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Synthesis and polymerization of fluorinated monomers bearing a reactive lateral group. Part 3[1] – synthesis of trifluorovinyl hydroxy and acetoxy monomers

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Abstract

The preparation of two functional perfluorovinyl monomers useful as comonomers in the copolymerization of commercially available monomers is presented. First, 1-iodo-1,2-dichloro-1,2,2-trifluoro ethane (**1**) was added to allyl alcohol under several initiating conditions and it was found that AIBN is the best initiator. Then, the selective reduction of the iodine atom in the presence of tributyl stannane gave $ClCF_2CFClC_3H_6OH$ quantitatively and its dechlorination was optimized leading to $F_2C{=}CFC_3H_6OH$ in 50% overall yield from (**1**). This monomer was quantitatively acetylated by acetyl chloride. All these products and intermediates were characterized by ^1H, ^{19}F and ^{13}C-NMR spectroscopy, and simulated spectra were in very good agreement with those observed experimentally.

Keywords: Perfluorovinyl monomers; Functional monomers; 1-iodo-1,2-dichloro-1,2,2-trifluoro ethane; Fluoroalcohol; Radical addition; Dechlorination

1. Introduction

Perfluorovinyl functional monomers have already been shown to be of great interest in copolymerization with fluorinated or non fluorinated commercially available comonomers [1–5]. The functional group which is subsequently introduced in a lateral position about the backbone of the copolymer brings specific and complementary properties: adhesion for a carboxylic function [6], solubility from a cyclohexyl group [7], curability from hydroxyl or epoxide functions [8–11] or surface properties from a perfluorinated group [12]. We have recently shown that the preparation of new functional perfluorovinyl monomers could be simply performed by a photochemical addition of functional mercaptans (e.g., thioglycolic acid, 2-mercaptoethanol, or thiol acetic acid) to 1,1,2-trifluoro-1,4-pentadiene [13,14]. To synthesize another series of trifluorovinyl hydroxy or acetoxy monomers, another strategy was planned, starting from the radical addition of 1-iodo-1,2,2-trifluoro-1,2-dichloroethane to either allyl acetate or allyl alcohol. Such an iodinated halogenated transfer agent was prepared by radical addition of iodine monochloride to chlorotrifluoroethylene [15–20]. In contrast to the series of monomers previously described [13,14], a further objective of this paper was the obtaining of a new acetoxy-containing fluoro-monomer.

2. Experimental

2.1. General comments

Chlorotrifluoroethylene was kindly supplied by Solvay. Iodine monochloride, allyl alcohol, tributyl stannane, triphenyl phosphine, isopropyl amine, cuprous chloride, copper and zinc were provided by Aldrich and did not require any purification prior to use. Dibenzoyl peroxide and AIBN were supplied by Akzo and Merck, respectively.

$Cl(C_2F_3Cl)I$ was prepared by a batch photochemical addition of iodine monochloride to chlorotrifluoroethylene [20].

After reaction, the products were worked-up with an alkaline sodium bisulfite solution and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an SE-30 column, 3 m×1/8 in (i.d.). The nitrogen pressure at the entrance to the column was

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[1]Part 2, see [21].

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maintained at 0.6 bar and the detector and injector temperatures were 260°C and 255°C, respectively. The temperature program started from 50°C and reached 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 ^{1}H, ^{13}C and ^{19}F-NMR spectroscopy at room temperature. The ^{19}F, ^{13}C and ^{1}H-NMR spectra were recorded on a Bruker AC-200, -250 or WM-360 instruments, using deuterated chloroform and $CFCl_3$ as solvent and internal reference, respectively. The letters s, d, t, qi and m designate singlet, doublet, triplet quintet and multiplet, respectively. NMR simulation was performed with gNMR software [37].

2.2. Radical addition of 1-iodo-1,2-dichlorotrifluoroethane to allyl alcohol

2.2.1. Reaction at atmospheric pressure

In a three necked round bottom flask equipped with a condenser and a thermometer was stirred a mixture of 171.1 g (0.617 mol) of $Cl(C_2F_3Cl)I$ and 98.3 g (1.69 mol) of allyl alcohol. The mixture was heated up to 80°C and 2.30 g (0.014 mol) of AIBN was added every hour. The reaction was monitored by GC until the quasi total consumption of the iodinated reactant. Then, the iodohydrin was distilled. 167.5 g (0.497 mol) of a yellow orange liquid was obtained. Yield =81%. Bp=64–66°C/0.2 mm Hg.

2-iodo-4,5,5-trifluoro-4,5-dichloropentanol (A): ^{1}H-NMR ($CDCl_3$) δ: 2.5 (broad s, shifted with dilution, OH, 1H); 2.6–3.3 (m, CH_2CFCl, 2H); 3.8 (m, shifted to 4.7 ppm in the presence of Cl_3CNCO, CH_2OH, 2H); 4.5 (complex system and qi, $^{3}J_{HH}$=6.2 Hz, CHI, 1H).

