H_6F_{13}O_2)^{+\bullet}$]; 399 [36, $(C_{12}H_8F_{13})^{+\bullet}$]; 73 (17); 58 (22).

Compound **5b** could be rearranged thermally to **6b**.

4-Iodomethyl-2(2,2,3,3,4,4,5,5,6,6,7,7,7-tridecafluorohexyl-1,4-diacetoxybutane (**6b**): Analysis: Found: C, 28.9; H, 2.0; F, 36.7%. cf **5b** (C, 29.7; H, 2.5; F, 38.2%). ^{1}H NMR ($CDCl_3$) δ: 1.95 (m, 2H, CH_2CHO); 2.05 (2s, 6H, CH_3); 2.15 (m, 1H, CH); 2.40 (dt, 2H, CH_2CF_2); 3.25 (2dd, 2H, CH_2I); 4.10 (2dd, 2H, CH_2O); 4.75 (m, 1H, CHO) ppm. ^{19}F NMR ($CDCl_3$) δ: −81.18 (t, 3F, CF_3); −113.16 (m, 2F, CF_2CH_2); −122.20 (m, 2F, $CH_2CF_2CF_2$); −123.30 (m, 2F, CF_2); −124.2 (m, 2F, $C_2F_5CF_2$); −126.6 (m, 2F, CF_3CF_2) ppm. MS *m/z* (% rel. int.): 526 [70, $(M-2CH_3CO_2H)^{+\bullet}$]; 519 [52, $(M-I)^{+\bullet}$]; 477 [18, $(M-C_3F_7)^{+\bullet}$]; 459 [10, $(C_{14}H_{12}F_{13}O_2)^{+\bullet}$]; 417 [55, $(C_{11}H_6F_{13}O_2)^{+\bullet}$]; 400 (46).

3.2.3. From perfluorooctyl iodide

As previously, the addition of perfluoro-octyl iodide (28.4 g, 44 mmol) on to allyl acetate (4.4 g, 44 mmol) was performed in the presence of 0.0009 mol of the required initiator at an appropriate temperature. As a result, compound **2c** was obtained and purified by distillation.

2-Iodo-4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoro-undecyl acetate (**2c**): b.p. 61–65 °C/0.005 mmHg (lit. value [6]: 91–99 °C/0.07 Torr). Analysis: Found: C, 24.0; H, 1.2; F, 50.2%. $C_{13}H_8F_{17}IO_2$ requires: C, 24.2; H, 1.2; F, 50.0%; M, 646.1. ^{1}H NMR ($CDCl_3$) δ: 2.08 (s, 3H, CH_3); 2.82 (dt, 2H, CH_2CF_2); 4.30 (2dd, 2H, CH_2O); 4.38 (m, 1H, CHI) ppm. ^{13}C NMR ($CDCl_3$) δ: 11.57 (s, 1C, CHI); 20.13 (s, 1C, CH_3); 37.98 (t, 1C, CH_2CF_2, $^2J_{CF}=21$ Hz); 68.22 (s, 1C, CH_2O); 105–125 (m, 8C, C_8F_{17}); 169.70 (s, 1C, CO) ppm. ^{19}F NMR ($CDCl_3$) δ: −81.89 (t, 3F, CF_3); −113.50, −115.5 (2m, 2F, CF_2CH_2); −122.42 (m, 2F, $CF_2CF_2CH_2$); −122.76 (m, 4F, $C_4F_9CF_2CF_2$); −123.61 (m, 2F, $CF_3C_2F_4CF_2$); −124.32 (m, 2F, $C_2F_5CF_2$); −127.14 (m, 2F, CF_3CF_2) ppm. MS *m/z* (% rel. int.): 646 (0.2, $M^{+\bullet}$); 627 [1.5, $(C_{13}H_8F_{16}IO_2)^{+\bullet}$]; 586 [79, $(M-CH_3CO_2H)^{+\bullet}$]; 567 [10, $(C_{11}H_4F_{16}I)^{+\bullet}$]; 519 [100, $(M-I)^{+\bullet}$]; 459 [12, $(C_{11}H_4F_{17})^{+\bullet}$]; 413 [14, $(C_9HF_{16})^{+\bullet}$]; 167 [15, $(C_3H_4I)^{+\bullet}$]; 141 [11, $(CH_2I)^{+\bullet}$]; 127 (75, $I^{+\bullet}$); 91 (26); 90 (14); 77 (19); 69 [35, $(CF_3)^{+\bullet}$]; 58 (30).

