

# A telechelic fluorinated diol from 1,6-diiodoperfluorohexane

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Received 9 September 1999; accepted 11 September 2000

## Abstract

The radical addition of 1-iodoperfluorohexane (**1**) to allyl alcohol (2-propen-1-ol) (**2**) was investigated in the presence of various initiating systems (photochemically or in the presence of redox catalysts or organic initiators), leading to  $C_6F_{13}CH_2CHICH_2OH$  (**3**) in various yields. A scale of efficiency of the involved radical system was proposed, triphenylphosphine and AIBN yielding the best conversions of **1**. Interestingly, AIBN, when added three times in the course of the reaction was the most suitable for an almost quantitative consumption of **1**. Then, **3** was reduced to  $C_6F_{13}C_3H_6OH$  (**4**) in high yields by tributylstannane. Such a two-step procedure was extrapolated to the preparation of the fluorinated telechelic diol from 1,6-diiodoperfluorohexane (**5**). First, the formations of both the 1-to-1 monoadduct (**6**) and 1-to-2  $\alpha,\omega$ -diadduct (**7**) were noted and discussed: optimised conditions enabled production of **7** in 81% yield with a complete conversion of **5**. Then, telechelic diol  $HOC_3H_6C_6F_{12}C_3H_6OH$  (**8**) was synthesised selectively in 88% yield, from the reduction of the iodine atoms of **7** by tributylstannane.  $^1H$ ,  $^{19}F$  and  $^{13}C$  NMR spectroscopies allowed characterisation of all the intermediates and products without ambiguity. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Telechelic diol; 1,6-Diiodoperfluorohexane; 1-Iodoperfluorohexane; Allyl alcohol; Radical addition; AIBN; NMR

## 1. Introduction

Fluorinated polymers exhibit a unique combination of high thermal stability, chemical inertness (to acids, bases, solvents and petroleum), low dielectric constants and dissipation factors, low water absorptivity, excellent weatherability and a good resistance to oxidation and ageing, low flammabilities and very interesting surface properties [1–3]. Therefore, such products are involved in many applications (aerospace, aeronautics, engineering, optics, textile finishing, microelectronics) in spite of their high price and are showing an increasing market.

Well-architected polymers can be prepared either from controlled radical polymerisation [4,5] or from polycondensation or polyaddition. In these two last processes, telechelic or  $\alpha,\omega$ -difunctional (i.e. the functional groups are located at both extremities of the chain) precursors are required to obtain high molecular weight materials with satisfactory properties [6]. In the case of fluorinated telechelics, literature describing their synthesis is abundant and was reviewed several years ago [7,8]. They have been obtained more recently from  $\alpha,\omega$ -diiodides [9].

Two kinds of fluorinated telechelics exhibiting different properties are suggested and hence the polymers prepared from them can be involved in different applications. On the one hand, those possessing the fluorinated branched group (i.e. in a lateral position about the polymeric backbone) are searched for their enhanced surface properties but cannot be used as thermostable materials resistant to oxidation and to chemicals. On the other hand, those containing the fluorinated chain in the backbone exhibit much better thermal properties and are also resistant to oxidation, to aggressive media, to UV radiation and to ageing.

Various strategies have been proposed to prepare this second family of fluorinated telechelics. In 1969, Rice and Sandberg [10,11] used the dead-end copolymerisation of vinylidene fluoride and hexafluoropropene in the presence of telechelic peresters. More recently, such a process was successfully achieved from hydrogen peroxide [12].

Nowadays, among fluorinated telechelics prepared on an industrial scale only four commercially available polyethers have already been obtained: these are Krytox<sup>®</sup> [13,14], Fomblin<sup>®</sup> [15,16], Aflunox<sup>®</sup> and Demnum<sup>®</sup> [17] produced from the Du Pont, Ausimont, Nippon Mektran (NOK) and Daikin Companies, respectively.

Apart from fluorinated polyethers, new fluorotelechelic oligodiols as random copolymers containing vinylidene

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fluoride (VDF) and HFP base units, e.g.  $\text{HOCH}_2\text{CF}_2(\text{CH}_2\text{CF}_2)_p[\text{CF}(\text{CF}_3)\text{CF}_2]_q\text{CF}_2\text{CH}_2\text{OH}$  have been synthesised by Chan et al. [18].

In addition, the synthesis of telechelic fluorinated diols from direct fluorination of hydrogenated diols, produced in pilot plants, has been successfully achieved [19].

In spite of the lack of industrial fluorotelechelic (as distinct from polyethers) for fluorinated non-functional homo and copolymers, the present tendency shows that a growing interest is still required, as evidenced by numerous investigations [7–9]. It seems that many reactions involve  $\alpha,\omega$ -diiodoperfluoroalkanes as reactants, to prepare telechelic intermediates preserving the fluorinated chain in the backbone. A summary of various methods of syntheses of these diiodides was recently made [9]. In addition, several examples of syntheses of fluorotelechelic from  $\text{IR}_F\text{I}$  have been described: the bis(ethylenation) of these diiodides followed by a hydrolysis in the presence of DMF/ $\text{H}_2\text{O}$  [20,21],  $\text{CuSO}_4$  or  $\text{AgOAc}$  [22],  $\text{H}_2\text{SO}_4/\text{SO}_3$  [23] or  $\text{NaNO}_2/\text{betaine}$  as surfactant [24] led to  $\text{HOC}_2\text{H}_4\text{-R}_F\text{-C}_2\text{H}_4\text{OH}$  in fair yields. As reviewed by Brace [25,26], the functionalisation of fluorinated telechelic diiodides has been successfully attempted by various authors, leading to original fluorotelechelic [9] (Table 1).