^{19}F-NMR ($CDCl_3$) δ: −67.9 (AB part of ABX system; Fa at −67.5, $^{2}J_{FaFb}$=169.3 Hz, $^{3}J_{FaFc}$=9.2 Hz; Fb at −68.2, $^{2}J_{FbFa}$=169.3 Hz, $^{3}J_{FbFc}$=4.1 Hz, $ClCF_2$, 2F); X part at −118.65 (dq, $^{3}J_{FcHa}$=35.7 Hz, $^{3}J_{FcHb}$ = $^{3}J_{FcFa}$=9.1 Hz) and −121.25 (m, $^{3}J_{FcFa}$=9.7); CFCl, 1F.

^{19}F-NMR ($CDCl_3$, irradiation of the protons of CH_aH_b adjacent to CFCl group) δ: −67.9 (as above); −118.65(t, $^{3}J_{FcFa}$=9.1 Hz) and −121.25 (t, $^{3}J_{FcFa}$=9.7 Hz).

^{13}C-NMR ($CDCl_3$) δ: 22.3 (s, CHI); 42.2 (t, $^{2}J_{CF}$= 22.1 Hz, $CFClCH_2$); 68.3 (s, CH_2OH); 110.3 (dt, $^{1}J_{CF}$= 258.9 Hz, $^{2}J_{CF}$=31.8 Hz, $^{2}J_{CF'}$=31.6 Hz, CFCl); 125.1 (td, $^{1}J_{CF}$=299.1 Hz, $^{2}J_{CF}$=32.9 Hz).

2.2.2. Reaction performed in Carius tube

A Carius tube saturated with nitrogen was filled with 40.0 g (0.14 mol) of $Cl(C_2F_3Cl)I$, 17.1 g (0.28 mol) of allyl alcohol and 0.92 g (0.014 mol) of powdered copper. The tube was degassed by 5 thaw-freeze cycles and then sealed. It was placed in a shaking oven and heated at 120°C for 7 h. After reaction and cooling to room temperature, the tube was frozen in liquid nitrogen and then opened. After the gross warmed up to room temperature, it was diluted in diethyl ether and the copper was filtered off.

After an acidic treatment, neutralization and evaporation of the solvent, the gross was analyzed by GC. The yield was estimated to be 62%.

2.3. Reduction of the above iodhydrin (A) to A,1

80.0 g (0.27 mol) of tributyl stannane were dropwise added under stirring to 88.9 g (0.26 mol) of iodohydrin **A** placed in an ampoule cooled in an ice bath, saturated of argon and equipped with a septum. The addition took 30 min, the ice bath being progressively lowered. Then, the mixture was stirred for 3 additional hours at room temperature. Afterwards, the reduced derivative **A,1** was distilled under reduced pressure. 47.2 g (0.225 mol) of a clear yellow liquid was obtained (yield=86.5%). Bp= 80°C–82°C/23 mm Hg.

4,5-dichloro-4,5,5-trifluoro pentanol (**A,1**): ^{1}H-NMR ($CDCl_3$) δ:1.90 (m, BB′ part of AA′BB′ system, $C\underline{H}_2CH_2OH$, 2H); 2.15 (broad signal, shifted with dilution or to 7–9 ppm with Cl_3CNCO, OH, 1H); 2.40 (m, AA′ part, $CFClCH_2$, 2H), 3.72 (t, $^{3}J_{HH}$=6.4 Hz, $C\underline{H}_2OH$ shifted to 4.6 ppm in the presence of Cl_3CNCO, 2H).

^{1}H-NMR (acetone d_6) δ: 1.85 (m, $C\underline{H}_2CH_2OH$, 2H); 2.45 (m, $CFClCH_2$, 2H); 3.65 (t, $^{3}J_{HH}$=6.0 Hz, CH_2OH, 1 ppm low field shifted with Cl_3CNCO, 2H); 2.30 (broad signal, shifted with dilution, OH, 1H).

^{19}F-NMR ($CDCl_3$) δ: −67.4 (AB part of an ABX system); −120.6 (ddt, $^{3}J_{FcFa}$=9.4 Hz, $^{3}J_{FcFb}$=9.7 Hz, $^{3}J_{FcH}$=6.6 Hz, CFCl).

^{19}F-NMR (acetone d_6) δ: −64.2 (AB part, same coupling constants as above); −117.2 (same coupling constants as above).

^{19}F-NMR ($CDCl_3$, with irradiation of CH_2 of $CFClCH_2$ group) δ: −67.3 (AB system, $^{2}J_{FaFb}$=169.3 Hz, $^{3}J_{FaFc}$ = $^{3}J_{FbFc}$=9.7 Hz, $ClCF_2$); −120.7 (dd, $^{3}J_{FcFa}$=9.4 Hz, $^{3}J_{FcFb}$=9.7 Hz, CFCl).

^{13}C – NMR ($CDCl_3$) δ: 25.6 (s, $C\underline{H}_2CH_2OH$); 33.0 (d, $^{2}J_{CF}$=21.4 Hz, $CFCl\underline{C}H_2$); 61.0 (s, CH_2OH); 111.3 (dt, $^{1}J_{CF}$=255.5 Hz, $^{2}J_{CF}$=31.5 Hz,CFCl); 125.8 (td, $^{1}J_{CF}$=298.8 Hz, $^{2}J_{CF}$=33.4 Hz, $ClCF_2$).

