

Radical additions to fluoroolefins. Thermal reaction of perfluoroallyl chloride with perfluoroalkyl iodides as a selective synthesis of terminal perfluoroolefins

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Abstract

Reaction of perfluoroallyl chloride with perfluoroalkyl iodides, R_fI ($R_f = C_4F_9, C_6F_{13}, C_8F_{17}$), in an autoclave at 180–250 °C gave terminal perfluoroolefins, $CF_2=CF-CF_2-R_f$ (**2–4**) as the sole reaction products. Isomeric fluoroolefins containing an internal double bond and telomeric products were not observed in the reaction mixture. The yields were dependent on the reaction temperature and on the chain length of R_fI : the highest preparative yield of olefin **2** ($R_f = C_4F_9$) was obtained at 200 °C (26%), while in the syntheses of olefins **3** and **4** ($R_f = C_6F_{13}$ and C_8F_{17} , respectively) highest yields were achieved at 250 °C (41% and 74%, respectively). The presence of CuI or a peroxide initiator had a negative influence on the yield of products. Formulae have been assigned to the fragments in the mass spectra of products **2–4**, and fragmentation sequences have been proposed.

Keywords: Perfluoroallyl chloride; Perfluoroalkyl iodides; Perfluoro-1-alkenes; Radical addition; Thermal initiation; Mass spectrometry

1. Introduction

Perfluoroolefins are known as very interesting reactants and intermediates for the syntheses of highly fluorinated oligomers, telomers and polymers. Several methods for the preparation of perfluoro-1-alkenes are described. However, some of them have appeared to be not completely selective and afforded terminal olefins together with different amounts of isomeric perfluoroalkenes having internal double bonds. The oldest method known is the pyrolysis of alkali metal salts of perfluorocarboxylic acids [1–3] that gave a mixture of perfluoroolefins with internal olefins that sometimes prevailed. Perfluorocarboxylic acids [4] and their anhydrides [5] can also be pyrolysed to form mixture of perfluoroalkenes, generally with a different result from the decarboxylation of the salts. A mixture of isomeric internal and terminal perfluoroolefins was also obtained by the fluorination of telomeric chlorofluoroalkanes with potassium fluoride [6]. Fluorination of chlorofluorocarboxylic acid esters with potassium fluoride afforded a mixture of structural isomers of

perfluoroolefins in an overall yield of 90% [7]. The preparation of 1-perfluoroalkenes by the reaction of perfluoroalkyl iodides with organomagnesium [8] and organozinc [9–11] reagents is generally not a selective method. However, when phenylmagnesium bromide was used as the agent, 1-perfluoroalkenes were obtained [12] as the sole products in 95% yield.

It was thus interesting to look for a useful and simple method based on regioselective radical addition of industrially available perfluoroalkyl iodides on to suitable fluoroolefins. Perfluoroallyl chloride (PAC) was chosen as the fluoroolefin since it allows the possibility to synthesize odd-number perfluoro-1-alkenes and this was the objective of this work.

Our aim to prepare these 1-alkenes was confronted with some published observations: the very low yield in the thermal reaction of trifluoroiodomethane with hexafluoropropene [13] and the formation of a mixture of products in a tube reaction [14], 'discrete' telomerisation of hexafluoropropene with perfluoroalkyl iodides [15], easy telomerisation of hexafluoropropene with perfluoroalkyl iodides [16,17] and with α,ω -diiodoperfluoroalkanes [18,19] and non-regioselective reaction of perfluoroalkyl iodides with hexafluoropropene [16,17,20]. Only two reactions have been reported as

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Table 1
Thermal addition reaction of R_FI with perfluoroallyl chloride