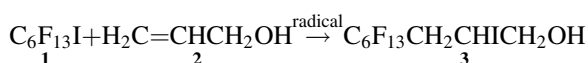
In addition, fluorinated telechelic diols are interesting precursors of fluorinated polyurethanes [23,39,40], polyesters [41], triazines (via telechelic cyanates [42–44]) or cured networks (via telechelic (meth)acrylates [45–47]). Few fluorodiols are commercially available. Although Li and Chen [32,33] succeeded in preparing low fluorine content  $(\text{HOCH}_2\text{CHICH}_2)_2\text{CF}_2$  from the addition of diiododifluoromethane to allyl alcohol (2-propen-1-ol), we found it worth increasing the fluorine amount and one of the solutions concerns the bismonoaddition of 1,6-diiodoperfluorohexane to this unsaturated alcohol followed by the reduction of both iodine atoms to produce  $\text{HOC}_3\text{H}_6\text{C}_6\text{F}_{12}\text{-C}_3\text{H}_6\text{OH}$ , as the objective of this article. First, a model reaction dealing with the addition of perfluorohexyl iodide to allyl alcohol was optimised, before transferring the best results towards the addition of the telechelic fluorodiiodide.

## 2. Results and discussion

Before synthesising the fluorinated telechelic diol, a model reaction considering the radical addition of 1-iodoperfluorohexane (**1**) to allyl alcohol (**2**) was attempted. Various ways of initiation have been chosen and the best condition will be used for the bis(monoaddition) of  $\alpha,\omega$ -diiodoperfluoroalkane to allyl alcohol.

### 2.1. Radical addition of 1-iodoperfluorohexane to allyl alcohol

Perfluoroalkyl iodides are known to exhibit a low  $\text{CF}_2\text{-I}$  bond dissociation energy [48,49]; the C–I bond can easily be cleaved in the presence of various systems [25,26,50,51]: thermally, photochemically, biochemically, electrochemically, from various initiators or catalysts. Three various types of initiation to allow this bond to generate  $\text{C}_6\text{F}_{13}\cdot$  radicals have been chosen: photochemical, from the use of redox systems or radical initiators. Copper metal has been used at a temperature higher than the threshold of thermal initiation ( $120^\circ\text{C}$ ) while initiators were used at a temperature for which their half lives were ca. 1 h (Table 2). The assumed radicals generated from those initiators are also listed in Table 2. The chosen reaction-time was at least 5 half lives of each initiator. The reaction was as follows:



Most reactions were performed at atmospheric pressure (Table 3) in contrast to those carried out in sealed Carius tubes when the temperature was higher than  $94^\circ\text{C}$  (i.e. bp of allyl alcohol). Since allyl alcohol is a monomer which does not homopolymerise [52], it was used in a slight excess (Table 4) to favour a faster consumption of 1-iodoperfluorohexane.

After reaction, the total product mixture was analysed by gas chromatography. For instance, from the reaction initiated by AIBN, the gas chromatogram of the final mixture shows the presence of the monomeric alcohol

Table 1  
Radical addition of  $\alpha,\omega$ -diiodo(per)fluoroalkanes to unsaturated compounds

$\text{R}_F$ of $\text{IR}_F\text{I}$	Monomer	Intermediate	Product	Reference
$\text{C}_6\text{F}_{12}$	Vinyl acetate	–	$(\text{AcOCHICH}_2\text{C}_3\text{F}_6)_2$	[27]
$(\text{C}_2\text{F}_4)_n$ $n = 1,2$	Allyl acetate	–	$[\text{AcOCH}_2\text{CHICH}_2(\text{CF}_2)_n]_2$	[28]
$\text{C}_6\text{F}_{12}$	Allyl acetate	$(\text{AcOCH}_2\text{CHICH}_2\text{C}_3\text{F}_6)$ with rearranged isomers	Diepoxide	[29]
$(\text{C}_2\text{F}_4)_n$ $n = 2,3$	Allyl acetate	As above	$[\text{H}_2\text{C}=\text{CHCH}_2(\text{CF}_2)_n]_2$	[30]
TFE/HFP/VDF cotelomer $\text{CF}_2$	Allyl acetate	As above	As above (various $\text{R}_F$ )	[31]
$\text{CF}_2$	Allyl alcohol	–	$(\text{HOCH}_2\text{CHICH}_2)_2\text{CF}_2$	[32,33]
$(\text{C}_2\text{F}_4)_n$ $n = 1,2$	Allyl alcohol	–	$[\text{HOCH}_2\text{CHICH}_2(\text{CF}_2)_n]_2$	[28]
$\text{C}_6\text{F}_{12}$	$(\text{CH}_3)_3\text{SiC}\equiv\text{CSi}(\text{CH}_3)_3$	Fluorodiiodo diene	$\alpha,\omega$ -Diacetylenic	[34]
$\text{C}_6\text{F}_{12}$	Norbornene	–	Fluoro bis(norbornane)	[35]
$\text{C}_6\text{F}_{12}$	$\omega$ -Unsaturated sterol	–	Fluoro bisterol	[36]
$(\text{C}_2\text{F}_4)_n$ $\bar{n} = 3.1$	Methyl 10-undecenoate	Fluorodiiodo diester	Telechelic diester	[37,38]