As shown in Table 1, an equimolar amount of $C_8F_{17}I$ and allyl acetate led to an exotherm at 170 °C, producing the rearranged compound **3c**.

1-Iodomethyl-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl acetate (**3c**): b.p. 79–81 °C/0.2 mmHg. Analysis: Found: C, 24.2; H, 1.3; F, 49.8%. Requires (C, 24.2; H, 1.2; F, 50.0%). ^{1}H NMR ($CDCl_3$) δ: 2.05 (s, 3H, CH_3); 2.55 (m, 2H, CH_2CF_2); 3.38 (2dd, 2H, CH_2I); 5.12 (dq, 1H, CHO) ppm. ^{13}C NMR ($CDCl_3$) δ: 6.64 (s, 1C, CH_2I); 20.29 (s, 1C, CH_3); 37.98 (t, 1C, CH_2CF_2, $^2J_{CF}=21$ Hz); 65.30 (s, 1C, CHO); 105–125 (m, 8C, C_8F_{17}); 169.70 (s, 1C, CO) ppm. The ^{19}F NMR spectrum was identical to that of compound **2c**. MS *m/z* (% rel. int.): 627 [0.6, $(C_{13}H_8F_{16}IO_2)^{+\bullet}$]; 586 [100, $(M-CH_3CO_2H)^{+\bullet}$]; 567 [10, $(C_{11}H_4F_{16}I)^{+\bullet}$]; 520 (14); 519 [100, $(M-I)^{+\bullet}$]; 459 [4, $(C_{11}H_4F_{17})^{+\bullet}$]; 413 [13, $(C_9HF_{16})^{+\bullet}$]; 167 [40, $(C_3H_4I)^{+\bullet}$]; 141 [10, $(CH_2I)^{+\bullet}$]; 127 (13, $I^{+\bullet}$); 121 (16); 91 (21); 69 [37, $(CF)^{+\bullet}$]; 58 (29).

As in the previous case, the 2:1 telomer **5c** was also obtained from the reaction of an excess of allyl acetate with $C_8F_{17}I$ (Table 1).

2-Iodo-4-acetoxymethyl-6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-heptadecafluorotridecyl acetate (**5c**): Analysis: Found: C, 29.0; H, 2.1; F, 44.4; I, 15.4%. $C_{18}H_{16}F_{17}IO_4$ requires: C, 29.0; H, 2.2; F, 43.3; I, 17.0%; M, 746.2. The ^{1}H NMR spectrum was similar to that of compound **5b** while the ^{19}F NMR spectrum was similar to that of compound **2c**. MS *m/z* (% rel. int.): 620 (23); 619 [100, $(M-I)^{+\bullet}$]; 577 [10, $(M-C_3F_7)^{+\bullet}$]; 559 [8, $(C_{16}H_{12}F_{17}O_2)^{+\bullet}$]; 517 [16, $(C_{13}H_6F_{17}O_2)^{+\bullet}$]; 499 [43, $(C_{14}H_8F_{17})^{+\bullet}$]; 103 (20); 86 (30); 73 (20); 66 (10); 58 (29).

Telomer **5c** also rearranged thermally to compound **6c**.

1-Iodomethyl-3-acetoxymethyl-5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-heptadecafluorododecyl acetate (**6c**): ^{1}H NMR spectrum similar to that of compound **6b** while the ^{19}F NMR spectrum was similar to that of compound **5c**.

