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Synthesis of telechelic dienes from fluorinated α,ω-diiodoalkanes. Part I. Divinyl and diallyl derivatives from model $I(C_2F_4)_nI$ compounds

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Abstract

The synthesis of five fluorinated non-conjugated dienes from commercially available α,ω-diiodoperfluoroalkanes is described. Preparation of the fluorinated divinyl derivatives $H_2C{=}CH(CF_2)_nCH{=}CH_2$ ($n=2$, 4, 6) (**2,2**, **2,4** and **2,6**) was effected by ethylenation of these diiodinated compounds in various ways followed by dehydroiodination in ethanolic potassium hydroxide. Allyl diolefines, $H_2C{=}CHCH_2(CF_2)_nCH_2CH{=}CH_2$ (**4,4** and **4,6**) were produced by the α,ω-bis-telomerization of allyl acetate followed by deiodoacetoxylation in the presence of zinc. The diacetate precursors **3,4** and **3,6** of the respective diallyls **4,4** and **4,6** were obtained rather than diacetate **3,2** because of the eventual decomposition of α,ω-diiodoperfluoroethane by β-scission. These five fluorinated non-conjugated dienes have been characterized by ^1H, ^{13}C and ^{19}F NMR spectroscopy.

Keywords: Telechelic dienes; Fluorinated vinyl dienes; Fluorinated allyl dienes; α,ω-Diiodoperfluoroalkanes; NMR spectroscopy

1. Introduction

Although perfluoroalkyl iodides are widely used as reactants for the synthesis of fluorinated derivatives [1], this is not the case for α,ω-diiodoperfluoroalkanes because of the difficulty of synthesis and their corresponding price. The major interesting applications include fluorinated elastomers [2–4] or rubbers [5], block copolymers [4], silicon-containing polymers [6,7] or monomer precursors of membranes, as produced by Asahi Glass [8].

The literature describes several ways of synthesis of α,ω-diiodoperfluoroalkanes and a few examples are given below.

The method most used is thermal telomerization of tetrafluoroethylene, TFE, with iodine as reviewed recently by Tortelli and Tonelli [9] who optimized the process (best conditions are in an autoclave at 180–200 °C for 8 h with a 2–3-fold excess of TFE) performed industrially by Asahi Glass [10]. It should be noted that heating 1,2-diiodoperfluoroethane leads to higher telomeric adducts because of the well-known β-scission of the starting material [11,12]. In addition, the γ-ray (from a ^{60}Co source) induced telomerization of TFE with IC_2F_4I [13] and the use of radical initiators [14] also lead to diiodoperfluorobutane and hexane.

The second method involves the Hunsdiecker reaction of fluorinated dicarboxylic silver salts in the presence of iodine [15] which produced the expected fluorinated diiodides in moderate yield. Halogen exchange is also a possible way of obtaining such iodinated derivatives. For example, telomers of TFE with I–Cl [16,17] and I–Br [17] afford the corresponding diiodides by further reaction with iodine. Similarly, Riley et al. [7] obtained new diiodides containing perfluorinated ether linkages via the iodination of α,ω-diacid fluorides in the presence of potassium fluoride. This reaction can also be performed thermally from perfluorinated diacid chlorides [18] with preheated crystallized KI. The UV photolysis of $BrCF_2I$ with TFE led to $I(CF_2)_nI$ ($n=2$–5) after 45 min at 100 °C [19].

Interestingly, several functionalizations have been achieved from α,ω-diiodoperfluoroalkanes after the introduction of a spacer between the perfluorinated chain and the iodine atoms: for example, the synthesis of telechelic diols [3,20], dicarboxylic acids or dinitriles [21], diamines or diisocyanates [3,22] which are for obtaining fluorinated polymers. Furthermore, Piccardi et al. [23] have produced fluorinated α,ω-di(trichloromethylated) derivatives from the bis-monoaddition of carbon tetrachloride on to 3,3,4,4-tetrafluoro-1,5-hexadiene.

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However, little work has been undertaken on the preparation of fluorinated non-conjugated dienes, as has recently been reviewed by Chambers [24]. These dienes are useful for various applications: epoxy resins for coatings which exhibit good weathering resistance [25,26], oil and water-repellent elastomers [27], clothing protection [26,28] and silicones which exhibit good properties at low temperatures [7].

Syntheses of α,ω-divinyl derivatives, $H_2C{=}CH{-}R_F{-}CH{=}CH_2$, have been performed by Knunyants et al. [29], Brace [30] and Kim et al. [7] from the thermal bis-monoaddition of ethylene on to IR_FI, followed by a dehydroiodination in ethanolic potassium hydroxide [7,29] or tributylamine [30]. Similar reactions from α,ω-dibromoperfluoroalkanes leading to divinyl compounds have also been investigated [7,31,32]. In certain cases, the ethylenation was more efficient in the presence of catalysts such as ruthenium, chromium or manganese complexes [33–35].