Table 2

Initiators used, temperature ( $T_1$ ) for their half life of 1 h and radicals generated from their decomposition, in the radical addition of 1-iodoperfluorohexane (**1**) to allyl alcohol (**2**)

Initiator	Formulae	$T_1$ (°C)	Nature of the radicals generated
Bis(4- <i>tert</i> -butyl cyclohexyl)percarbonate	$[(\text{CH}_3)_3\text{CC}_6\text{H}_{10}\text{OCO}_2]_2$	60	$(\text{CH}_3)_3\text{C}-\text{C}_6\text{H}_{10}-\text{OCO}_2^\bullet + (\text{CH}_3)_3\text{C}-\text{C}_6\text{H}_{10}\text{O}^\bullet$
<i>Tert</i> -butyl peroxyphthalate	$(\text{CH}_3)_3\text{COOCOC}(\text{CH}_3)_3$	74	$(\text{CH}_3)_3\text{CO}^\bullet + (\text{CH}_3)_3\text{CCO}_2^\bullet + (\text{CH}_3)_3\text{C}^\bullet + \bullet\text{CH}_3$
Triphenylphosphine	$\text{PPh}_3$	75	$[\text{PPh}_3]^\bullet$
AIBN	$[(\text{CH}_3)_2\text{C}(\text{CN})\text{N}]_2$	80	$(\text{CH}_3)_2\text{C}^\bullet\text{CN}$
Triethyl phosphite	$\text{P}(\text{OEt})_3$	85	$[\text{P}(\text{OEt})_3]^\bullet$
Hydrogen peroxide	$\text{H}_2\text{O}_2$	100–130	$\text{HO}^\bullet$
<i>Tert</i> -butyl cumyl peroxide	$(\text{CH}_3)_3\text{COOC}(\text{CH}_3)_2\text{Ph}$	131	$(\text{CH}_3)_3\text{CO}^\bullet + \text{PhC}(\text{CH}_3)_2\text{O}^\bullet + \bullet\text{CH}_3$
<i>Tert</i> -butyl peroxide	$(\text{CH}_3)_3\text{CO}-\text{OC}(\text{CH}_3)_3$	145	$(\text{CH}_3)_3\text{CO}^\bullet + \bullet\text{CH}_3$

Table 3

Radical addition of 1-iodoperfluorohexane (**1**) to allyl alcohol (**2**) in the presence of various initiators and catalyst (reaction performed in Carius tube or in round bottom flask) and yields of adduct **3**

Initiator or catalyst	Apparatus	$[\text{C}_6\text{F}_{13}\text{I}]_0/[\text{allyl alcohol}]_0$	$[\text{Initiator or catalyst}]_0/[\text{allyl alcohol}]_0$ (%)	$T$ (°C)	$t$ (h)	Yield (%)
Benzophenone/UV	Carius tube	1.02	2.0	25	8	40
Bis(4- <i>tert</i> -butyl cyclohexyl)percarbonate	Round bottom flask	0.94	0.6	60	8	8
$\text{PPh}_3$	Round bottom flask	0.94	9.8	75	8	78
<i>Tert</i> -butyl peroxyphthalate	Round bottom flask	0.94	8.8	75	8	42
AIBN	Round bottom flask	1.01	1.2	80	8	62
AIBN	Round bottom flask	0.77	2.0 + 2.0 + 2.0	80	3 + 3 + 3	91
$\text{P}(\text{OEt})_3$	Round bottom flask	0.80	9.6	85	10	45
$\text{PPh}_3$	Round bottom flask	0.86	19.9	85	8	80
$\text{H}_2\text{O}_2$	Carius tube	0.92	6.0	110	15	38
Cu	Carius tube	0.90	9.4	130	12	65
<i>Tert</i> -butyl cumyl peroxide	Carius tube	0.98	2.0	132	6	25
( <i>t</i> -BuO) <sub>2</sub>	Carius tube	0.97	2.0	145	7	35

(retention time (rt): 0.85 min), of the 1-iodo-perfluorohexane (rt: 2.62 min) and a major peak centred at rt: 10.68 min assigned to **3** monoadduct.

When the reactions were performed at atmospheric pressure, the formation of iodohydrin **3** was monitored by GC, using 1H,1H,2H,2H-perfluorooctanol as the standard. Beforehand, the  $M_I/M_S$  versus  $A_I/A_S$  calibration curve was drawn ( $M_I$ ,  $M_S$ ,  $A_I$  and  $A_S$  represent the moles of iodohydrin and standard and the areas of the peaks of the gas chromatogram assigned to the iodohydrin and the standard, respectively).

For those carried out in sealed Carius tubes, the conversion of **1** was assessed at the end of the reaction.

The results are gathered in Table 3. In most cases, the reaction produced is clean since except the peaks corresponding to the reactant, the standard and the iodohydrin, no other signal was present on the gas chromatogram. Even for a slight initial excess of **2**, no peak assigned to the diadduct was noted at higher retention times.