3.3. General procedure for the radical addition of diiodoperfluoroalkanes to allyl acetate

A mixture of the diiodoperfluoroalkane (0.03 mol) and allyl acetate (6.01 g, 0.06 mol) was placed in a 50-ml three-necked flask equipped with a reflux condenser and a thermometer, and warmed up to ca. 115 °C with mixing when dibenzoyl peroxide (0.3 g, 1.24 mmol) was added. A sudden increase in the reaction temperature to 125–140 °C occurred and after 1 min the dark colour of the mixture turned to a light lilac colour indicating that the reaction was almost complete. The mixture was then mixed for an additional 15 min without heating when the temperature fell to 90–100 °C. GLC analysis indicated complete conversion of the starting diiodide at this point and a 60%–72% relative content of the diadduct in the mixture with the monoadduct. Volatile components were distilled off in vacuo (ca. 100 °C/1 kPa). Pure products, i.e. monoadducts and diadducts, were isolated by simple column chromatography (silica gel; hexane, chloroform) to give the yields listed in Table 2.

3.3.1. From 1,4-diiodoperfluorobutane

This reaction led to the formation of compounds **9a** and **10a**.

2,7-Diiodo-4,4,5,5,6,6,7,7-octafluoroheptyl acetate ($CH_3COOCH_2CHICH_2CF_2CF_2CF_2CF_2I$) (**9a**): ^{1}H NMR ($CDCl_3$) δ: 2.13 (s, 3H, CH_3); 2.81 (ddt, 1H, CH_2–CF_2, $^2J_{HH}=12$ Hz, $^3J_{HF}=11$ Hz, $^3J_{HH}=6$ Hz); 2.89 (ddt, 1H, CH_2–CF_2, $^2J_{HH}=12$ Hz, $^3J_{HF}=13$ Hz, $^3J_{HH}=6$ Hz); 4.29, 4.37 (2dd, 2H, CH_2–O, $^2J_{HH}=12$ Hz, $^3J_{HH}=6$ Hz); 4.42 (kv, 1H, CHI, $^3J_{HH}=6$ Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −59.31 (tt, 2F, CF_2I, $^3J_{FF}=5$ Hz, $^4J_{FF}=13$ Hz); −113.18 (m, 2F, CF_2CF_2I); −113.38 (dkv, 1F, CF_2CH_2, $^2J_{FF}=270$ Hz, $^3J_{FF}=14$ Hz, $^3J_{HF}=13$ Hz); −114.65 (dkv, 1F, CF_2CH_2, $^2J_{FF}=270$ Hz, $^3J_{FF}=12$ Hz, $^3J_{HF}=11$ Hz);

Table 2
Yields of mono- and di-adducts obtained in the radical addition of diiodoperfluoroalkanes to allyl acetate

Starting diiodide [a]	g	Preparative yield					
		Monoadduct	g	%	Diadduct	g	%
$I(CF_2)_4I$	13.61	**9a**	5.35	32.2	**10a**	12.62	64.3
$I(CF_2)_6I$	16.62	**9b**	4.75	24.2	**10b**	16.31	72.1

[a] Initial molarity 0.03 M in both cases.

−123.15 (q, 2F, $CH_2CF_2CF_2$, $^3J_{FF}$ = 12 Hz, $^4J_{FF}$ = 12 Hz) ppm. MS *m/z* (% rel. int.): 494 [6, $(M-CH_3CO_2H)^{+\bullet}$]; 493 [48, $(C_7H_3F_8I_2)^{+\bullet}$]; 428 (10); 427 [100, $(M-I)^{+\bullet}$]; 367 [6, $(C_7H_4F_8I)^{+\bullet}$]; 240 [12, $(C_7H_4F_8)^{+\bullet}$]; 195 (12); 121 (12); 58 (16).