2.4. Dechlorination of A,1

In a three necked round bottom flask swept by an argon flow and equipped with a condenser was introduced via a septum 100 ml of dry DMF. Under vigourous stirring, 46.8 g (0.72 mol) of zinc activated by 5 cm^3 of acetic acid and 5 cm^3 of acetic anhydride were placed in the flask and then the slurry was heated up to 90°C. 50.0 g (0.237 mol) of halogenated alcohol **A,1** was then added dropwise and the temperature was maintained at 90°C. For 4 h after complete addition the reaction was monitored by GC, the respective retention time for the trifluorovinyl and chlorinated alcohols being, 2.75 and 5.04 min. After cooling, the excess of zinc was filtered off and the gross was treated with HCl 10% and the fluorinated part extracted with diethyl ether. After

distillation of this solvent, 4,5,5-trifluoro-4-ene pentanol (**A,2**) was rectified. 23.3 g (0.166 mol) of colorless liquid were obtained. Bp=53°C–55°C/24 mm Hg (literature value [10]: 95°C/155 mm Hg). Yield=70%.

A similar procedure as given above was made for the other experiments (Table 2) changing the initial [zinc]/[**A,1**] molar ratio, the temperature or the solvent. For experiment 2 the amount required for $ZnCl_2$ was 5.0 g (0.04 mol) whereas for experiments 6 and 8 the initial [Zn]/[oxalic acid] and [Zn]/[propionic acid] molar ratios were 8:1 and 1:1, respectively. The chemical shifts and the coupling constants from corresponding ^1H, ^{19}F and ^{13}C-NMR spectra are listed in Table 3.

Simulated ^1H-NMR spectrum of CH_2 adjacent to the trifluorovinyl group: 2.35 ppm, dddt, $^3J_{HFc}$=22.3 Hz, $^4J_{HFa}$=2.8 Hz, $^4J_{HFb}$=4.2 Hz, $^3J_{HH}$=7.2 Hz.

2.5. *Acetylation of* A,2

In a two necked round bottom flask equipped with a condenser (linked to a trap containing potassium carbonate), containing 50.1 g (0.36 mol) of trifluorovinyl alcohol **A,2**, and cooled in an ice bath were dropwise added into 31.7 g (0.41 mol) of acetyl chloride. The reactivity of both starting materials was checked by HCl bubbling in the trap. After complete addition, the reaction was left stirring at room temperature until no more HCl bubbles appeared (ca. 4 h). After distillation, 59.3 g (0.326 mol) of 4,5,5-trifluoro-4-ene pentyl acetate (**A,3**) (colorless liquid) were obtained. Bp=56°C–58°C/21 mm Hg. (Yield=91%).

^1H-NMR ($CDCl_3$) δ: 1.84 (qi, $^3J_{HH}$=6.9 Hz, $C\underline{H}_2CH_2OAc$, 2H); 2.03 (s, $COCH_3$, 3H); 2.30 (dddt, $CFCH_2$, $^3J_{HF}$=21.9 Hz, $^3J_{HH}$=6.9 Hz, $^4J_{HF}$=3.8 Hz, $^4J_{HF}$=2.5 Hz,2H); 4.06 (t, $^3J_{HH}$=6.9 Hz, CH_2OAc, 2H).

^{19}F-NMR ($CDCl_3$) δ: −105.5 (ddt, $^2J_{FF}$=89.0 Hz, $^3J_{FF}$=31.9 Hz, $^4J_{FaH}$=2.5 Hz, F_a); −125.0 (ddt, $^2J_{FF}$= 89.0 Hz, $^3J_{FF}$=114.2 Hz, $^4J_{FH}$=3.8 Hz, F_b); −175.3(ddt, $^3J_{FF}$=31.9 Hz, $^3J_{FF}$ =114.2 Hz, $^3J_{FH}$=20.9 Hz, F_c).

^{13}C-NMR ($CDCl_3$) δ: 19.93 (s, CH_3); 21.89 (dd, $^2J_{CF}$= 22.3 Hz, $^3J_{CF}$=2.5 Hz, $CF\underline{C}H_2$); 24.15 (ddd, $^3J_{CF}$= 2.8 Hz, $^4J_{CF}$=2.7 Hz; $^4J_{CF}$=1.0 Hz,$CFCH_2\underline{C}H_2$); 63.02 (s, CH_2OH); 127.5 (ddt, $^1J_{CF}$=234.4 Hz, $^2J_{CF}$=53.4 Hz, $^2J_{CF}$= 15.7 Hz, =CF); 153.0 (ddd, $^1J_{CF}$=285.8 Hz, $^1J_{CF}$= 272.4 Hz, $^2J_{CF}$=47.0 Hz,$=CF_2$); 170.38 (s, C=O).