Among the various catalysts or initiators, AIBN and triphenylphosphine were the most efficient since the corresponding yields ranged between 60 and 90%. The yield is

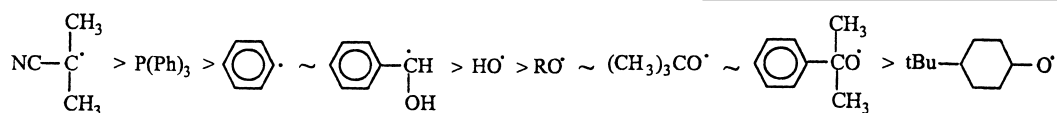
Table 4

Amounts of reactants used in the radical addition of 1-iodoperfluorohexane (**1**) to allyl alcohol (**2**)

Catalyst or initiator (g)	$T$ (°C)	( <b>1</b> ) (g)/(mole)	( <b>2</b> ) (g)/(mole)	Solvent (g)	Yield (%)
UV/benzophenone (0.28)	25	35.3/0.079	4.5/0.077	5.4 $\text{CH}_3\text{CN}$	40
Bis(4- <i>tert</i> -butyl cyclohexyl)percarbonate (0.21)	60	36.3/0.081	5.0/0.086	None	8
<i>Tert</i> -butyl peroxyphthalate (2.40)	74	49.0/0.110	6.8/0.117	19.0 $\text{C}_6\text{F}_{13}(\text{CH}_2)_2\text{OH}$	42
$\text{PPh}_3$ (2.20)	75	36.1/0.081	5.0/0.086	8.0 $\text{CH}_3\text{CN}$	78
AIBN (0.34)	80	75.0/0.168	9.7/0.167	None	62
AIBN added three times (0.64 × 3)	80	67.1/0.150	11.13/0.195	10.8 $\text{C}_6\text{F}_{13}(\text{CH}_2)_2\text{OH}$	91
$\text{PPh}_3$ (4.95)	85	36.6/0.082	5.5/0.095	None	80
$\text{P}(\text{OEt})_3$ (0.44)	85	9.8/0.022	1.6/0.028	3.9 $\text{C}_6\text{F}_{13}(\text{CH}_2)_2\text{OH}$	45
$\text{H}_2\text{O}_2$ (0.15)	110	30.4/0.068	4.3/0.074	4.2 $\text{CH}_3\text{CN}$	38
<i>Tert</i> -butyl cumyl peroxide (0.28)	131	29.5/0.066	3.9/0.067	10.0 $\text{CH}_3\text{CN}$	25
( <i>t</i> -BuO) <sub>2</sub> (0.20)	145	29.8/0.067	4.0/0.069	8.9 $\text{CH}_3\text{CN}$	35
Cu (0.43)	130	29.1/0.065	4.2/0.072	4.6 $\text{CH}_3\text{CN}$	65

quasi-optimal when AIBN was added every 3 h, and better than that noted when PPh<sub>3</sub> was also added during the reaction.

According to the observed yields of that reaction, the following decreasing reactivity scale of the efficiency of the radical generated from the initiator was suggested:



After distillation, iodohydrin **3** was characterised by <sup>1</sup>H, <sup>19</sup>F and <sup>13</sup>C NMR without any ambiguity. The <sup>1</sup>H NMR spectrum shows the absence of ethylenic protons (in the 5.4–6.1 ppm range) and the presence of a complex system (doubled AB system) centred at 2.9 ppm assigned to the methylene group adjacent to the perfluorinated chain. The multiplet centred at 4.4 ppm gives the evidence of the CHI group while the broad singlet at 2.2 ppm shifting with dilution or with CCl<sub>3</sub>NCO is attributed to the hydroxy function. The methylene group adjacent to this OH function leads to a multiplet centred at 3.8 ppm. Indeed, adding one or two drops of Cl<sub>3</sub>CNCO in the NMR tube gave a low field shift of ca. 1 ppm as noted in HOCH<sub>2</sub>(VDF)<sub>n</sub>H telomers [53].

The most interesting feature in the <sup>19</sup>F NMR spectrum concerns the high field shift from –59.2 ppm (CF<sub>2</sub>I end-group of C<sub>6</sub>F<sub>13</sub>I) to –114.9 ppm (assigned to CF<sub>2</sub>CH<sub>2</sub>CHI) as an AB system because of the presence of both stereoisomers and the bulky iodine atom.

Finally, the <sup>13</sup>C NMR spectrum exhibits the characteristic triplets or quartet in the 102 to 124 ppm range assigned to the perfluorinated group. The methylene group adjacent to it gave an expected triplet (<sup>2</sup>J<sub>CF</sub> = 21.1 Hz) centred at 39.2 ppm while that adjacent to the OH function is represented by a singlet at 69.1 ppm. As expected, the presence of the iodine atom gives the attached carbon atom a high field shifted singlet at 21.5 ppm. In contrast to the other signals which appear as positive peaks since they are assigned to secondary and quaternary carbon atoms, this singlet has a negative orientation (for a tertiary carbon atom) on the 80 MHz multiplicity <sup>13</sup>C NMR spectrum.

Hence, the NMR spectra show that C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CHICH<sub>2</sub>OH (**3**) was produced selectively and gave evidence that the perfluorohexyl radical reacted selectively to the less hindered side of the unsaturated alcohol. This is in good agreement with the results noted from the radical addition of ClCF<sub>2</sub>CFCII to allyl alcohol for which AIBN gave the best yields [54].

