

Journal of Fluorine Chemistry 93 (1999) 117-127



# Synthesis and polymerisation of fluorinated monomers bearing a reactive lateral group. Part $5^1$ – Radical addition of iodine monobromide to chlorotrifluoroethylene to form a useful intermediate in the synthesis of 4,5,5-trifluoro-4-ene-pentanol

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Received 19 June 1998; accepted 11 September 1998

#### Abstract

The synthesis of the new halogenated alcohol  $BrCF_2CFCICH_2CHICH_2OH$  as a precursor of 4,5,5 trifluoro-4-ene pentanol  $F_2C=CFC_3H_6OH$  is based on a two-step process. First, the radical addition of iodine monobromide to chlorotrifluoroethylene (CTFE) led to the expected  $BrCF_2CFCII$  (I) and  $ICF_2CFCIBr$  (II), but also to  $BrCF_2CFCIBr$  (III) and  $ICF_2CFCII$  (IV), the amount of which determined by <sup>19</sup>F NMR depended on the reaction conditions: by feeding CTFE into IBr continuously or in batches; photochemical or thermal initiations, and with various initial  $[IBr]_0/[CTFE]_0$  molar ratios. In most cases, isomer (I) was mainly produced. The second step concerned the addition of such a mixture to allyl alcohol yielding the polyhalogenoalcohol with a quantitative conversion of (I). The reactivity of different halogeno end-groups of these isomers toward the allyl alcohol was discussed. Reduction of the iodine atom into hydrogen and the halogenated alcohol was accompanied by that of the bromine atom leading to  $BrCF_2CFCIC_3H_6OH$  while dehydrochlorination of (V) into trifluorovinyl hydroxy monomers was achieved in the presence of potassium hydroxide but in poor yields. Strategies starting from the radical additions of iodine monochloride and of iodine monobromide were compared showing that the former led to better overall yields of trifluorovinyl alcohol than the latter. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Chlorotrifluoroethylene; Iodine monobromide; Radical addition; <sup>19</sup>F NMR spectroscopy; Reduction; Functional trifluorovinyl monomer

#### 1. Introduction

Previous papers have demonstrated the high reactivity of 1,2-dichloroiodotrifluoroethane (ClCF<sub>2</sub>CFCII) in the telomerisation reactions of various fluoroolefins such as vinylidene fluoride (VDF) [1], trifluoroethylene [2,3], 1-chloro-2,2-difluoroethylene [4], chlorotrifluoroethylene (CTFE) [4–7], tetrafluoroethylene [3,8–10], 1,1-difluoropropene [11] or hexafluoropropene [6,12]; or the cotelomerisation of VDF and CTFE [13]. Furthermore, this compound can undergo radical additions to dienes [14], allyl trialkylsilanes [15] or functional olefins such as allyl acetate [16,17] or allyl alcohol [18], and also coupling reactions [19].

Allyl acetate and allyl alcohol were thus involved in keyreactions as starting points for the synthesis of functional trifluorovinyl monomers [16–18]. However, the last step, the dechlorination of ClCF<sub>2</sub>CFCl–R– $\bigcirc$  (where R and  $\bigcirc$  designate a spacer and a functional group, respectively) did not exceed 70% yield, even after a pseudo-optimisation of this reaction [18]. This may arise from the high strength of the Cl–CF<sub>2</sub> bond. It is known that debromination [20] or dechlorobromination [21,22] are easier and usually gave high yields of trifluorovinylic compounds. Hence, our interest was focused on a similar way of synthesis of trifluorovinyl functional monomers from brominated reactants, and especially, iodine monobromide. Its addition to chlorotrifluoroethylene (CTFE) mainly led to BrCF<sub>2</sub>CFCII that reacted with allyl alcohol or allyl acetate. The former reaction is described in this paper whereas the latter one will be detailed in a forthcoming paper.

In contrast to the addition of iodine monochloride to CTFE carried out by several authors [7,10,23–27] and recently optimised [28], that of iodine monobromide to

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<sup>&</sup>lt;sup>1</sup> Part 4, see [18]

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CTFE has drawn less attention. Several papers described this reaction, such as the pioneer work of Haszeldine [23] who claimed that IBr and CTFE yielded  $BrCF_2CFCII$ , but several years later, Chambers et al. [29] showed that this reaction led to  $BrCF_2CFCIBr$  and two isomers:  $BrCF_2CFCII$ and  $ICF_2CFCIBr$ . The formation of both isomers was proved by irradiating the mixture in the presence of mercury: the former isomer reacted quickly, leaving the latter one unchanged. This addition was also mentioned in a patent [30] but the authors did not indicate the presence of both isomers and by-products.