2,9-Diiodo-4,4,5,5,6,6,7,7-octafluoro-1,10-diacetoxydecane ($(CH_3COOCH_2CHICH_2CF_2CF_2)_2$) (**10a**): ^{1}H NMR ($CDCl_3$) δ: 2.13 (s, 3H, CH_3); 2.81 (ddt, 1H, CH_2–CF_2, $^2J_{HH}$ = 12 Hz, $^3J_{HF}$ = 11 Hz, $^3J_{HH}$ = 6 Hz); 2.89 (ddt, 1H, CH_2–CF_2, $^2J_{HH}$ = 12 Hz, $^3J_{HF}$ = 13 Hz, $^3J_{HH}$ = 6 Hz); 4.29, 4.37 (2dd, 2H, CH_2–O, $^2J_{HH}$ = 12 Hz, $^3J_{HH}$ = 6 Hz); 4.43 (kv, 1H, CHI, $^3J_{HH}$ = 6 Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −113.38, −114.70 (2d, 4F, CF_2CH_2, $^2J_{FF}$ = 270 Hz); −123.91 (m, 4F, $CH_2CF_2CF_2$) ppm. MS *m/z* (% rel. int.): 526 [100, $(M-HI)^{+\bullet}$]; 466 [35, $(C_{12}H_{11}F_8IO_2)^{+\bullet}$]; 341 [36, $(C_{12}H_{13}F_8O_2)^{+\bullet}$]; 238 [10, $(C_7H_2F_8)^{+\bullet}$]; 167 [10, $(C_3H_4I)^{+\bullet}$]; 127 (22, $I^{+\bullet}$); 121 (14); 109 (10); 91 (15); 77 (17); 58 (55).

3.3.2. From 1,6-diiodoperfluorohexane

This reaction led to the formation of compounds **9b** and **10b**.

2,9-Diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorononyl acetate ($CH_3COOCH_2CHICH_2CF_2CF_2CF_2CF_2CF_2CF_2I$) (**9b**): ^{1}H NMR spectrum similar to that of compound **9a**. ^{19}F NMR ($CDCl_3$) δ: 59.57 (tt, 2F, CF_2I, $^3J_{FF}$ = 5 Hz, $^4J_{FF}$ = 13 Hz); −113.18 (m, 2F, CF_2CF_2I); −113.4 (dkv, 1F, CH_2CF_2, $^2J_{FF}$ = 270 Hz, $^3J_{FF}$ = 14 Hz, $^3J_{HF}$ = 13 Hz); −114.7 (dkv, 1F, CH_2CF_2, $^2J_{FF}$ = 270 Hz, $^3J_{FF}$ = 12 Hz, $^3J_{HF}$ = 11 Hz); −122.10 (m, 2F, $CF_2C_3F_6I$); −122.30 (m, 2F, $IC_2F_4CF_2$); −124.12 (m, 2F, $CH_2CF_2CF_2$) ppm. MS *m/z* (% rel. int.): 593 [12, $(C_9H_3F_{12}I_2)^{+\bullet}$]; 528 (11); 527 [100 $(M-I)^{+\bullet}$]; 466 [7, $(C_9H_3F_{12}I)^{+\bullet}$]; 295 (12); 177 (12); 127 (24, $I^{+\bullet}$); 77 (15); 58 (20).

2,11-Diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-1,12-diacetoxydodecane ($(CH_3COOCH_2CHICH_2CF_2CF_2CF_2)_2$) (**10b**): ^{1}H NMR spectrum similar to that of compound **10a**. ^{19}F NMR ($CDCl_3$) δ: −113.40, −114.70 (2dm, 4F, CF_2CH_2, $^2J_{FF}$ = 270 Hz); −122.17 (m, 4F, $CH_2C_2F_4CF_2$); −124.08 (m, 4F, $CH_2CF_2CF_2$) ppm. MS *m/z* (% rel. int.): 626 [100, $(M-HI)^{+\bullet}$]; 566 [17, $(C_{14}H_{11}F_{12}IO_2)^{+\bullet}$]; 441 [15, $(C_{14}H_{13}F_{12}O_2)^{+\bullet}$]; 167 [6, $(C_3H_4I)^{+\bullet}$]; 58 (55).

3.4. General procedure for the thermal rearrangement of primary adducts of diiodoperfluoroalkanes

The primary adduct (**9a**, **10a**, **10b**, respectively; 2.5 mmol) was placed in a 5-ml round-bottom flask equipped with a reflux condenser, drying tube and a magnetic stirrer, and was heated for 5 h at 180 °C. The reaction mixture was purified by column chromatography (silica gel, hexane, yield 89%–94%) and the isomeric composition shown in Table 3 determined by GLC methods.

The NMR spectra of the compounds **11a**, **12a**, and **12b** were obtained using the isolated reaction mixtures.