Further, although allyl acetate is more reactive than allyl alcohol [55], this former monomer led to the unexpected rearranged C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>CH(OAc)CH<sub>2</sub>I by-product [50] which is not convenient to achieve a primary/primary telechelic diol from α,ω-diiodoperfluoroalkanes in similar conditions. Therefore, the system allyl alcohol/IC<sub>6</sub>F<sub>12</sub>I/AIBN is used

even if the reaction is performed at more longer reaction times.

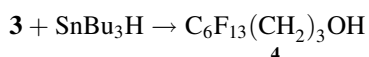
## 2.2. Selective reduction of the iodine atom in iodohydrin **3**

The literature gives various methods for the reduction of

iodine atoms: from a palladium/charcoal complex [37,38,56,57], from a zinc/HCl or zinc/NiCl<sub>2</sub> mixture [58,59] or by of tributylstannane [60].

This last method has already shown a great efficiency from fluoroalkyl iodides containing various fluoroolefin base units (vinylidene fluoride [61], trifluoroethylene [62] or hexafluoropropene [63,64]) or allyl alcohol [65] close to the iodine.

This method was successfully used to achieve the reduction of iodohydrin **3** by a stoichiometric molar amount of tributylstannane, as follows:



After distillation, the 1H,1H,2H,2H,3H,3H-perfluoronanol was obtained in 90% yield and was characterised by NMR.

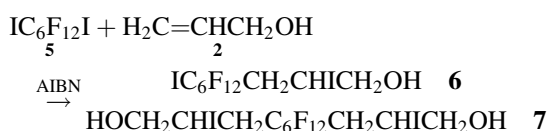
The absence of a CHI group was noted from the high field shifts from 4.4 to 1.8 ppm (<sup>1</sup>H NMR) and from 21.5 to 20.8 ppm (<sup>13</sup>C NMR).

## 2.3. Conclusion

This model reaction performed in a two-step procedure to obtain C<sub>6</sub>F<sub>13</sub>C<sub>3</sub>H<sub>6</sub>OH from C<sub>6</sub>F<sub>13</sub>I has been improved to achieve high yields of intermediate iodohydrin **3** and fluorinated alcohol **4**. Hence, this “optimised” two-step process was involved for the bismonoaddition of 1,6-diiodoperfluorohexane to allyl alcohol to obtain an α,ω-diols. The use of allyl alcohol motivated our choice for the synthesis of this telechelic since no rearranged by-product was formed in these conditions.

## 2.4. Bismonoaddition of 1,6-diiodoperfluorohexane to allyl alcohol

The optimal conditions in the radical addition of perfluorohexyl iodide were used to achieve this reaction:



The reaction was performed in bulk with a 2.5–4-fold excess of allyl alcohol over  $\text{IC}_6\text{F}_{12}\text{I}$  to favour the formation of bis(iodohydrin) **7** about monofunctional **6**. Further, it was noted that even with the largest excess of hydroxylated monomer, the diadduct containing one hydroxyl end-group,  $\text{IC}_6\text{F}_{12}[\text{CH}_2\text{CH}(\text{CH}_2\text{OH})]_2\text{I}$  was not produced and confirms the poor propagation behavior of the allyl alcohol monomer.

The reaction was monitored by GC, the chromatogram of which shows four peaks having the following retention-times: 0.37, 4.77, 10.76 and 15.23 min assigned to allyl alcohol,  $\text{IC}_6\text{F}_{12}\text{I}$ , alcohols **6** and **7**, respectively.

After a 3 h reaction, the conversion of **5** was assessed to be ca. 85% while the **6/7** products ratio was about 75/25. This ratio decreased to 50/50 after 5 h reaction with 95% of diiodide-conversion. After a 15 h reaction, it was noted both quantitative conversions of the diiodide and of monoadduct **6**. As in the case of the bismonoaddition of  $\alpha,\omega$ -bis(trichloromethyl) chlorotrifluoroethylene telomers to allyl acetate [55,66], the diiodide first reacted with allyl alcohol leading to the monoadduct **6**, until complete conversion of  $\text{IC}_6\text{F}_{12}\text{I}$ ; then, the excess of allyl alcohol reacted with product **6** yielding telechelic **7**. Although allyl alcohol is less reactive than allyl acetate, it seems that the  $\text{CF}_2\text{-I}$  bond is more reactive toward the former monomer in the presence of AIBN than a  $-\text{CCl}_3$  end-group toward the latter monomer in the presence of redox catalyst (i.e.  $\text{CuCl}$  or  $\text{CuCl}_2$ ). It took at least 48 h [66] and even 13 days [55] to achieved the selective formation of telechelic diacetate from bis(trichloromethyl) telomers.

After work-up and purification, telechelic **7** was characterised by NMR. The  $^{19}\text{F}$  NMR spectrum shows the absence of signal centred at  $-59.3$  ppm assigned to a  $\text{CF}_2\text{I}$  end-group giving evidence of the absence of both diiodide and monoadduct **6**. Three signals with the same integrals centred at  $-112.3$  (AB system),  $-121.1$  and  $-123.1$  are assigned to the difluoromethylene groups located in  $\alpha$ ,  $\beta$  and  $\gamma$  to the methylene groups. The  $^1\text{H}$  NMR spectrum is rather similar to that of iodohydrin **3**.