Hence, we have planned to perform a deeper investigation of this reaction to elucidate the above observations and to quantify the products. The second objective of this paper is based on the reactivity of these products to allyl alcohol in order to prepare key intermediates for the synthesis of functional trifluorovinyl monomers. Such monomers were previously obtained [18,31] from precursors based on the radical addition of iodine monochloride to CTFE [28]. Thus, both reactions involving iodine halides are to be compared as are the reactivities of their products with allyl alcohol.

#### 2. Results and discussion

The synthesis of new halogenated alcohols was performed in two steps (Scheme 1) which are detailed hereafter.

# 2.1. Addition of iodine monobromide to chlorotrifluoroethylene

According to the literature discussed above, it is clear that at least two isomers were produced (Scheme 1); but the authors considered only the monoaddition reaction of IBr to chlorotrifluoroethylene (CTFE) without taking into account the possibility of telomerisation or the reaction mechanism [23,29].

The radical addition of iodine monobromide to CTFE was carried out in various ways, IBr being from a commercial source or generated in situ from a mixture of iodine and bromine: by either ensuring a continuous bubbling of CTFE into IBr or the use of a batch process in a Carius tube or an autoclave. Initiation occurred either thermally or photochemically, and in this latter case, benzophenone was used as the photoinitiator. These conditions of initiation were suggested from the literature [23,29] or from the previous work (e.g., those dealing with the radical additions of iodine monochloride to CTFE [28] or to trifluoroethylene [32]). However, neither redox catalyst nor radical initiator was used since such systems were not reported to bring any improvement in the yield or regioselectivity of addition.

The results are listed in Table 1. The amounts of the three products were determined by gas chromatography, after identifying ICF<sub>2</sub>CFCII [8,11,24,28,33] and recently synthesised BrCF<sub>2</sub>CFCIBr [34–36], which have retention times of 11.7 and 6.3 mn, respectively (Fig. 1). In addition, the presence of the expected I(CTFE)Br was checked by GC/MS and by <sup>19</sup>F NMR spectroscopy. The mass spectrum confirms the formation of BrCF<sub>2</sub>CFCIBr and ICF<sub>2</sub>CFCII by their characteristic fragments (see Section 4) whereas those of I(CTFE)Br clearly identify the presence of both isomers: fragments at 193, 195, 197 and 145, 147 assigned to (BrCF<sub>2</sub>CFCI)<sup>++</sup>; and (CFCIBr)<sup>++</sup>; end-groups of (I) and (II), respectively.

In addition, the <sup>19</sup>F NMR spectrum (Fig. 2) provides firm evidence for the existence of these three products and allowed us to distinguish two isomers for I(CTFE)Br. First, ICF<sub>2</sub>CFCII was formed as a minor compound, shown by

Table 1

Radical addition of iodine monobromide to chlorotrifluoroethylene (CTFE): experimental conditions and results

Vessel									
	Weight of IBr (g)	Weight of CTFE (g)	$[IBr]_0/$ [CTFE]_0	Initiation (°C)	Time (h)	Br(C <sub>2</sub> F <sub>3</sub> Cl)I (%)	BrCF <sub>2</sub> CFClBr (%)	ICF <sub>2</sub> CFCII (%)	Overall yield (%)
F	in situ	bubbling	_	th, 50–70	2	26	74	0	6
А	in situ	75.0	<0.77	th, 100	2	63	33	4	n.d.
А	in situ	65.0	<0.90	th, 100	1	55	25	20	31 <sup>a</sup>
А	in situ	65.0	< 0.90	th, 90	12	55	23	22	n.d.
CT	71.0	40.0	1.00	th, 100	72	51	44	5	35 <sup>a</sup>
CT	76.4	56.0	0.77	th, 90	16	61 <sup>b</sup>	31	8	n.d.
CT	70.4	56.6	0.70	th, 80	5	73	20	7	n.d.
CT	37.0	30.4	0.70	th, 80	5	76	20	4	n.d.
СТ	120.0	69.8	0.97	photoch. Ph <sub>2</sub> CO, RT	14	75 <sup>c,d</sup>	24	1	39 <sup>a</sup>
СТ	36.5	21.6	0.95	photoch. DPPH <sup>e</sup> Ph <sub>2</sub> CO, RT	15	72	26	2	8 <sup>a</sup>
	F A A CT CT CT CT CT CT CT	Vessel weight of IBr (g)   F in situ   A in situ   A in situ   CT 71.0   CT 76.4   CT 70.4   CT 37.0   CT 120.0   CT 36.5	Version Weight of IBr (g) Weight of CTFE (g)   F in situ 50.0   A in situ 65.0   A in situ 65.0   CT 71.0 40.0   CT 76.4 56.0   CT 70.4 56.6   CT 37.0 30.4   CT 120.0 69.8   CT 36.5 21.6	Vesselweight of IBr (g)weight of CTFE (g) $[IBI]_{0}/$ $[CTFE]_0$ Fin sitububbling-Ain situ75.0<0.77	Vesselweight of IBr (g)weight of CTFE (g) $[IBI]_{0/}$ [CTFE]_0initiation (°C)Fin sitububbling-th, 50–70Ain situ75.0<0.77	Vesselweight of IBr (g)weight of CTFE (g) $[CTFE]_0$ Initiation (°C)Initiation InitiationFin sitububbling-th, 50–702Ain situ75.0<0.77	Vesselweight of IBr (g)weight of CTFE (g) $[CTFE]_0$ InitiationInite Initiation $BI(C_2F_3CI)I$ Fin sitububbling-th, 50–70226Ain situ75.0<0.77	Vesselweight of IBr (g)weight of CTFE (g) $[CTFE]_0$ (°C)(h)(%) $BICF_2CFCIBI$ Fin sitububbling-th, 50–7022674Ain situ75.0<0.77	Vesselweight of IBr (g)inflig/ (CTFE (g)initiation [CTFE]0initiation (°C)initiation (%)initiation 