Yamamoto et al. [36,37] obtained the interesting fluoropolyoxyalkylene glycol diallyl ether $H_2C{=}CHCH_2OR_F{-}OCH_2CH{=}CH_2$, where R_F is a tetrafluoroethylene (TFE) block or TFE/hexafluoropropylene oxide cotelomer prepared from a caesium fluoride/oxalic acid fluoride system [36] or $[CsOCF_2CF(CF_3)OCF_2]_2$ [37], respectively, followed by the addition of allyl bromide. In addition, Thompson and Hoover [28] have described the synthesis of fluorocarbon-containing diallyl ammonium compounds which have been used as hydrophobic and oleophobic materials for textiles.

To our knowledge the literature does not report any reaction leading to fluorinated allyl dienes from α,ω-diiodoperfluoroalkanes. Nevertheless, interesting routes involving perfluoroalkyl iodides (R_FI) have been described: thus Cornforth et al. [38] prepared an allyl olefin via a fluorinated epoxide, whereas Matsubara et al. [39] added R_FI on to an allyl organotin derivative in the presence of palladium.

Brace [40] and more recently Huang [41] have presented interesting two-step syntheses of fluorinated allyl olefins, by performing the monoaddition of perfluoroalkyl iodides on to allyl acetate, followed by a 'deiodoacetoxylation'. Two patents [42] also mention the preparation of such fluorinated monomers from fluorinated iodohydrin. Similarly, the synthesis of α,ω-bis(iodoacetate) was successfully achieved from IR_FI by radical initiation [43] or in the presence of R_FSO_2Na [44], but no further reaction was investigated.

The object of the present work was the preparation and characterization of new fluorinated α,ω-divinyl and diallyl olefin from commercially available telechelic diiodoperfluoroalkanes.

2. Results and discussion

Syntheses of the fluorinated divinyl or diallyl non-conjugated dienes were performed by different two-step processes, each reaction being described below.

2.1. Synthesis of divinyl non-conjugated dienes

As described in the literature [29,30,33–35], the divinyl diolefins were synthesized by the α,ω-bis(monoethylenation) of diiodoperfluoroalkanes followed by a bis(dehydroiodination) as follows:

$$I(CF_2)_nI + H_2C{=}CH_2 \longrightarrow \quad (n=2,\ 4,\ 6)$$

$$IC_2H_4(CF_2)_nI + IC_2H_4(CF_2)_nC_2H_4I \quad (\mathbf{1,}\boldsymbol{n})$$

$$\mathbf{1,}\boldsymbol{n} + KOH + EtOH \longrightarrow H_2C{=}CH(CF_2)_nCH{=}CH_2 \quad (\mathbf{2,}\boldsymbol{n})$$

2.1.1. Ethylenation of fluoroiodides

The ethylenation of perfluoroalkyl iodides is well known but it was interesting to investigate such a reaction on a model and then to apply the best conditions to the α,ω-diiodoperfluoroalkanes.

(*a*) *Modelling from perfluoroalkyl iodides*

As reported in the literature, this reaction can be initiated thermally [29,30] or in the presence of metallic salts [22,33–35] or initiators [14]. Modelling on the ethylenation of commercially available perfluorohexyl iodides was first conducted under different conditions. Three reactions were carried out thermally at 140, 170 and 210 °C for 10 h in each case without any initiator or catalyst, being present whereas three other reactions were undertaken in the presence of redox systems. Finally, five further ethylenations involved the following radical initiators which were used separately at a temperature at which their half-life was close to 1 h: bis(4-t-butylcyclohexyl)peroxydicarbonate (Perkadox-16) (60 °C), t-butylperoxypivalate (Trigonox 25) (74 °C), AIBN (80 °C), dibenzoyl peroxide (DBP) (92 °C) and di(t-butyl)peroxide (135 °C). t-Butanol was used as solvent and chlorobenzene was chosen as the internal standard to determine the reaction yield by gas chromatography.

The results are listed in Table 1. It can be seen that thermal ethylenation (without any initiator or catalysts) could only be achieved in moderate yield above 200 °C. The use of CuI or CuCl in the presence of a 10-fold excess of ethanolamine as a ligand led to high monoadduct yield. The results obtained using radical initiators are more complex. AIBN and dibenzoyl peroxide are insoluble in $C_6F_{13}I$ are room temperature and led to poor results as observed by Vergé [45] in the telomerization of tetrafluoroethylene with $C_6F_{13}I$. However, di(t-butyl)peroxide gave fair results as previously noted in the ethylenation of 1,2-dibromo-perfluoroethane [7].