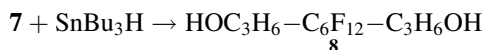
The  $^{13}\text{C}$  NMR spectrum is also similar to that of **3** with however a shorter zone characteristic of the difluoromethylene carbon atoms at 110–125 ppm. Although two diastereoisomers could be expected because of two asymmetrical carbon atoms of **7**, the peaks observed are not doubled. Hence, **7** could be regarded as a symmetrical molecule ( $\text{C}_2$  symmetry) arising from the regioselective addition of  $\text{IC}_6\text{F}_{12}\cdot$  and  $\text{HOCH}_2\text{CHICH}_2\text{C}_6\text{F}_{12}\cdot$  radicals to allyl alcohol.

As in the case above, these radicals reacted to the less hindered side of allyl alcohol without any rearranged by-product (also noted when allyl acetate was used as the monomer [30,31,50,67]).

### 2.5. Reduction of **4**

The selective reduction of both iodine atoms was performed by tributylstannane, as in the model reaction above,

using a 3.1-fold excess of the tin complex over **7**, as follows:



After reaction and treatment (the tin complex was precipitated from diethyl ether), diol **8** was characterised by NMR. The most important features were noted in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra showing the high field shift of the signal centred at 4.4 (CHI groups) to 1.8 ppm in **8** and the slight low field shift of the singlet at 21.5 to 24.8 ppm, respectively. Further, the shape of the signal centred at  $-113.5$  ppm assigned to  $\text{CH}_2\text{CF}_2$  groups became simpler than the slightly low field shifted complex AB system noted in the  $^{19}\text{F}$  NMR spectrum of **7**.

The bis(reduction) was carried out in 73% yield and the overall yield of diol **8** was 61% starting from 1,6-diiodoperfluorohexane.

### 3. Conclusion

This work, composed of two dependant parts, deals with a model “optimisation” reaction involving a perfluoroalkyl iodide, before transferring it to a further procedure utilising an expensive  $\alpha,\omega$ -diiodoperfluoroalkane for the preparation of a fluorotelechelic diol.

First, the model reaction describes a two-step procedure to synthesise  $\text{C}_6\text{F}_{13}\text{C}_3\text{H}_6\text{OH}$ , from the radical addition of  $\text{C}_6\text{F}_{13}\text{I}$  to allyl acetate, followed by the selective reduction of the iodine atom in the produced iodohydrin. Various initiating systems (photochemical, redox or from organic initiators) were attempted showing that radical initiators were most efficient, and that AIBN and triphenylphosphine led to the best yields. Interestingly, the result was improved when AIBN was added during the reaction. Although allyl alcohol (a.a.) demonstrated a slightly lower reactivity than allyl acetate (91% in 10 h for a.a. versus 84–95% in 1–5 min [67]) it did not allow the formation of any  $\text{C}_6\text{F}_{13}\text{CH}_2\text{CH}(\text{OAc})\text{CH}_2\text{I}$  rearranged by-product. The second step, involving tributylstannane as a highly selective iodine reducing agent, was achieved in high yield. From  $\text{C}_6\text{F}_{13}\text{I}$ , the overall yield of 1H,1H,2H,2H,3H,3H-perfluoronanol was 82%.

This model reaction was successfully applied to 1,6-diiodoperfluorohexane for obtaining a telechelic diol containing a  $\text{C}_6\text{F}_{12}$  group in the backbone. The first step led to a fluorinated bis(iodohydrin) in 81% yield and even a four-fold excess of allyl alcohol did not lead to any trace of  $\text{IC}_6\text{F}_{12}(\text{a.a.})_2\text{I}$ . As above, no rearranged by-product was noted and this allowed the formation of telechelic diol after the selective bis(reduction) of both iodine atoms, achieved in 75% yield. The overall yield of  $\text{HOC}_3\text{H}_6\text{C}_6\text{F}_{12}\text{C}_3\text{H}_6\text{OH}$  was 61% from 1,6-diiodoperfluorohexane.

This telechelic diol is an interesting precursor of fluorinated  $\alpha,\omega$ -di(meth)acrylate, dicyanate, but also polyurethane or polyester.

## 4. Experimental details

### 4.1. General comments

#### 4.1.1. Reactants

1-Iodoperfluorohexane and 1H,1H,2H,2H-perfluorooctanol were kindly supplied by Elf Atochem (Pierre Benite, France); 1,6-diiodoperfluorohexane (**5**) by Daikin (Japan); 4-*tert*-butylcyclohexylperoxydicarbonate (Perkadox-16) by Akzo (Neederland) and *tert*-butyl peroxyvalate by La Chalonnaise des Peroxydes (France). 2,2-Azobisisobutyronitrile (AIBN) was purchased from Merck, acetonitrile from SDS. Allyl alcohol (or 2-propen-1-ol), **2**, benzophenone, copper, hydrogen peroxide, *tert*-butyl cumyl peroxide, di-*tert*-butyl peroxide, triethylphosphite and triphenylphosphine were supplied by Aldrich.

The iodinated reactants were worked up with sodium thiosulfate, dried and distilled prior to use. All other chemicals (except allyl alcohol, distilled) were used as received.

#### 4.1.2. Reactions

The photochemical reaction was performed under a mercury lamp Philips HPK 125 W, the tube being stood vertically, magnetically stirred and irradiated at 10 cm from it.