3. Results and discussion

Perfluorovinyl functional monomers comprising of hydroxy or acetoxy end-groups were synthesized from $Cl(C_2F_3Cl)CH_2CHICH_2OH$ generated by the radical addition of $Cl(C_2F_3Cl)I$ to allyl alcohol. The synthesis of $Cl(C_2F_3Cl)I$ was recently optimized by photochemical addition of iodine monochloride to chlorotrifluoroethylene (CTFE) in batch [20]. Previous experiments showed that the addition of $Cl(C_2F_3Cl)I$ to allyl acetate initiated by dibenzoyl peroxide at 90°C led to the expected $Cl(C_2F_3Cl)CH_2CHICH_2OAc$ which underwent a thermal five-member-rearrangement yielding up to 30% $Cl(C_2F_3Cl)CH_2CH(OAc)CH_2I$ [21]. In order to synthesize trifluorovinyl monomers containing a functional group on a primary carbon atom, two alternatives have been proposed to avoid the thermal rearrangement: either the iodinated compound reacts to allyl acetate at a temperature below 90°C or it reacts to allyl alcohol. The first topic will be described in a forthcoming paper [22] whereas the second strategy is detailed below. Scheme 1 represents the routes leading to the obtaining of ω-hydroxy and ω-acetoxy trifluorovinyl monomers.

The syntheses of 4,5,5-trifluoro-4-ene pentanol (**A,2**) and 4,5,5-trifluoro-4-ene pentyl acetate (**A,3**) were performed in three or four steps, respectively, from 1-iodo-1,2,2-trifluoro-1,2-dichloroethane (Scheme 1). First, it required the radical addition of this iodinated transfer agent to allyl alcohol leading to iodohydrin **A** that underwent a reduction to yield **A,1**. Dechlorination of this latter intermediate led to trifluorovinyl alcohol **A,2** that was acetylated into $F_2C{=}CFC_3H_6OCOCH_3$ (**A,3**). Each step is described hereafter.

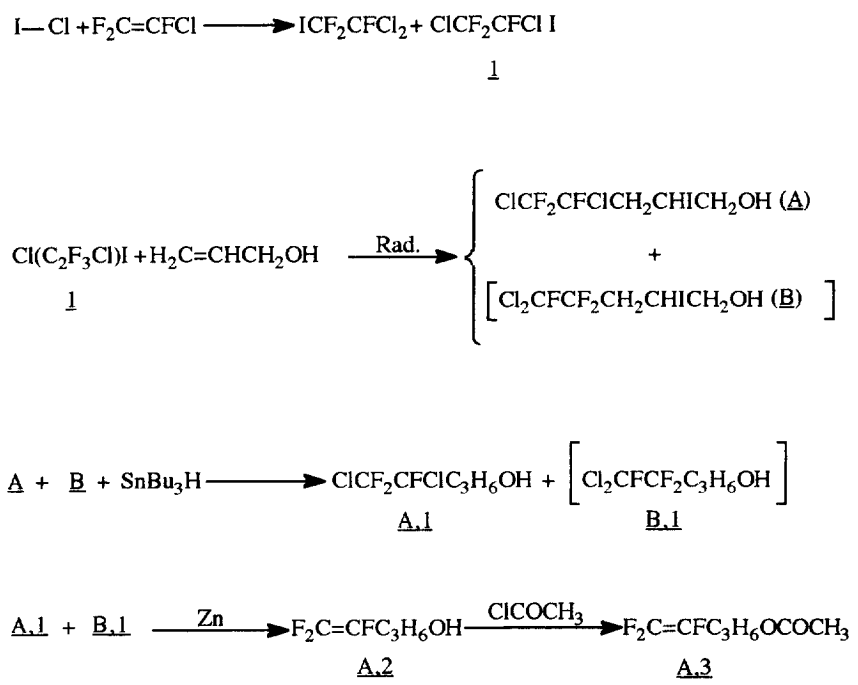
3.1. *Radical addition of 1-iodo-1,2,2-trifluoro-1,2-dichloroethane to allyl alcohol*

The reaction, yielding iodohydrin **A** was induced by several initiators or catalysts. Table 1 summarizes the experimental conditions and the yields of the radical addition of $Cl(C_2F_3Cl)I$ to allyl alcohol. Several initiating systems were chosen as mentioned in the literature starting from perfluoroalkyl iodides [23–30], the radical initiators being used at a temperature for which the half-life is about 1 h. Copper metal or copper salt were used at a temperature higher than 120°C. Copper powder was shown to be efficient for catalyzing the addition of perfluoroalkyl iodide (R_FI) to allyl alcohol [23] but the yield was not as high as

Table 1
Conditions of reactions and yields of the addition of $C_2F_3Cl_2I$ to allyl alcohol (DBP means dibenzoyl peroxide, R_0 and C_0 stand for initial $[C_2F_3Cl_2I]_0$/[allyl alcohol]$_0$ and [initiator]$_0$/[allyl alcohol]$_0$ molar ratios, respectively

Initiating system	R_0	C_0	T (°C)	t (h)	Yield (%)
Cu (powder)	1.0	0.10	120	7	62
$CuCl/iPrNH_2$	1.0	0.05/0.10	130	3	46
PPh_3	0.5	0.10	85	8	39
PPh_3/CH_3CN	0.5	0.10	85	16	50
DBP	1.0	0.07	95	2	22[a]
DBP	1.0	0.03	95	18	31
DBP	0.8	0.05	96	15	38[a]
AIBN	0.9	0.03	80	8	63[a]
AIBN	1.0	0.04	90	14	70
AIBN	0.4	0.12[b]	80	10	81[a]

[a] Distilled product.
[b] 0.012 added every hour.