1-Iodomethyl-6-iodo-3,3,4,4,5,5,6,6-octafluorohexyl acetate ($ICH_2CH(OCOCH_3)CH_2CF_2CF_2CF_2CF_2I$) (**11a**): ^{1}H NMR ($CDCl_3$) δ: 2.11 (s, 3H, CH_3); 2.47, 2.53 (2m, 2H, CH_2–CF_2); 3.35 (dd, 1H, CH_2I, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 5 Hz); 3.44 (dd, 1H, CH_2I, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 6 Hz); 5.13 (kv, 1H, CH−O, $^3J_{HH}$ = 5 Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −59.27 (m, 2F, CF_2I); −113.18 (m, 2F, CF_2CF_2I); −113.12, −114.23 (dkv, 2F, CF_2CH_2); −123.10 (m, 2F, $CH_2CF_2CF_2$) ppm. MS *m/z* (% rel. int.): 554 (0.4, $M^{+\bullet}$); 496 (11); 494 [100, $(M-CH_3CO_2H)^{+\bullet}$]; 429 (13); 427 [87, $(M-I)^{+\bullet}$]; 367 [11, $(C_7H_4F_8I)^{+\bullet}$]; 240 [30, $(C_7H_4F_8)^{+\bullet}$]; 195 (12); 127 (16, $I^{+\bullet}$); 121 (14); 58 (16).

1,8-Di(iodomethyl)-1,10-diiodo-3,3,4,4,5,5,6,6-octafluoro-2,9-diacetoxyoctane ($(ICH_2CH(OCOCH_3)CH_2CF_2CF_2)_2$) (**12a**): ^{1}H NMR ($CDCl_3$) δ: 2.11 (s, 3H, CH_3); 2.48, 2.52 (m, 2H, CH_2–CF_2); 3.55 (dd, 1H, CH_2I, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 5 Hz); 3.44 (dd, 1H, CH_2I, $^2J_{HH}$ = 11 Hz, $^3J_{HH}$ = 6 Hz); 5.14 (kv, 1H, CH−O, $^3J_{HH}$ = 5 Hz) ppm. ^{19}F NMR ($CDCl_3$) δ: −113.05, −114.45 (2dm, 4F, CF_2CH_2, $^2J_{FF}$ = 270 Hz); −123.89 (m, 4F, $CH_2CF_2CF_2$) ppm. MS *m/z* (% rel. int.): 527 [100, $(M-I)^{+\bullet}$]; 467 [41, $(C_{12}H_{12}F_8IO_2)^{+\bullet}$]; 399 [5, $(C_{14}H_{15}F_8O_4)^{+\bullet}$]; 341 [23, $(C_{12}H_{13}F_8O_2)^{+\bullet}$]; 279 [6, $(C_{10}H_7F_8)^{+\bullet}$]; 238 [6, $(C_7H_2F_8)^{+\bullet}$]; 167 [10, $(C_3H_4I)^{+\bullet}$]; 127 (32, $I^{+\bullet}$); 121 (6); 58 (32).

1,10-Di(iodomethyl)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diacetoxydecane ($(ICH_2CH(OCOCH_3)CH_2CF_2CF_2CF_2)_2$) (**12b**): ^{1}H NMR spectrum similar to that of compound **12a**. ^{19}F NMR ($CDCl_3$) δ: −113.05, −114.24

Table 3
Isomeric composition of reaction mixtures arising from thermal rearrangement of primary adducts of diiodoperfluoroalkanes

Starting compound	%	Equilibrium mixture	%
9a	13	**9a/11a**	87
10a	14	**10a/12a**	86
10b	14	**10b/12b**	86

(2dm, 4F, CF_2CH_2, $^2J_{FF}=270$ Hz); −122.24 (m, 4F, $CH_2C_2F_4CF_2$); −124.12 (m, 4F, $CH_2CF_2CF_2$) ppm. MS *m/z* (% rel. int.): 627 [97, $(M-I)^{+\bullet}$]; 567 [24, $(C_{14}H_{12}F_{12}IO_2)^{+\bullet}$]; 441 [18, $(C_{14}H_{13}F_{12}O_2)^{+\bullet}$]; 167 [14, $(C_3H_4I)^{+\bullet}$]; 127 (17, $I^{+\bullet}$); 58 (20).