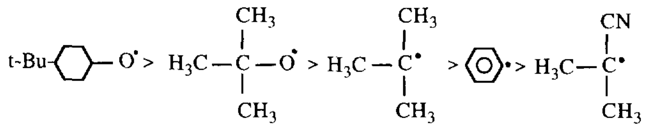
The radical reactivity series in decreasing order is Perkadox-16 (60 °C) > $(^tBuO)_2$ (135 °C) > t-butylperoxypivalate (74 °C) > DBP (92 °C) > AIBN (80 °C). This shows that the temperature is not a key factor in the reaction but rather the nature of the radical created by the decomposition of the initiator. Thus, it may be concluded that alkoxy radicals are

Table 1
Ethylenation of commercially available perfluorohexyl iodide [a]

R_0	Initiator or catalyst	c_0	c'_0	Temp. (°C)	Time (h)	Yield (GC) (%)
0.4	–	–	–	140	12	0
0.4	–	–	–	170	12	5
0.4	–	–	–	210	12	60
0.4	CuI	0.02	–	165	15	90
0.4	CuCl	0.02	2	140	14	75
0.4	CuCl	0.02	10	140	14	90
0.4	$RuCl_2(PPh_3)_3$	0.01	–	110	16	0
0.4	Perkadox-16	0.02	–	60	4	70
0.4	Trigonox 25	0.02	–	75	4	8
0.4	AIBN	0.02	–	80	4	2
0.4	DBP	0.02	–	90	4	5
0.4	$(^tBuO)_2$	0.02	–	135	4	55

[a] Experimental conditions employed: (R_0 = [iodide]$_0$/[ethylene]$_0$; c_0 = [initiator or catalyst]$_0$/[ethylene]$_0$; Perkadox-16 = bis(4-t-butylcyclohexyl)peroxydicarbonate; DBP = dibenzoyl peroxide; Trigonox 25 = t-butylperoxypivalate; c'_0 = [ethanolamine]$_0$/[CuCl]$_0$; yields calculated by GC methods using chlorobenzene as internal standard.

more reactive towards R_FI than alkyl radicals, allowing the following series of reactivity to be proposed:



By-products formed could not be identified by GC/MS, NMR or FT-IR spectroscopy, and the absence of C_6F_{13}–C_6F_{13} showed that the C_6F_{13} radical does not undergo recombination. Finally, it should be noted that although Perkadox-16 seems to be the most efficient reagent, it was necessary to recharge the autoclave two or three times with this reagent to effect the reaction.

(*b*) *Ethylenation of α,ω-diiodoperfluoroalkanes*

Modelling was also used for the bis(ethylenation) of α,ω-diiodoperfluoroalkanes. When the reaction was carried out in the presence of CuI, good yields of $IC_2H_4(CF_2)_nC_2H_4I$ were obtained irrespective of the chain length of the diiodide (see Table 2). The good efficiency of copper salts as catalysts in the ethylenation reaction confirms previous results for similar reactions starting from $Cl_3CCF_2CCl_3$, which led to $ClC_2H_4CCl_2CF_2CCl_2C_2H_4Cl$ in very high yield [46].

The three bis(ethylenated) α,ω-diiodoperfluoroalkanes **1,2**, **1,4** and **1,6** were characterized by ^1H and ^{19}F NMR spectroscopy (Table 3). The ^1H NMR spectra showed triplet and complex systems centred at δ 3.25 and 2.65 ppm which are assigned to the methylene end-groups and to the CH_2 group adjacent to the fluorinated chain, respectively.

The ^{19}F NMR spectra exhibited a high-field shift of the CF_2I end-group of the telogen ($\delta = -53$ or -60 ppm for 1,2-diiodoperfluoroethane or higher molecular weight diiodides, respectively) to $CF_2CH_2CH_2I$ ($\delta = -115.8$ or -124 ppm, respectively) of the ethylenated derivatives.

2.1.2. Synthesis of fluorinated divinyl compounds

Preparations of these fluorinated non-conjugated dienes were performed by dehydroiodination of the ethylenated products obtained above in an alkaline medium. Modelling was performed using the commercially available 1-iodo-1,1,2,2-tetrahydroperfluoro-octane under different experimental conditions. The results are summarized in Table 4 and show that the highest yield was obtained in the presence of ethanolic potassium hydroxide.

Application of these results to the bis(ethylenated) diiodoperfluoroalkanes gave yields of fluorinated non-conjugated

Table 2
Ethylenation of commercially available α,ω-diiodoperfluoroalkanes [a]

Iodide	Initiator or catalyst	c_0	c'_0	Temp. (°C)	Time (h)	Yield (%)
IC_2F_4I	$(^tBuO)_2$[b]	0.06	–	135	6	52
	CuCl	0.02	10	145	14	73
	CuI	0.02	–	160	14	75
IC_4F_8I	CuI	0.02	–	160	4	74
$IC_6F_{12}I$	CuI	0.02	–	165	15	80

[a] Experimental conditions employed; R_0 = 0.2; yields calculated after distillation.
[b] The autoclave was charged three times with c_0 = 0.02.