Scheme 1. Synthesis of 1,1,2-trifluoropentene-5-ol and 4,5,5-trifluoro-4-ene pentylacetate (the products in brackets have not been produced experimentally).

expected (62% only). Triphenylphosphine in the presence of acetonitrile was described by Huang and Zhang [24] leading to high yield of monoadduct from the addition of R_FI to unsaturated compounds but the maximum yield reached was 50%. In contrast to the addition of $Cl(C_2F_3Cl)I$ to allyl acetate which was quick and quantitative in the presence of dibenzoyl peroxide (DBP) [21], that to allyl alcohol under the same conditions only led to a highest yield of 38%, with no rearranged isomer.

The best initiator for such a reaction was azobisisobutyronitrile (AIBN), especially when this azo compound was continuously added during the reaction. The scale up of this reaction detailed in the experiment gave a yield of 81% after distillation of **A**. As indicated above, no exotherm occurred and no rearranged product was observed. Considering the efficiency of the initiators/catalysts, the following decreasing order is as follows:

$$\underset{\text{continuous addition}}{\text{AIBN}} > \underset{\text{batch}}{\text{AIBN}} = \underset{\text{powder}}{\text{Cu}} > PPh_3 > CuCl/iPrNH_2 > DBP$$

Both isomers were characterized by ^1H and ^{19}F-NMR. The ^1H-NMR spectrum of **A** exhibits two complex signals in the 2.6–3.3 ppm range and at 3.8 ppm, and a doublet of multiplets centered at 4.5 ppm assigned to the methylene groups adjacent to the CFCl group (the signal is more complex than that of R_FCH_2) and to the hydroxy function (AB part of ABX system), and the methyne group. Interestingly, adding one drop of Cl_3CNCO in the NMR tube shifted the signal at 3.8 ppm assigned to $C\underline{H}_2OH$ to low field to 4.7 ppm. Such a technique was also used successfully to characterize hydroxymethyl end-groups of $HOCH_2(C_2H_2F_2)_n$-H telomers [31]. The complex NMR spectra can be explained by the mixture of two diastereoisomers in $ClCF_2C{*}FClCH_2C{*}HICH_2OH$ because of the presence of two asymmetric carbon atoms. Indeed, such a mixture can be observed from the gas chromatrogram of this product showing two close peaks at 7.9 and 8.2 min. Actually, the CHI group of one diastereoisomer is represented by a quintet ($^3J_{HH}$=6.8 Hz) whereas the same group of the other diastereoisomer is more complex. According to the integrations of these signals, the amount of the diastereoisomers is 46.5/53.5. In addition, a broad signal centered at 2.5 ppm, low field shifted to 7–9 ppm in the presence of CCl_3NCO, corresponds to the hydroxy end-group.

The ^{19}F-NMR spectrum shows the AB part of an ABX system ($^2J_{FaFb}$=169.3 Hz, $^3J_{FaFc}$=9.2 Hz and $^3J_{FbFc}$= 4.1 Hz) centered at −67.9 ppm assigned to a $ClCF_2$ end-group and two signals centered at −118.65 and −121.25 ppm corresponding to CFCl group (X part) of both diastereoisomers. The former is representated by a doublet ($^3J_{FcH}$=35.7 Hz, Fc and H being in antiposition) of quartets ($^3J_{FH}$ = $^3J_{FcFa}$=9.1 Hz) whereas the second one is more complex. Such an interpretation was clear when the protons H_a and H_b adjacent to CFCl group were irradiated: the ^{19}F-NMR spectrum showed two triplets centered at −118.65 (J=9.15 Hz) and −121.25 ppm (J=9.66 Hz), and obviously the unmodified AB part at −67.9 ppm.

As from the integration in the ^1H-NMR spectrum, the ratio of these peaks is about 46.0/54.0.

The ^{13}C-NMR spectrum also confirms the structure of iodinated alcohol **A** by the high field signal at 22.3 ppm assigned to a CHI group, by the CH_2OH end-group represented by a singlet at 68.3 ppm and by the methylene group

adjacent to the chlorofluorinated group showing a triplet ($^2J_{CF}$=22 Hz) centered at 42.2 ppm. More interesting are the signals assigned to the carbon atoms bearing the fluorine atoms. This spectrum exhibits two distinct groups of signals, centered at 110 and 125 ppm assigned to the CFCl and CF_2 groups, respectively. The former signal is a doublet ($^1J_{CF}$=259 Hz) of triplets ($^2J_{CF}$=31.8 Hz) of triplets ($^2J_{CF'}$=31.6 Hz) assigned to the presence of both diastereoisomers and for the same reason, the latter shows two triplets ($^1J_{CF}$=299 Hz) of doublets ($^2J_{CF}$=32.9 Hz).

In contrast to the formation of $Cl_2CFCF_2CH_2CHI$-CH_2OAc resulting from the radical addition of Cl_2CFCF_2I to allyl acetate [21], no evidence for $Cl_2CFCF_2CH_2CHI$-CH_2OH (**B**) in Scheme 1 was shown either in the ^{19}F-NMR spectra (absence of signals at −110 and −74 ppm assigned to CF_2 and $CFCl_2$ groups, respectively [21]) or in the ^{13}C-NMR spectrum. This may result from the greater reactivity of allyl acetate over allyl alcohol confirming the previous work of Boutevin et al., and Améduri et al. [32,33] and the less efficient activity of radical initiators to induce addition of perfluoroalkyl iodides to allyl alcohol [23].