R _F I ^a	Catalyst ^b	Temperature (°C)	Time (h)	Raw product ^c		Perfluoroalkene yield		
				Amount (g)	Alkene content (%)	Product	(g)	(%)
C ₄ F ₉ I	–	120	48	8.60	0	2	0	0.
	CuI	120	48	9.60	0	2	0	0
	–	180	40	9.18	13	2	1.13	8.8
	CuI	200	40	10.10	12	2	1.05	8.2
	T-145	200	40	9.61	17	2	1.49	11.6
	–	200	40	10.24	38	2	3.33	26.0
	–	230	40	9.95	32	2	2.80	21.9
	–	250	40	9.92	30	2	2.63	20.5
C ₆ F ₁₃ I	–	200	40	11.75	16	3	1.80	11.8
	–	230	40	12.25	27	3	3.04	19.9
	–	250	40	13.47	56	3	6.30	41.1
C ₈ F ₁₇ I	–	250	40	16.70	74	4	10.18	74.1

^a Perfluoroalkyl iodide, 0.025 mol; C₄F₉I, 8.65 g; C₆F₁₃I, 11.15 g; C₈F₁₇I, 13.65 g.

^b CuI, 0.95 g (0.005 mol); T-145, i.e. Trigonox 145 [2,5-bis(t-butylperoxy)-2,5-dimethyl-3-hexyne], 0.57 g (0.002 mol).

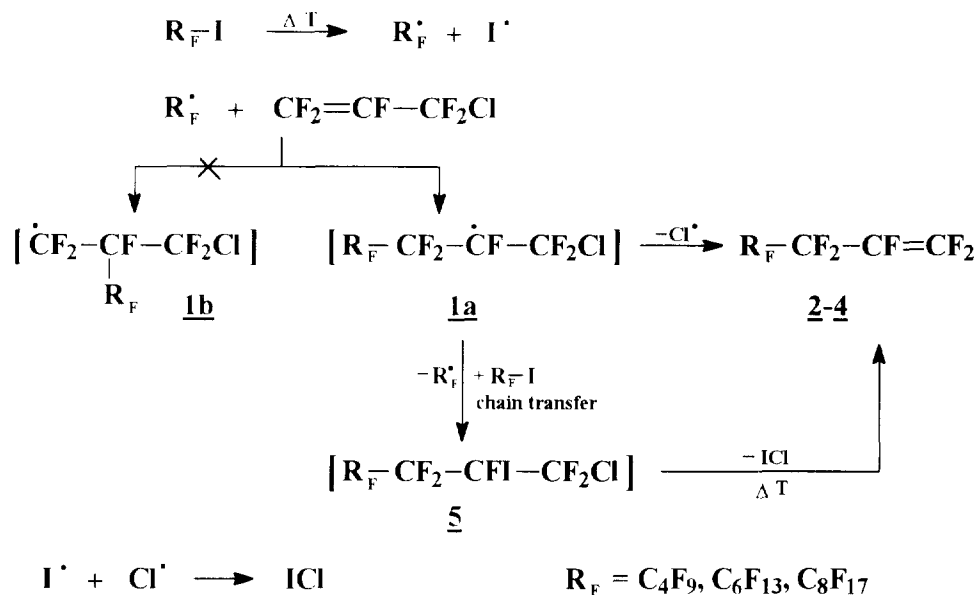
^c GC analysis, calibration curve for perfluoroolefin content.

being completely regioselective: the gas-phase photochemical reaction of trifluoromethyl iodide with hexafluoropropene [21] and the reaction of telomeric fluoroalkyl iodides, which were prepared from vinylidene fluoride, with hexafluoropropene [22]; these results gave a favourable forecast for our reaction.