Table 3
^{19}F and ^{1}H NMR parameters of commercially available α,ω-diiodoperfluoroalkanes and of the ethylenated divinyl and diallyl derivatives obtained

I	CF_2	CF_2	I									
	−53.3											
I	CH_2	CH_2	CF_2	CF_2	CH_2	CH_2	I					
	3.25	2.65	−115.8									
H_2C	=	CH	CF_2	CF_2	CH	=	CH_2					
6.0		5.8	−116.5									
I	CF_2	CF_2	CF_2	CF_2	I							
	−59.0	−112.3										
I	CH_2	CH_2	CF_2	CF_2	CF_2	CF_2	CH_2	CH_2	I			
	3.2	2.6	−123.8	−115.4								
	(tt)	(ttt)										
H_2C	=	CH	CF_2	CF_2	CF_2	CF_2	CH	=	CH_2			
6.0		5.8	−124.7	−115.0								
H_2C	=	CH	CH_2	CF_2	CF_2	C_2F_4	CH_2	CH	=	CH_2		
5.3		5.8	2.7	−123.8	−113.8							
			td									
I	CF_2	CF_2	CF_2	CF_2	CF_2	CF_2	I					
	−59.5	−113.5	−121.4									
I	CH_2	CH_2	CF_2	CF_2	CF_2	CF_2	CF_2	CF_2	CH_2	CH_2	I	
	3.2	2.7	−123.8	−115.3	−122.1							
H_2C	=	CH	CF_2	CF_2	CF_2	CF_2	CF_2	CF_2	CH	=	CH_2	
6.0		5.8	−124.6	−114.9	−122.4							
H_2C	=	CH	CH_2	CF_2	CF_2	CF_2	C_3F_6	CH_2	CH	=	CH_2	
5.35		5.80	2.85	−124	−114	−122						
			td									

dienes higher than 70%, except for the lower molecular weight olefin for which the yield was only 55%.

These dienes were also characterized by ^{1}H and ^{19}F NMR spectroscopy and their chemical shifts are listed in Table 2. For all these three compounds, the ^{1}H NMR spectra exhibited characteristic signals at δ 6.0 and 5.8 ppm, which were assigned to the H_2C and $CH{-}R_F$ groups, respectively.

2.2. Synthesis of fluorinated diallyl diolefins

Preparations of the fluorinated diallyl derivatives were performed via a two-step reaction. The first step involved the radical addition of α,ω-diiodoperfluoroalkane to allyl acetate forming the 2:1 adduct, which was then deiodoacetylated with activated zinc to yield the new fluorinated non-conjugated diene according to the following scheme:

$$I(CF_2)_nI + H_2C{=}CHCH_2OCOCH_3 \longrightarrow$$
$$(n=2,\ 4,\ 6)$$

$$CH_3CO_2CH_2CHICH_2(CF_2)_nCH_2CHICH_2OCOCH_3$$
$$(\mathbf{3},\boldsymbol{n})$$

$$\mathbf{3},\boldsymbol{n} + Zn + CH_3OH \longrightarrow$$

$$H_2C{=}CHCH_2(CF_2)_nCH_2CH{=}CH_2$$
$$(\mathbf{4},\boldsymbol{n})$$

Table 4
Dehydroiodination of 1-iodo-1,1,2,2-tetrahydroperfluoro-octane or bis(ethylenated) α,ω-diiodoperfluoroalkanes in the presence of different alkaline media

$R_FC_2H_4I$	Alkali	Temp. (°C)	Time (h)	Yield (%)
$C_6F_{13}C_2H_4I$	KOH	70	4	90
$C_6F_{13}C_2H_4I$	NaOH	70	4	80
$C_6F_{13}C_2H_4I$	Pyridine	90	3	12
$C_6F_{13}C_2H_4I$	NEt_3	90	4	82
$C_6F_{13}C_2H_4I$	NBu_3	90	4	80
$IC_2H_4C_2F_4C_2H_4I$	KOH	70	5	55
$IC_2H_4C_4F_8C_2H_4I$	KOH	70	5	72
$IC_2H_4C_6F_{12}C_2H_4I$	KOH	75	5	75

2.2.1. Preparation of fluorinated bis(iodoacetate) derivatives

As shown previously [47], many methods of initiation can be used for the addition of perfluoroalkyl iodides to allyl acetate. In this work, dibenzoyl peroxide was chosen for the first step and employed at 95 °C, at which temperature its half-life is ca. 1 h. However, this initial reaction may also produce the undesirable 1:1 monoadduct as well as the expected 2:1 adduct **3**,***n***. In order to obtain the highest possible amount of **3**,***n***, an initial $[\text{allyl acetate}]_0/[\text{diiodoperfluoroalkane}]_0$ molar ratio equal to 4 was chosen and three portions of radical initiator were used during the reaction. The total amount of initiator was less than one-tenth of the molar amount of diiodoperfluoroalkane.

The radical addition of 1,2-diiodoperfluoroethane to allyl acetate failed whatever the nature of the radical initiator [dibenzoyl peroxide, AIBN or bis(4-t-butylcyclohexyl)-peroxydicarbonate] or the quality of the diiodide (distilled or worked-up with a sodium thiosulphate solution). A similar effect was noted by Brace [12] for the radical addition of IC_2F_4I on to vinyl acetate. This unsuccessful reaction can be explained by the eventual exotherm above 160 °C [48] produced by the reaction [47], which may provoke the well-known β-scission of the 1,2-diiodoperfluoroethane [11,12,30] as a result of the formation of the unstable $ICF_2\dot{C}F_2$ radical.