3.2. Synthesis of 4,5,5-trifluoro-4,5-dichloropentanol (A,1)

2-iodo-4,5,5-trifluoro-4,5-dichloropentanol (**A**) was reduced into **A,1** in the presence of a stoichiometric amount of tributyl stannane without solvent. Such a tin compound has already shown its high efficiency in the selective substitution of iodine to hydrogen [34].

The reaction was monitored by gas chromatography indicating one peak only, having a shorter retention time (5.04 mn) than that of the iodinated precursor (7.9 and 8.2 mn). This showed that the conversion of **A** was quantitative after 1 h, and was confirmed by NMR spectroscopy. After distillation, the alcohol was obtained in a yield (87%) higher than that observed by Ohmori et al. [10] in the presence of $LiAlH_4$ (65%).

The structure of **A,1** was confirmed by ^{1}H-NMR by the high field shift of the doublet of multiplets assigned to the CHI group (δ=4.5 ppm) to a complex BB′ part of an AA′BB′ system centered at 1.90 ppm. The AA′ part appeared at 2.40 ppm by comparing the spectrum to that of $Cl_3C(CH_2)_3OCOCH_3$ synthesized previously [33], and assigned as follows:

$$\underset{}{Cl_3C\text{-}}\underset{2.70}{CH_2}\text{-}\underset{2.05}{CH_2}\text{-}\underset{4.10}{CH_2}\text{-}OAc$$

$$\underset{}{ClCF_2CFCl\text{-}}\underset{2.40}{CH_2}\text{-}\underset{1.90}{CH_2}\text{-}\underset{3.72}{CH_2}\text{-}OH$$

Its ^{19}F-NMR spectrum was more simple than that of the iodinated precursor especially the signal centered at −120.6 ppm assigned to CFCl and giving a unique signal: a doublet ($^3J_{FcFa}$=9.4 Hz) of doublets ($^3J_{FcFb}$=9.7 Hz) of triplets ($^3J_{FcH}$=6.6 Hz). After irradiation of the methylene group adjacent to the CFCl, this signal became a doublet ($^3J_{FcFa}$=9.4 Hz) of doublets ($^3J_{FcFb}$=9.7 Hz) whereas that assigned to $ClCF_2$ showed an AB system at −67.3 ppm: $^2J_{FaFb}$=169.1 Hz and identical coupling constants: $^3J_{FaFc}$ = $^3J_{FbFc}$=9.7 Hz.

Interestingly, recording the spectrum in deuterated acetone led to a low field shift of both signals: −117.2 (−120.6 ppm in $CDCl_3$) and −64.2 (−67.4 ppm in $CDCl_3$).

The structure of the reduced compound was confirmed by ^{13}C-NMR. Its spectrum exhibits a triplet ($^1J_{CF}$=298.8 Hz) of doublets ($^2J_{CF}$=33.4 Hz) and a doublet ($^1J_{CF}$=255.5 Hz) of triplets ($^2J_{CF}$=31.5 Hz) centered at 125.8 and 111.3 ppm, assigned to $ClCF_2$ and CFCl groups, respectively. The CH_2 group adjacent to the latter group was represented by a doublet ($^2J_{CF}$=21.4 Hz) centered at 33.0 ppm whereas the methylene group α and β to the hydroxy function gave two singlets at 61.0 and 25.6 ppm, respectively.

The synthesis of halogenated alcohol **A,1** was thus performed selectively, with a quantitative conversion of the iodohydrin **A** at 2°C–25°C only, and without any use of AIBN heated at 60°C as noted from the literature [35,36].

3.3. Synthesis of 4,5,5-trifluoro-4-pentene-1-ol (A,2)

The dechlorination of **A,1** into **A,2** was performed in the presence of zinc in various solvents and the results are listed in Table 2. Drastic activation of zinc was necessary to get an acceptable yield but the nature of the solvent also played a great part. All reactants and the solvent require to be

Table 2
Experimental conditions and yields of the dechlorination of **A,1** into 4,5,5-trifluoro-4-ene pentanol (**A,2**)

Run	$[Zn]_0/[R_{F,Cl}C_3H_6OH]_0$	T (°C)	t (h)	Solvent	Yield (%)
1	2.0	60	15	Methanol	43
2	2.0 (+$ZnCl_2$)	70	72	Methanol	38
3	2.0 (+HCl)	64	24	Methanol	47
4	2.0 (+HCl added continously)	60	21	Methanol	42
5	4.0 (id.)	65	30	Methanol	38
6	3.5 (+oxalic acid)	35	100	Anhydrous Et_2O	0
7	3.0	80	24	Ethanol	44
8	2.0 (+propionic acid)	100	24	Dioxane	29
9	3.0	120	24	Dioxane	46
10	2.0	90	4	Anhydrous DMF	65
11	3.0	90	4	Anhydrous DMF	70

Table 3
^{1}H, ^{19}F and ^{13}C-NMR characteristics of 4,5,5-trifluoro-4-ene pentanol from Ohmori et al. [10] (ref. ^{19}F-NMR: CF_3CO_2H) and from the present work (ref. ^{19}F-NMR: $CFCl_3$)