F, A, CT, th, photoch. and n.d. mean flask, autoclave, Carius tube, thermal, photochemical and not determined, respectively.

<sup>a</sup>After distillation.

<sup>b</sup>%BrCF<sub>2</sub>CFClI=58- %ICF<sub>2</sub>CFClBr=3.

<sup>c</sup>Relative yields determined by <sup>19</sup>F NMR.

<sup>d</sup>%BrCF<sub>2</sub>CFClI=70, %ICF<sub>2</sub>CFClBr=5.

<sup>e</sup>2,2-Diphenyl-1-picrylhydrazyl.



Scheme 1. Preparation of halogenated alcohols from the products of addition of iodine monobromide to chlorotrifluoroethylene.

three different signals centred at -43.45, -52.27 and -65.85 ppm assigned to the three fluorine atoms of an AMX system. This confirms the characterisation of Chambers et al. [33]. Second, BrCF<sub>2</sub>CFClBr was also easily noted by the characteristic AB part of an ABX system ( $\delta_{FA}$ =-59.13 ppm and  $\delta_{FB}$ =-60.85 ppm) and the triplet

 $({}^{3}J_{FF}=13.9 \text{ Hz})$  centred at -69.25 ppm. The conditions used for recording this spectrum allowed us to observe this triplet only, rather than the expected doublet of doublets with close coupling constants (13.5 and 14.1 Hz). Finally, both isomers of I(CTFE)Br are also formed. The major one, BrCF<sub>2</sub>CFCII (I), exhibits the following <sup>19</sup>F NMR character-



Fig. 1. Gas chromatogram of the total product mixture of the addition of iodine monobromide to CTFE of experiment 2 (the experimental conditions are in Table 1). A and B represent the peaks assigned to CTFE and methylene chloride, respectively.

istics: the AB part of an ABX system, assigned to the BrCF<sub>2</sub> end-group overlaps with the signal of the same group of BrCF<sub>2</sub>CFClBr, giving a doublet ( ${}^{2}J_{FbFa}$ =165.9 Hz) of doublets ( ${}^{3}J_{FcFb}$ =20.4 Hz) and centred at -58.95 ppm, and a doublet ( ${}^{2}J_{FaFb}$ =165.9 Hz) of doublets ( ${}^{3}J_{FaFc}$ =15.1 Hz) at -53.74 ppm. The X part of the ABX system shows a doublet ( ${}^{3}J_{FcFa}$ =15.6 Hz) of doublets ( ${}^{3}J_{FbFc}$ =20.2 Hz) centred at -69.81 ppm. Interestingly, these NMR characteristics show the difference of shapes of signals assigned to XCF<sub>2</sub> and CFClX end-groups (where X is I or Br), the bulkier iodine atom enhancing the differences between the coupling constants  ${}^{2}J_{FF}$  (188.5 and 165.9 Hz for I and Br

atoms respectively, compared to 163.9 Hz for a chlorine atom [17]) and between the  ${}^{3}J_{\text{FaFc}}$  and the  ${}^{3}J_{\text{FbFc}}$ .

The minor isomer, ICF<sub>2</sub>CFClBr, also had distinct signals. The AB part of the ABX system, assigned to the ICF<sub>2</sub> group, is a low field shifted compared with that for BrCF<sub>2</sub>, but high field shifted compared to the same end-group of ICF<sub>2</sub>CFCII. The X part (CFClBr group) is represented by a triplet ( ${}^{3}J_{FF}$ =16.1 Hz) centred at -66.20 ppm.