However, the reaction was performed in 71% yield from 1,4-diiodoperfluorobutane in the presence of dibenzoyl peroxide. Since the α,ω-diiodinated conversion was quantitative, it can be assumed that the remaining amounts arise from the 1:1 and eventual 3:1 adducts as observed in the radical addition of perfluoroalkyl iodides in the presence of a large excess of allyl acetate [49], where $R_FC_2H_4(CH_2OAc)CH_2CHICH_2OAc$ was isolated.

Interestingly, the reaction was quick, selective and led to high yields, contrary to the redox telomerization of allyl acetate with α,ω-bis(trichloromethylated) chlorofluorotelogens which produce the corresponding telechelic diacetates only under more extreme experimental conditions (e.g. greater amounts of catalyst and higher temperatures) and after several days [50].

Furthermore, heating the 2:1 adduct (**3,*n***) for a longer time at elevated temperatures led to rearrangement of the iodoacetoxy group [47] leading to **3′,*n*** as follows:

$$\underset{(\mathbf{3},n)}{AcOCH_2CHICH_2(CF_2)_nCH_2CHICH_2OAc} \longrightarrow$$

$$\underset{(\mathbf{3'},n)}{AcOCH_2CHICH_2(CF_2)_nCH_2CH(OAc)CH_2I}$$

$(n=4, 6)$

This rearrangement can also proceed at both ends of the molecule. It may also come from the exotherm produced by the high reactivity of diiodoperfluoroalkane towards allyl acetate. As observed in the ^1H NMR spectrum of the resulting **3,6** compound, the presence of a multiplet and of an AB system centred at δ 5.10 and 3.35 ppm assigned to CH(OAc) and CH_2I groups, respectively, provide good evidence for the formation of such a rearranged isomer.

2.2.2. Fluorinated diallyl non-conjugated dienes

Synthesis of the fluorinated diallyl dienes was achieved in the presence of activated zinc in methanol. The different functional groups in **3,*n*** and **3′,*n*** did not affect the yield of diallyl, which was higher than 75%.

The ^1H NMR spectrum exhibited the presence of a triplet of doublets at δ 2.85 ppm, corresponding to the methylene group adjacent to the fluorinated chain, and characteristic multiplets at δ 5.35 and 5.80 ppm assigned to the ethylenic protons. In the ^{19}F NMR spectrum the expected multiplets were observed at $\delta = -114$, -122 and -124 ppm and are assigned to the difluoromethylene groups (Table 2).

3. Experimental details

3.1. General comments

Diiodoperfluoroalkanes were supplied by the Mihama Corp. (Japan) and were washed with a sodium thiosulphate solution, dried over $MgSO_4$ and distilled. Ethylene was supplied by Air Liquide. Allyl acetate and zinc were provided by Aldrich and required no purification prior to use. Perfluorohexyl iodide and 1-iodo-1,1,2,2,-tetrahydroperfluorooctane were kindly provided by Elf Atochem.

Ethylenations were carried out in 200 or 500 cm^3 Hastelloy Vinci Technologies autoclaves. After introduction of the non-volatile reactants, the vessel was closed, frozen in an acetone/liquid nitrogen mixture and then placed under vacuum for several minutes. The required amount of ethylene was then added.

After reaction, the product were worked-up and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an SE30 column, 1 m×1/8 in (i.d.). The nitrogen pressure at the entrance to the column was maintained at 0.6 bar with a detector and injector temperature of 260 °C and 255 °C, respectively. The temperature programme commenced at 50 °C and attained 250 °C at a heating rate of 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.

The products were characterized by ^1H and ^{19}F NMR spectroscopy, all undertaken at room temperature. The ^{19}F and ^1H NMR spectra were recorded on a Bruker CW-60 apparatus, with $CFCl_3$ and TMS as the respective internal references, or at higher resolution on Bruker AC-200, -250 or WM-360 instruments, using deuterated chloroform as solvent and internal reference. The letters s, d, t, q and m designate singlet, doublet, triplet, quartet and multiplet, respectively.

New compounds were analyzed at the Microanalysis Laboratory (CNRS) of the ENSCM.

3.2. Synthesis of fluorinated α,ω-divinyl dienes

3.2.1. Preparation of α,ω-bis(ethylenated) diiodo derivatives

*(a) 1,6-Diiodo-3,3,4,4-tetrafluorohexane (**1,2**)*

Into a 200 cm^3 Hastelloy autoclave were placed 0.084 mol (30 g) of 1,2-diiodoperfluoroethane, 0.0042 mol (0.8 g) of cuprous iodide and 20 g of acetonitrile. After freezing the vessel, 0.35 mol (10 g) of ethylene was introduced. The autoclave was then allowed to warm up to room temperature and heated up to 160 °C for 14 h. After reaction and cooling in ice, the vessel was degassed and opened. The copper catalyst was worked-up with an acid solution, neutralized with saturated sodium carbonate solution, washed with water and dried over magnesium sulphate. After evaporation of the solvent, the solid residue was recrystallized from hexane to give 25.8 g of white crystals.