4. Conclusions

Peroxide- or percarbonate-induced initiation of the addition of perfluoroalkyl iodides, R_FI, to allyl acetate leads to the formation of addition and 2:1 telomeric products whose proportion depends upon the nature of the initiator, the reaction temperature and the stoichiometric ratio of the reactants. In all the cases, the R_FI conversion was very high and usually quantitative.

In addition, the choice of initiator influences the reaction temperature on which the formation of the rearranged products formed in the subsequent thermal rearrangement of the primary adducts and telomers is dependent. Diiodoperfluoroalkanes, I−Q−I, react in a similar manner to perfluoroalkyl iodides, forming monoadducts and diadducts with allyl acetate which both undergo subsequent rearrangement. The mass spectra of the corresponding regioisomeric primary and rearranged products display characteristic signals allowing them to be distinguished by these means.

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References

[1] K. Baum, C.D. Bedford and R.J. Hunadi, *J. Org. Chem., 47* (1982) 2251.
[2] T. Ikeya and T. Kitazume, *12th Symp. Fluorine Chem.*, Hakata, Japan, October 1987, Abs. No. 3R17.
[3] P. Calas, P. Moreau and A. Commeyras, *J. Chem. Soc., Chem. Commun.*, (1982) 433.
[4] L.G. Anello, R.F. Sweeney and M.H. Litt, US Pat. 3 647 887, 1972; [*Chem. Abs., 77* (1972) 75 008q].
[5] N.O. Brace, *J. Fluorine Chem., 20* (1982) 313.
[6] M. Kotora, J. Kvicala, B. Améduri, M. Hajek and B. Boutevin, *J. Fluorine Chem., 64* (1993) 259.
[7] M. Napoli, A. Scipioni, L. Conte, E. Legnaro and L.N. Krotz, *J. Fluorine Chem., 66* (1994) 249.
[8] Q.Y. Chen and M.F. Chen, *Chin. J. Chem., 9* (1991) 186.
[9] K. Miura, Y. Takeyama, K. Oshima and K. Utimoto, *Bull. Chem. Soc. Jpn., 64* (1991) 1542.
[10] W.Y. Huang and H.Z. Zhang, *J. Fluorine Chem., 50* (1990) 133; *Chin. Chem. Lett., 1* (1990) 153.
[11] K. Von Werner, *J. Fluorine Chem., 28* (1985) 229.
[12] Q.Y. Chen, Z.A. Qiu and Z.Y. Yang, *J. Fluorine Chem., 36* (1987) 149.
[13] M. Kurobashi and T. Ishihara, *J. Fluorine Chem., 39* (1988) 299.
[14] M. Kotora, M. Hajek, B. Améduri and B. Boutevin, *J. Fluorine Chem., 68* (1994) 49.
[15] P. Laurent, H. Blancou and A. Commeyras, *J. Fluorine Chem., 62* (1993) 161.
[16] T. Fuchikami and I. Ojima, *Tetrahedron Lett., 25* (1984) 303.
[17] Z.Y. Yang and D.J. Burton, *J. Fluorine Chem., 45* (1989) 435.
[18] S. Matsubara, M. Mitani and K. Utimoto, *Tetrahedron Lett., 28* (1987) 5857.
[19] H. Bertrais, B. Boutevin, M. Malicewicz, Y. Pietrasanta and J.L. Vernet, *Eur. Poly. J., 18* (1982) 791.
[20] B. Améduri and B. Boutevin, *Macromolecules, 24* (1991) 2475.
[21] S.P. Khrlakyan, V.V. Shokina and I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1964) 72.
[22] A. Manseri, B. Améduri, B. Boutevin, M. Kotora, M. Hajek and G. Caporiccio, *J. Fluorine Chem., 73* (1995) 151.
[23] R.A. Jackson, *Tetrahedron, 47* (1991) 6777.
[24] J. Balague, B. Améduri and B. Boutevin, unpublished results.