While a set of reactions were carried out in a two-necked round-bottom flask equipped with a condenser and a nitrogen flow after all the reactants were weighed into the flask, other reactions occurred in sealed borosilicate Carius tubes (CT) (thickness: 25 mm, i.d.: 23 mm and length: 260 mm). After introduction of the reactants, the CT was immersed into liquid nitrogen and degased under vacuum to get rid oxygen. Five thaw freeze cycles were done and then the CT was sealed and placed into the cavity of an aluminium block put in a shaking oven. After reaction, the CT was taken out of the block, cooled to room temperature, immersed into liquid nitrogen and opened.

Both these sets of reactions were carried out in similar conditions.

#### 4.1.3. Apparatus

After reaction and evaporation of the solvent, the total product mixture was worked up (when the reaction was catalysed with copper) with acidic water and NaHCO<sub>3</sub> and analysed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with a SE 30 column, 3 m × 1/8 in. (i.d.). The nitrogen pressure at the entrance to the column was maintained at 0.6 bar and the detector and injector temperatures were 260 and 255 °C, respectively. The temperature programme started from 50 and reached 250 °C at a heating rate of 15 °C/min. The GC apparatus was connected to a Hewlett Packard integrator (model 3390).

The products were characterised by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy at 20 °C. Spectra were recorded on Bruker AC-200, AC-250 or WM-360 instruments, using deuterated chloroform or acetone as the solvents. All chemical shifts

are given in ppm/TMS for <sup>1</sup>H and in ppm/CFCl<sub>3</sub> for <sup>19</sup>F NMR, the coupling constants being in Hz.

### 4.2. Synthesis of C<sub>6</sub>F<sub>13</sub>C<sub>3</sub>H<sub>6</sub>OH (**4**)

The reaction was carried out in two steps.

#### 4.2.1. Radical addition of 1-iodoperfluorohexane (**1**) to allyl alcohol (**2**)

Various weights of reactants are listed in Table 4.

After reaction, iodohydrin **3** was distilled bp: 69–72 °C/0.15 mm Hg, (lit. [65]: 70–76 °C/2 torr); *T*<sub>m</sub>: 44 °C (lit. [65]: 43–44 °C), beige solid.

4.2.1.1. 2-Iodo-4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononanol (**3**). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 4.4(m,CH,1H); 3.8(m,CH<sub>2</sub>OH down field shifted of 1.0 ppm with Cl<sub>3</sub>CNCO,2H); 2.9(m,CH<sub>2</sub>CH,2H); 2.2(broad s, shifted with dilution and with Cl<sub>3</sub>CNCO, CH<sub>2</sub>OH,1H).

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ: –81.9(m,CF<sub>3</sub>CF<sub>2</sub>,3F); –115.2(m,CF<sub>2</sub>–CH<sub>2</sub>,2F); –122.3(m,CF<sub>2</sub>–CF<sub>2</sub>–CH<sub>2</sub>,2F); –123.1(m,CF<sub>2</sub>–(CF<sub>2</sub>)<sub>2</sub>–CH<sub>2</sub>,2F); –124.4(m,CF<sub>2</sub>–(CF<sub>2</sub>)<sub>3</sub>–CH<sub>2</sub>,2F); –126.2(m,CF<sub>2</sub>–(CF<sub>2</sub>)<sub>4</sub>–CH<sub>2</sub>,2F).

80 MHz multiplicity <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 102–124(positive triplets and quartets, C<sub>6</sub>F<sub>13</sub>–CH<sub>2</sub>,6C); 69.1(pos.s,CH<sub>2</sub>–OH,1C); 39.2(pos.t, <sup>2</sup>J<sub>CF</sub> = 21.1 Hz, C<sub>6</sub>F<sub>13</sub>–CH<sub>2</sub>,1C); 21.5(negative s,CH,1C).

#### 4.2.2. Reduction of **3**

Iodohydrin **3**, 5.21 g (0.010 mol) of which was dissolved in anhydrous toluene in a two-necked round-bottom flask equipped with a condenser and swept with an argon flow. Tributylstannane (3.1 ml, 3.35 g, 0.011 mol) was transferred under argon to a dropping funnel, added dropwise into the iodohydrin cooled at 5 °C. Then the solution was magnetically stirred for 12 h at room temperature. After elimination of toluene, the upper phase containing the tin salt was separated from the organic fluorinated phase by extraction with pentane. The organic part of 3.50 g of colourless liquid was distilled, bp: 69–71 °C/23 mm Hg, yield: 90%.

4.2.2.1. 4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononanol (**4**). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ: 3.70(down field shifted t of 1.0 ppm in the presence of Cl<sub>3</sub>CNCO, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz, CH<sub>2</sub>OH,2H); 2.2(m,R<sub>F</sub>CH<sub>2</sub>,2H); 1.8(m,CH<sub>2</sub>CH<sub>2</sub>OH,2H); 1.7(broad signal, low field shifted with Cl<sub>3</sub>CNCO or with dilution, CH<sub>2</sub>OH,1H).

<sup>19</sup>F NMR (CDCl<sub>3</sub>): same chemical shifts as those of **3**. <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ: 120–95(m,CF<sub>3</sub> and CF<sub>2</sub> groups, C<sub>6</sub>F<sub>13</sub>); 67.6(s,CH<sub>2</sub>OH,1C); 36.3(t, <sup>2</sup>J<sub>CF</sub> = 21.6 Hz, C<sub>6</sub>F<sub>13</sub>CH<sub>2</sub>,1C); 20.8(s,CH<sub>2</sub>CH<sub>2</sub>OH,1C).