$\mathrm{C_6H_8F_4I_2}$ (409.92): m.p. 116 °C (hexane) (lit. value: 112.5–113.5 °C [30]; 115 °C [29]), yield 75%. ^{19}F NMR ($\mathrm{CDCl_3}$) δ: -115.8 (t, $J = 11.4$ Hz, 4F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 2.65 (m, $\mathrm{CH_2CF_2}$, 4H); 3.25 (m, $\mathrm{ICH_2}$, 4H) ppm. Analysis: calc. for $\mathrm{C_6H_8F_4I_2}$: C, 17.58; F, 18.53; H, 1.96%. Found: C, 17.7; F, 18.70; H, 1.8%.

*(b) 1,8-Diiodo-3,3,4,4,5,5,6,6-octafluoro-octane (**1,4**)*

A similar reaction was performed using 0.066 mol (30 g) of 1,4-diiodoperfluorobutane, 0.004 mol (0.8 g) of cuprous iodide, 20 g of acetonitrile and 0.35 mol (10 g) of ethylene. The bis(ethylenated) product (23.6 g of white crystals) was recrystallized from hexane.

$\mathrm{C_8H_8F_8I_2}$ (509.94): m.p. 94 °C (hexane) (lit. value [29]: 93 °C), yield 70%. ^{19}F NMR ($\mathrm{CDCl_3}$) δ: -115.4 (m, $\mathrm{CH_2CF_2C}F_2$, 4F); -123.8 (m, $\mathrm{CF_2CH_2}$, 4F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 2.6 (ttt, $\mathrm{ICH_2C}H_2$, 4H); 3.2 (m, $\mathrm{ICH_2}$, 4H) ppm. ^{13}C NMR ($\mathrm{CDCl_3}$) δ: -11.08 (s, $\mathrm{CH_2I}$, 2C); 36.59 (t, $\mathrm{CF_2CH_2}$, 2C, $J_{\mathrm{CF}} = 22.5$ Hz); 105–125 (t and m, $\mathrm{C_4F_8}$, 4C, $J_{\mathrm{CF}} = 33.1$ Hz) ppm. Analysis: calc. for $\mathrm{C_8H_8F_8I_2}$: C, 18.84; F, 29.80; H, 1.58%. Found: C, 19.1; F, 29.4; H, 1.4%.

*(c) 1,10-Diiodo-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane (**1,6**)*

The same experimental procedure was performed as above, using 0.054 mol (30.0 g) of 1,6-diiodoperfluorohexane, 0.004 mol (0.9 g) of CuI, 20 g of acetonitrile and 0.35 mol (10 g) of ethylene. The brown solid was recrystallized from hexane when 24.6 g of white crystals were obtained.

$\mathrm{C_{10}H_8F_{12}I_2}$ (609.95); m.p. 89 °C (hexane) (lit. value [29]: 90 °C), yield 75%. ^{19}F NMR ($\mathrm{CDCl_3}$) δ: -115.3 (m, $\mathrm{CH_2CF_2C}F_2$, 4F); -122.1 (m, $\mathrm{CH_2C_2F_4C}F_2$, 4F); -123.8 (m, $\mathrm{CH_2CF_2}$, 4F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 2.75 (m, $\mathrm{CH_2CF_2}$, 4H); 3.25 (m, $\mathrm{ICH_2}$, 4H) ppm. Analysis: calc. for $\mathrm{C_{10}H_8F_{12}I_2}$: C, 19.69; F, 37.37; H, 1.32%. Found: C, 19.7; F, 37.6; H, 1.3%.

3.2.2. Preparation of fluorinated α,ω-divinyl non-conjugated dienes

*(a) 3,3,4,4-Tetrafluoro-1,5-hexadiene (**2,2**)*

Into a two-necked round bottom flask equipped with a condenser and a dropping funnel was introduced 0.1 mol (5.6 g) of potassium hydroxide in 20 ml of ethanol. A solution composed of 0.05 mol (20 g) of 1,6-diiodo-3,3,4,4-tetrafluorohexane in 50 ml of ethanol was added dropwise from the dropping funnel with stirring at room temperature over about 45 min. The reaction medium was then heated up to 60 °C for 4 h. After cooling, the whole was diluted with 100 ml of water, extracted with Freon-113, poured into a saturated solution of $\mathrm{Na_2CO_3}$, washed with water, dried over $\mathrm{MgSO_4}$ and distilled. A colourless liquid (4.23 g) was obtained.

$\mathrm{C_6H_6F_4}$ (154.10): b.p. 71–72 °C (lit. value [29,30]: 72 °C), yield 55%. ^{19}F NMR ($\mathrm{CDCl_3}$) δ: -116.5 (d, $J_{\mathrm{HF}} = 14.8$ Hz, 4F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 6.0 (m, $\mathrm{H_2C}$, 4H); 5.8 (m, CH=, 2H) ppm. Analysis: calc. for $\mathrm{C_6H_6F_4}$: C, 46.76; F, 49.31; H, 3.92%. Found: C, 47.0; F, 49.8; H, 3.6%.