Fa\ 1 2 /Fc C=C 3 4 5 Fb / CH_2—CH_2—CH_2OH	Fa	Fb	C^1	C^2	Fc	C^3
Ohmori et al. [10]	+29.9, ddt $^2J_{FaFb}$=92 $^3J_{FaFc}$=33 $^4J_{FaH}$=2	+48.5, ddt $^2J_{FbFa}$=92 $^3J_{FbFc}$=116 $^4J_{FbH}$=4	n.g.	n.g.	+97.5, ddt $^3J_{FcFa}$=33 $^3J_{FcFb}$=116 $^3J_{FcH}$=22	n.g.
This work	−106.05, ddt $^2J_{FaFb}$=88.2 $^3J_{FaFc}$=31.8 $^4J_{FaH}$=2.4	−125.23, ddt $^2J_{FbFa}$=88.2 $^3J_{FbFc}$=113.3 $^4J_{FbH}$=4.0	153.24, ddd $^1J_{C1F}$=272.3 $^1J_{C1F'}$=285.6 $^2J_{C1Fc}$=47.3	128.48, ddd $^1J_{C2Fc}$=234.1 $^2J_{C2F'}$=53.5 $^2J_{C2F}$ =15.5	−174.92, ddt $^3J_{FcFa}$=31.8 $^3J_{FcFb}$=113.3 $^3J_{FcH}$=22.5	21.91, dd $^2J_{CFc}$=22.2 $^3J_{CF}$=2.2
	C^3H_2	C^4	C^4H_2	C^5	C^5H_2	OH
Ohmori et al. [10]	2.6, dm $^3J_{HFc}$=22	n.g.	2.05, qi $^3J_{HH}$=7	n.g.	3.86, t $^3J_{HH}$=7	5.33, s
This work	2.35, dddt $^3J_{HFc}$=22.5 $^4J_{HFa}$=2.4 $^4J_{HFb}$=4.0 $^3J_{HH}$=6.8	28.23, d $^3J_{CF}$=2.3	1.78, qi $^3J_{HH}$=6.8	61.25, s	3.65, t $^3J_{HH}$=6.3	3.08, s

Chemical shifts and coupling constants are in ppm and Hertz, respectively. (n.g. means not given).

saturated by nitrogen or argon. The presence of a coreagent (e.g., $ZnCl_2$; hydrochloric, oxalic or propionic acid) did not improve the yield of dechlorination, in contrast to the initial [Zn]/[halogenated alcohol] molar ratio and the temperature which are key-parameters. The optimal yield was obtained in experiment 11. Monitoring this reaction by gas chromatography showed a quasi-complete conversion of **A,1** after 4 h.

The synthesis of this trifluorovinyl alcohol was previously described by Ohmori et al. [10] who found spectroscopic values slightly different from ours (Table 3). This might come from the nature of the deuterated solvent used by the Japanese researchers who did not mention it in their patent.

We have found further data in the characterization by ^{1}H-NMR, the spectrum of which exhibits 19 bands as an interesting doublet ($^3J_{HF}$=22.5 Hz) of doublets ($^4J_{HF}$= 2.4 Hz) of doublets ($^4J_{HF}$=4.0 Hz) of triplets Hz ($^3J_{HH}$= 6.8 Hz) assigned to the methylene group adjacent to the trifluorovinyl end-group (Table 3). Further, the simulation [37] of this group from the above coupling constants led to identical shape of signal and similar coupling constants (Fig. 1).

To further characterize the monomer, ^{13}C-NMR spectroscopy was also performed in contrast to Ohmori et al. [10] who did not study it. The chemical shifts and the coupling constants are in good agreement with the structure of this fluoroalcohol (Table 3). However, the assignments of the peaks observed on the ^{13}C-NMR spectrum may be ambiguous for carbon atoms in α or β positions about the trifluorinated double bond. However, from the spectrum of 2,3,3-trifluoroallyl alcohol for which the carbon atom of the hydroxymethyl group shows a doublet ($^2J_{CF}$=

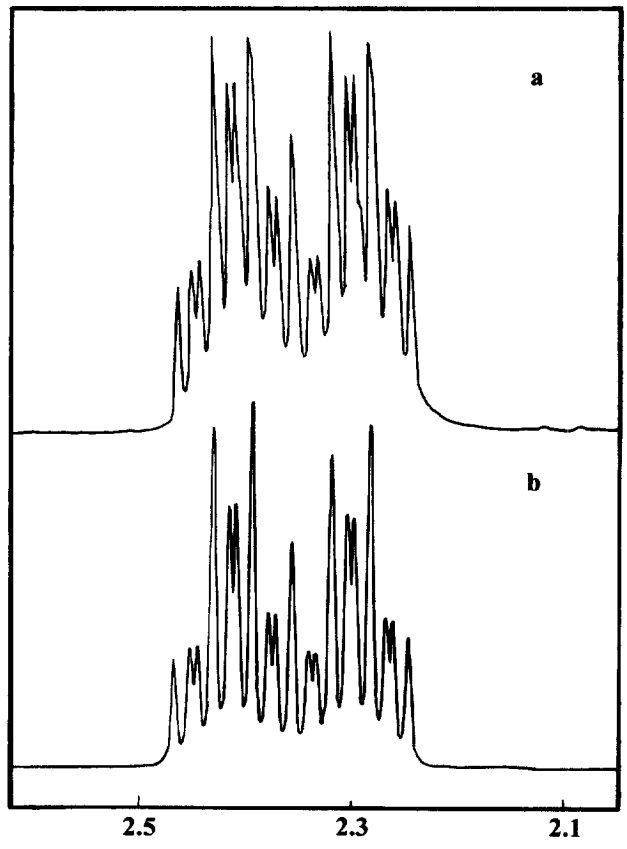


Fig. 1. Part of experimental (a) and simulated (b) ^{1}H-NMR spectra of 4,5,5-trifluoro-4-enepentanol.