### 4.3. Synthesis of telechelic fluorinated diol **8**

As above, the preparation of diol **8** was carried out in two steps.

#### 4.3.1. Radical bis(monoaddition) of 1,6-diiodoperfluorohexane (**5**) to allyl alcohol (**2**)

A similar experiment as that starting from **1** was performed in a two-necked round-bottom flask using 50.05 g (0.09 mol) of **5**, 11.12 g (0.19 mol) of **2** and 0.697 g (43 mmol) of AIBN magnetically stirred. The same amounts of AIBN and of **2** were added every 4 h while the reaction was monitored by gas chromatography (GC). After 10 h, the conversion of **5** was quantitative. After evaporation of excess of **2** until constant weight, 49.2 g (73 mmol, 81% yield) of an orange wax was obtained showing the formation of the  $\alpha,\omega$ -diiodohydrin **7** by GC.

4.3.1.1. 2,11-Diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-1,12-dodecanediol (**7**).  $^1\text{H}$  NMR ( $(\text{D}_3\text{C})_2\text{CO}$ )  $\delta$ : 4.4(m,CHI,2H); 3.8(m, down field shifted with  $\text{Cl}_3\text{CNCO}$ ,  $\text{CH}_2\text{OH}$ ,4H); 2.8(m, $\text{CH}_2\text{CHI}$ ,4H); 2.2(broad singlet shifted in the presence of  $\text{Cl}_3\text{CNCO}$  or with dilution, OH,2H).

$^{19}\text{F}$  NMR ( $(\text{D}_3\text{C})_2\text{CO}$ )  $\delta$ : -111.3(complex AB system, $\text{CF}_2\text{-CH}_2\text{CHI}$ ,4F); -121.1(m, $\text{CF}_2\text{-CF}_2\text{-CH}_2\text{CHI}$ ,4F); -123.1(m, $\text{CF}_2\text{-(CF}_2\text{)}_2\text{-CH}_2\text{CHI}$ ,4F).

$^{13}\text{C}$  NMR ( $(\text{D}_3\text{C})_2\text{CO}$ ) similar chemical shifts as those of **3**.

#### 4.3.2. Reduction of **7** into **8**

Similarly to the reduction of **3**, 61 ml (0.227 mol) of tributylstannane were added dropwise into 48.32 g (71.9 mmol) of **7** saturated with argon, and cooled in an ice bath.

After total addition, the mixture was left stirring and progressively heated up to room temperature for 8 h. 145 mg of potassium fluoride and 150 ml of diethyl ether were added into the mixture and stirred at room temperature for 3 h. A complex of  $\text{KF}$  and  $\text{SnBu}_3\text{X}$  ( $\text{X} = \text{I}, \text{H}$ ) precipitated and was filtered off. After almost total evaporation of  $\text{Et}_2\text{O}$ , diol **8** was precipitated from water, and then recrystallised from  $\text{ClCF}_2\text{CFCl}_2$ . 22.1 g (53 mmol) of yellow crystals were obtained in 73% yield.  $T_m$ : 71°C ( $\text{ClCF}_2\text{CFCl}_2$ ).

4.3.2.1. 4,4,5,5,6,6,7,7,8,8,9,9-Dodecafluoro-1,12-dodecanediol (**8**).  $^1\text{H}$  NMR ( $(\text{D}_3\text{C})_2\text{CO}$ )  $\delta$ : 3.9(broad signal, down field shifted with  $\text{Cl}_3\text{CNCO}$ ,2H,OH); 3.6(m,down field shifted of 1.0 ppm with  $\text{Cl}_3\text{CNCO}$ , $\text{CH}_2\text{OH}$ ,4H); 2.4(m, $\text{C}_6\text{F}_{12}\text{CH}_2$ ,4H); 1.8(q,  $^3J_{\text{HH}} = 6.9$  Hz,  $\text{CH}_2\text{CH}_2\text{C}_6\text{F}_{12}$ ,4H).

$^{19}\text{F}$  NMR ( $(\text{D}_3\text{C})_2\text{CO}$ ) same spectrum as that of **7**, except a more simple system centred at -113.5 ppm for  $\text{CH}_2\text{CF}_2$  groups.

$^{13}\text{C}$  NMR ( $(\text{D}_3\text{C})_2\text{CO}$ )  $\delta$ : 110–125(m, $\text{C}_6\text{F}_{12}$ ,6C); 61.2(s, $\text{CH}_2\text{OH}$ ,2C); 30.3(t,  $^2J_{\text{CF}} = 22.1$  Hz,  $\text{CH}_2\text{C}_6\text{F}_{12}$ ,2C); 24.8(s, $\text{CH}_2\text{CH}_2\text{OH}$ ,2C).

#### Acknowledgements

The authors would like to thank the Daikin Industries, Ltd. (Drs Shimizu, Morita and Yamamoto) for its financial

support and for the gift of 1,6-diiodoperfluorohexane, the Elf Atochem Company for the gift of 1-iodoperfluorohexane and 1H,1H,2H,2H-perfluorooctanol, Akzo for Perkadox 16 and La Chalonnaise des Peroxydes for *t*-butyl peroxy-pivalate.

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