*(b) 3,3,4,4,5,5,6,6-Octafluoro-1,7-octadiene (**2,4**)*

Using similar conditions as above, 0.039 mol (20 g) of 1,8-diiodo-3,3,4,4,5,5,6,6-octafluoro-octane diluted in 40 ml of ethanol were added dropwise into 0.076 mol (4.3 g) of potassium hydroxide in 20 ml of ethanol. After work-up, 7.1 g of a colourless liquid were obtained.

$\mathrm{C_8H_6F_8}$ (254.11): b.p. 122 °C (lit. value [29]: 123 °C), yield 72%. ^{19}F NMR ($\mathrm{CDCl_3}$) δ: -115.0 (m, $\mathrm{HCCF_2C}F_2$, 4F); -124.7 (m, $\mathrm{HCCF_2}$, 4F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 6.0 (m, $\mathrm{H_2C}$, 4H); 5.8 (m, HC, 2H) ppm. Analysis: calc. for $\mathrm{C_8H_6F_8}$: C, 37.81; F, 59.81; H, 2.38%. Found: C, 38.1; F, 60.1; H, 2.2%.

*(c) 3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,9-decadiene (**2,6**)*

A similar experiment was performed using 0.072 mol (4.05 g) of potassium hydroxide in 20 ml of ethanol and 0.036 mol (22 g) of **1,3** in 50 ml of ethanol. The same work-up led to 9.6 of a colourless liquid after distillation.

$\mathrm{C_{10}H_6F_{12}}$ (354.13): b.p. 58–61 °C/19 torr (lit. value [29]: 161 °C), yield 75%. ^{19}F NMR ($\mathrm{CDCl_3}$) δ: -114.9 (m, $\mathrm{CHCF_2C}F_2$, 4F); -122.4 (m, $\mathrm{CH{-}C_2F_4C}F_2$, 4F); -124.6 (m, $\mathrm{CH{-}CF_2}$, 4F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 6.0 (m, $\mathrm{H_2C}$, 4H); 5.8 (m, HC, 2H) ppm. ^{13}C NMR ($\mathrm{CDCl_3}$) δ: 105–120 (t and m, $\mathrm{C_6F_{12}}$, 6C, $J_{\mathrm{CF}} = 31.3$ Hz); 124.8 (m, $\mathrm{H_2}C\mathrm{{=}CH}$, 2C); 125.24 (t, $\mathrm{CF_2}C\mathrm{H}$, 2C, $J_{\mathrm{CF}} = 20.4$ Hz) ppm. Analysis: calc. for $\mathrm{C_{10}H_6F_{12}}$: C, 33.91; F, 64.37; H, 1.71%. Found: C, 34.1; F, 64.9; H, 1.5%.

3.3. Preparation of fluorinated α,ω-diallyl dienes

3.3.1. Synthesis of fluorinated iodoacetate derivatives

(a) Addition of 1,4-diiodoperfluorobutane to allyl acetate

A 250 ml three-necked round-bottom flask equipped with a condenser and a thermometer was charged with 0.142 mol (64 g) of 1,4-diiodoperfluorobutane, 0.568 mol (56.8 g) of allyl acetate and 0.00284 mol (0.7 g) of dibenzoyl peroxide. The reaction mixture was stirred at 95 °C and the temperature of the solution carefully checked. After 10–15 min, the mixture became clear and an exotherm up to 150 °C occurred leading to an instantaneous change of colour to violet–brown. Then, 0.00284 mol of dibenzoyl peroxide was added twice, every 30 min. The unreacted allyl acetate was distilled off and the monoadduct $\mathrm{IC_4F_8CH_2CHICH_2OCOCH_3}$ remaining distilled under reduced pressure. The residue in the distillation flask was the 2:1 adduct (**3,4**) (66 g) with 90% purity. The yield was 71%.

A similar reaction may be performed in the presence of butyronitrile as solvent, the initiator being added in small fractions into the solution after the temperature reaches 95 °C. ^{19}F NMR ($\mathrm{CDCl_3}$) δ: -114.8 (m, $\mathrm{CH_2CF_2C}F_2$, 4F); -123.6 (m, $\mathrm{CH_2CF_2}$, 4F) ppm. ^{1}H NMR ($\mathrm{CDCl_3}$) δ: 2.0 (s, $\mathrm{CH_3CO_2}$, 6H); 2.45 (m, $\mathrm{CHIC}H_2\mathrm{C_4F_8}$, 4H); 4.3 (m, CHI and $\mathrm{CH_2OAc}$, 6H) ppm. The presence of the rearranged product is demonstrated in the ^{1}H NMR spectrum by the existence of both a complex system and an AB system centred at δ 5.2

and 3.35 ppm, assigned to the CHOAc and CH_2I groups, respectively.