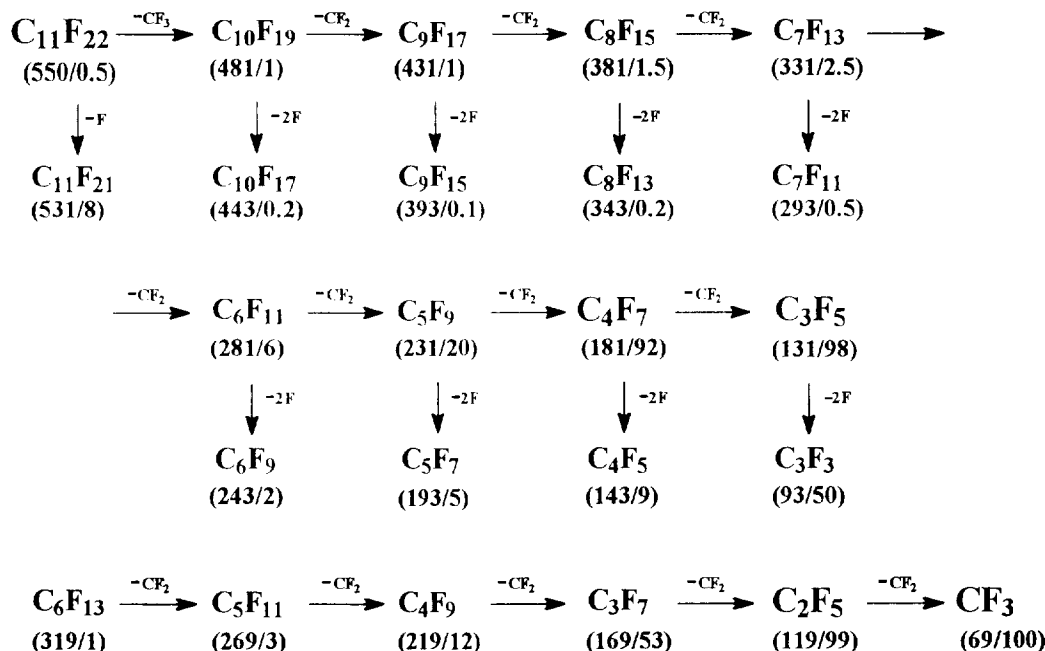
Perfluoroalkyl iodides are thermally stable below temperatures of 300 °C. However, above this temperature decomposition of the iodides to perfluoroolefins was observed [17]. Our studies contribute to the potential formation of perfluoroolefins directly in the reaction mixture in a similar fashion and to the question of regioselectivity of the addition of perfluoroalkyl iodides to PAC.

2. Results and discussion

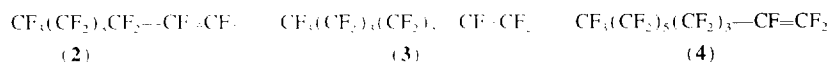
The reaction of perfluoroalkyl iodides with PAC was carried out in the temperature range 180–250 °C under autogenous pressure. As can be seen in Table 1, the conversion depends on the temperature and on the perfluoroalkyl iodide: generally, the conversion increased with higher temperature. In the reaction of perfluorobutyl iodide, no increase in conversion was observed in the temperature range 200–250 °C, whereas for perfluorohexyl and perfluorooctyl iodides the increase in conversion in this temperature range was quite high. The presence of copper iodide or peroxide (Trigonox 145) in the reaction mixture had a negative effect on the



Scheme 1.



Scheme 4. Fragmentation pattern for $\text{C}_n\text{F}_{2n-1}$ ($-\text{CF}_2$, $-\text{CF}=\text{CF}_2$, (4) (C_nF_{2n} , calc. MW 550.09). Figures in parentheses refer to m/z value and % abundance, respectively.



Scheme 5

directs the attack of the bulky $\text{R}_1\cdot$ radical to the terminal position of PAC. The steric effect can also include stereo-electronic interactions of both perhalogenated reactants. The existence of a similar steric effect of β -chlorine was confirmed [26] in acid hydrolysis of fluorinated esters.

The reactivity of PAC towards perfluoroalkyl radicals is very low when compared with that of allyl acetate [27] or allyl alcohol [24] towards the same radicals. The reason for this phenomenon can be found in polar effects: both reaction partners, the perfluoroalkyl radicals and the double bond in PAC, are of electrophilic character. In such cases, the reaction rate is decreased dramatically [28] in comparison with more favourable interactions between electrophilic and nucleophilic reactants.