23.1 Hz) of triplets ($^3J_{CF}$=2.5 Hz) at 54.88 ppm [39], there is no doubt on the attribution of the methylene groups: that adjacent to the fluorinated double bond resonates at

21.91 ppm. However, it seems that the long distance-coupling of such a carbon atom occurs with one fluorine atom only of the CF_2 end-group ($^3J_{CF}$=2.2 Hz) (Table 3), in contrast to the same methylene group of the fluoroallyl alcohol that gives a doublet ($^2J_{CF}$=23.1 Hz) of triplets ($^3J_{CF}$=2.5 Hz).

In our case, also, dechlorination occurred in higher yield than that obtained by Ohmori et al. [10] (70 vs. 55%) who used a 3.1 fold excess of zinc in water at 80°C.

It was worth performing the reduction step before the dechlorination otherwise the iodohydrin A would have undergone a deiodohydroxylation leading to CF_2=$CFCH_2CH$=CH_2 as observed by Gorbunova et al. [40].

Starting from 1-iodo-1,2-dichloro-1,2,2-trifluoroethane, the overall yield of the synthesis of the hydroxy fluoromonomer was about 50%.

3.4. *Synthesis of* **A,3** *by acetylation of* **A,2**

To our knowledge, 4,5,5-trifluoro-4-ene-pentyl acetate has not previously been synthesized. This acetoxy monomer is interesting for several reasons: (i) it is known that an acetoxy function has a higher electron-withdrawing effect than a hydroxy one; (ii) the hydrophilicity of an acetate function is lower than that of –OH end-group and hence is more suitable for homopolymerization or copolymerization in a hydrophobic medium (e.g., the copolymerization in solution of TFE with the hydroxy comonomer occured with difficulties [38]); (iii) an acetoxy end-group can behave as an interesting 'label' in ^{1}H-NMR and IR spectroscopies.

The acetylation of fluoroalcohol **A,2** was performed at 2°C–5°C and then at 25°C in the presence of a slight excess of acetyl chloride. Acetoxy monomer (**A,3**) was purified by distillation in 91% yield.

Its ^{1}H-NMR spectrum exhibits the absence of the broad signal assigned to the OH end-group of **A,2** and the presence of the acetyl group at 2.03 ppm. This latter group produced a slight low field shift of its adjacent methylene group from 1.78 to 1.84 ppm.

As expected, the ^{19}F-NMR spectrum of the acetylated trifluorovinyl monomer was identical to that of the hydroxylated precursor.

Beside expected singlets at 20.22 ppm and 170.65 ppm assigned to the carbon atoms of the acetoxy end-group, the ^{13}C-NMR spectrum confirms the assignments of the precursor (Table 3) in which the carbon atom adjacent to the trifluorinated double bond, centered at 21.89 ppm is represented by a doublet ($^2J_{CF}$=23.0 Hz) of doublet ($^3J_{CF}$= 2.2 Hz). Such a signal is similar to that of the precursor but different from that ascribed to the methylene group of 2,3,3-trifluoroallyl alcohol as shown above. In addition, the methylene group in β position gives a doublet ($^3J_{CF}$= 2.8 Hz) of doublets ($^4J_{CF}$=2.7 Hz) of doublets ($^4J_{CF}$= 1.0 Hz) centered at 24.15 ppm. As given above, it is surprising to observe the poor electron-withdrawing effect of this fluorinated double bond which does not low field-shift the carbon atom adjacent to it as might be expected.

4. Conclusions

An improved synthesis of ω-hydroxy or acetoxy trifluorovinyl monomer in three or four steps starting from Cl(C_2F_3Cl)I (**1**) was achieved in 50 or 46% overall yields, respectively. First, among various initiation-conditions for the addition of (**1**) to allyl alcohol, the best yields were obtained when AIBN was used as the initiator. In contrast to a similar reaction involving allyl acetate, no rearranged isomer was produced showing that the iodohydrin with a functional end-group was obtained selectively and Cl_2CFCF_2I isomer was formed inefficiently. Second, the reduction of the latter compound proceeded quantitatively in the presence of tributyl stannane without reacting with the chlorine atoms. Third, the dechlorination, being usually the most delicate step, was also optimized and reached a yield of 70% when a 3 fold excess of zinc was used in dry DMF. Interestingly, the acetylation of CF_2=CFC_3H_6OH in cool to ambient conditions proceeded in 91% yield thus offering a new trifluorovinyl monomer with a protected hydroxy end-group. The copolymerization of both functional perfluorovinyl comonomers with commercially available fluoroalkenes to synthesize original fluoroelastomers is under investigation.

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