(b) Synthesis of 1,12-diacetoxy-2,11-diiodo-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluorododecane (3,6)

The fluorinated bis(iodoacetate) was formed by the addition of 1,6-perfluorohexane to allyl acetate under similar conditions to those above using 0.0361 mol (20 g) of $IC_6F_{12}I$, 0.1445 mol (14.45 g) of allyl acetate and three amounts consisting of 0.00074 mol added separately (3×0.18 g) of dibenzoyl peroxide. A dark red product (19.85 g) was obtained after removal of excess allyl acetate and distillation of the 1:1 monoadduct. The yield was 73%. ^{19}F NMR ($CDCl_3$) δ: -113.5 (m, $CHCF_2CF_2$, 4F); -121.2 (m, $CH_2C_2F_4CF_2$, 4F); -124.1 (m, CH_2CF_2, 4F) ppm. ^1H NMR ($CDCl_3$) δ: 2.0 (s, CH_3CO_2); 2.5 (m, $HClCH_2C_6F_{12}$); 2.7 (m, $R_FCH_2CH(OAc)$; 3.3 (AB system CH_2I); 4.3 (m, CHI and CH_2OAc); 5.1 (m, CHOAc) ppm.

3.3.2. Synthesis of fluorinated diallyl non-conjugated dienes

(a) 4,4,5,5,6,6,7,7-Octafluoro-1,9-decadiene (4,4)

A 250 ml flask equipped with a condenser, magnetic stirrer and dropping funnel was charged with 0.22 mol of activated zinc powder (14.3 g) and 100 ml of methanol. The reaction mixture was then heated to boiling and 0.101 mol (66 g) of the 2:1 adduct (**3,2**) added dropwise. After such addition, the reaction mixture was maintained at reflux for 30 min. Unreacted zinc powder was removed by filtration and methanol was removed by distillation using a 30 cm Vigreaux column. The residue was washed with 800 ml of 10% HCl and the organic layer separated, dried with magnesium sulphate and distilled under reduced pressure. 4,4,5,5,6,6,7,7-Octafluoro-1,9-decadiene (17.96 g) was obtained as a colourless liquid.

$C_{10}H_{10}F_8$ (282.16): b.p. 61–65 °C/21 Torr, yield 63%. ^{19}F NMR ($CDCl_3$) δ: -113.8 (m, $CF_2CF_2CH_2$, 4F); -123.8 (m, CF_2CH_2, 4F) ppm. ^1H NMR ($CDCl_3$) δ: 2.7 (td, $J_1=6.8$ Hz, $J_2=19.4$ Hz, CF_2CH_2, 4H); 5.3 (m, $H_2C{=}$, 4H); 5.8 (m, $CH{=}$, 2H) ppm. ^{13}C NMR ($CDCl_3$) δ: 35.72 (t, CH_2CF_2, $J_{CF}=22.9$ Hz, 2C); 105–118 (t and m, C_4F_8, $J_{CF}=33.2$ Hz, 4C); 121.65 (s, $H_2C{=}CH$, 2C); 125.37 (t, $H_2C{=}CH$, $J_{CF}=4.1$ Hz, 2C) ppm. Analysis: calc. for $C_{10}H_{10}F_8$: C, 42.56; F, 53.86; H, 3.57%; Found: C, 42.9; F, 54.1; H, 3.4%.

(b) 4,4,5,5,6,6,7,7,8,8,9,9-Dodecafluoro-1,11-dodecadiene (4,6)

A similar experiment as above was performed using 0.020 mol (15.1 g) of bis(iodoacetate) **3,3**, 0.043 mol (2.38 g) of zinc in 80 ml of methanol. A colourless liquid (5.20 g) was distilled from the final reaction mixture.

$C_{12}H_{10}F_{12}$ (382.18): b.p. 74–77 °C/19 Torr, yield 68%. ^{19}F NMR ($CDCl_3$) δ: -114.9 (m, $CF_2CF_2CH_2$, 4F); -122.4 (m, $CH_2CF_2CF_2CF_2$, 4F); -124.6 (m, CH_2CF_2, 4F) ppm. ^1H NMR ($CDCl_3$) δ: 2.85 (td, $J_1=6.6$ Hz, $J_2=18.4$ Hz, CF_2CH_2, 4H); 5.35 (m, $CH_2{=}$, 4H); 5.80 (m, $HC{=}$, 2H) ppm. Analysis: calc. for $C_{12}H_{10}F_{12}$: C, 37.71; F, 59.65; H, 2.63%. Found: C, 37.9; F, 60.0; H, 2.4%.

4. Conclusions

The synthesis of new fluorinated divinyl or diallyl non-conjugated dienes has been successfully achieved from commercially available α,ω-diiodoperfluoroalkanes. Both preparations were conducted simply in two step-reactions. For the synthesis of vinyl olefins, ethylenation was mainly performed by redox catalysis whereas the second step from ethanolic potassium hydroxide led to the expected fluorinated dienes in the best yield.

In the preparation of the allyl monomers, radical addition of α,ω-diiodoperfluoroalkanes to an excess of allyl acetate produced the corresponding diacetates in high yield but a similar reaction was unsuccessful from 1,2-diiodoperfluoroethane. Such diacetates may undergo thermal rearrangement above 160 °C but this did not affect obtaining diallyl compounds in the presence of activated zinc. Interestingly, under such circumstances the diallyl compounds were obtained in greater yield. These non-conjugated dienes are valuable intermediates for further fluorinated telechelic compounds such as diepoxides, diols or disilanes which are under investigation.

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