The structure and isomeric purity of products 2–4 were checked by NMR spectroscopy and mass spectrometry. The NMR spectrum of perfluoroheptene (2) has been published [12] but the shifts are given relative to trifluoroacetic acid and therefore their values are different. In this paper the NMR spectra of products 2–4 are presented with shifts relative to CCl_3F (Table 2). All NMR spectra show no signals at about -60 ppm which could be assigned to the CF_2I end-groups of the perfluoroalkyl iodides [16]. Molecular weights of products 2–4 were verified by mass spectrometry. Moreover, formulae have been assigned to individual fragments in the mass spectra that enable us to deduce fragmentation schemes (Schemes 2–4):

It can be concluded from the fragmentation schemes that the initial mass spectral fragmentation of perfluoroolefins 2–4 takes place at two bonds in the molecules. The first splitting, which is similar for each perfluoroolefin, involves the bond between the CF_3 group and the rest of the molecule, whereas the second splitting takes place in the chain of the molecule and is specific for each molecule as shown in Scheme 5.

3. Experimental details

The temperature data were uncorrected. GC analyses were performed on a Delsi 330 instrument (FID, $1\text{ m} \times 1/8$ in column packed with Silicone SE-30, injector/detector temperature $120/100$ °C, nitrogen pressure 1 bar) connected to a Hewlett Packard integrator (model 3390). NMR spectra were recorded on a Bruker 400 AM (FT, ^{19}F at 376 MHz) apparatus: CFCl_3 as internal standard, chemical shifts in ppm (s singlet, d doublet, t triplet, m multiplet), solvent CDCl_3 . Mass spectra were scanned on a GC–MS tandem JEOL DX-303 instrument (JMA 5000, single focus, 70 eV, helium), GC inlet via a 1 m capillary column coated with silicone elastomer.

Chemicals used were as follows. Perfluoroalkyl iodides were kindly supplied by Elf Atochem S.A., Trigonox-145 and copper chloride were purchased from Merck and Aldrich,

and 3-chloro-1,1,2,3,3-pentafluoropropene (perfluoroalkyl chloride, PAC) was prepared as described previously [29].

3.1. General procedures

A Hastelloy autoclave (volume 200 ml) equipped with a magnetic stirrer and gas inlet was charged with perfluoroalkyl iodide (0.025 mol) and eventually with a catalyst or initiator. The reactor was then cooled to ca. $-50\text{ }^{\circ}\text{C}$ by immersion in a cooling bath, evacuated and perfluoroalkyl chloride (PAC, 5.0 g, 0.03 mol) was condensed into the vessel. The mixture was heated while stirring as given in Table 1. After the reaction, the autoclave was cooled to room temperature, unreacted PAC was trapped and the composition of the raw reaction mixture and conversion of the starting components were determined by GC on the basis of a calibration curve for the product/perfluoroalkyl iodide mixture. The raw reaction mixture was purified by passing through a short column (ca. 2.5 cm) of silica gel/charcoal/silica gel (1:0.5:1 cm) and fractionated by distillation. Products **2–4** were obtained in a purity of ca. 99%. Boiling points of products: 1,1,2,3,3,4,4,5,5,6,6,7,7,7-tetradecafluoro-1-heptene (**2**), 81–82 $^{\circ}\text{C}$ (lit. value [2], b.p. 81 $^{\circ}\text{C}$); 1,1,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-octadecafluoro-1-nonene (**3**), 123–124 $^{\circ}\text{C}$ (lit. value [30], b.p. 123 $^{\circ}\text{C}$); 1,1,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-docosafluoro-1-undecene, 160–163 $^{\circ}\text{C}$.

4. Conclusions

Thermally initiated addition reaction of perfluoroalkyl iodides with perfluoroalkyl chloride afforded odd-number perfluoro-1-alkenes as the sole organic products, no rearranged or branched products were detected in the reaction mixture. Preparative yields were dependent on the reaction temperature and chain length of $\text{R}_1\text{-I}$. Organic peroxide and cuprous iodide acted as reaction inhibitors.

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