From the integrations of the signals assigned to the CFClX group (X=I or Br) of each product centred at -65.85 (CFClI of IV), -66.20 (CFClBr of II), -69.25 (CFClBr of III) and -69.81 (CFClI of I), proportions of products in the mixture were determined. For example, experiment 9 (Table 1, Fig. 2) gives the following ratios of products: ICFClCF<sub>2</sub>Br (70%), BrCF<sub>2</sub>CFClBr (24%), ICF<sub>2</sub>CFClBr (5%) and ICF<sub>2</sub>CFClI (1%).

As shown previously [28,33], the diiodinated compound may undergo a  $\beta$ -scission (or reversion) above 40°C leading back to CTFE and iodine, but from 90°C, the CTFE produced may also react with ICF<sub>2</sub>CFCII leading to telomers [33] since we have previously shown the high reactivity of the CFCII end-group in the thermal telomerisation of CTFE [37]. Interestingly, the photochemical induced reaction enabled drastic decrease of diiodide but with a non-negligible amount of dibrominated by-product. This latter product was also observed by Chambers et al. [29] in 20% yield.

The yield obtained from the reaction performed at atmospheric pressure (exp. 1 in Table 1) was quite low whereas those from thermal initiation in sealed Carius tube were less than 35%. The best yield observed was for photochemical induced reaction (exp. 9). However, the yield of this reaction was worse than that obtained from the addition of iodine



Fig. 2. <sup>19</sup>F NMR spectrum of the product of the addition of iodine monobromide to CTFE as experiment 9 (see Table 1) BrCF<sub>2</sub>CFCII( $\mathbf{\nabla}$ ), ICF<sub>2</sub>CFCIBr( $\Delta$ ), BrCF<sub>2</sub>CFCIBr( $\bigcirc$ ) and ICF<sub>2</sub>CFCII( $\mathbf{\Theta}$ ).

monochloride to chlorotrifluoroethylene (leading to 70% and quantitative yields for photochemical and thermal initiations, respectively [28]).

An attempt of the mechanism of the reaction is suggested.

#### 2.2. Mechanism

To our knowledge, the mechanism of this reaction has not been described previously. It can be ionic:

$${}^{\circ-\circ+}_{\text{BrI}} + {}^{\circ+}_{\text{CF}_2} = {}^{\circ-}_{\text{CF}}\text{Cl} \rightarrow \text{BrCF}_2\text{CFClI}$$

or radical:

(a) From Br attack

Initiation

 $\operatorname{IBr}_{\Delta} \operatorname{Br}^{\bullet} + \operatorname{I}^{\bullet}$ 

 $Br' + F_2C = CFCI \rightarrow BrCF_2CFCI'$ 

**Termination** 

 $BrCF_2CFCI^{\bullet} + IBr \rightarrow BrCF_2CFCII + Br^{\bullet} \quad (I)$ 

Termination by recombination

 $Br^{{\scriptscriptstyle\bullet}}+Br^{{\scriptscriptstyle\bullet}} \to Br_2$ 

(b) From I attack

Initiation

$$\begin{split} & IBr \mathop{\rightarrow}\limits_{\Delta} I^{\bullet} + Br^{\bullet} \\ & I^{\bullet} + F_2C {=} CFCl \rightarrow ICF_2CFCl^{\bullet} \\ & ICF_2CFCl^{\bullet} + IBr \rightarrow ICF_2CFClBr + I^{\bullet} \quad (II) \end{split}$$

# Termination

 $I^{{\scriptscriptstyle\bullet}}+I^{{\scriptscriptstyle\bullet}} \to I_2$ 

As for the radical addition of ICl to CTFE, no CTFE diadduct was observed (Fig. 1) and thus the propagation step did not occur.

According to this radical mechanism, it can be deduced that if I reacts with CTFE, isomer (II) is produced, whereas the addition of Br leads to isomer (I). From the experimental work (Table 1), isomer (I) is favoured, probably because of a higher reactivity of Br than that of I. This behaviour is similar to those of most telomerisations of olefins with perfluoroalkyl iodides ( $R_FI$ ) for which  $R_F$  reacted preferentially, allowing the formation of I<sub>2</sub> by recombination of I, whereas  $R_F-R_F$  was not observed [37].

In addition, the greater formation of  $BrCF_2CFClBr$  (III), as compared with  $ICF_2CFClI$  (IV), is in good agreement with scheme (a) which generates more  $Br_2$ .

We have previously demonstrated that the addition of iodine monochloride to CTFE [28] or to trifluoroethylene (TrFE) [32] was through a radical mechanism. Both these reactions led to the major formation of two isomers, CICF<sub>2</sub>CFCII and CICF<sub>2</sub>CFHI in 95% and 97% yields, respectively. In both cases, the iodine atom preferred to add to the less fluorinated sides of the fluoroalkenes and thus on the more hindered part of CTFE. This was shown thermodynamically and confirms that these reactions are not controlled by steric effects [32]. In the case of addition of IBr to CTFE, both these observations are also noted. Semi-empirical calculations are in progress on the basis of orbital analysis.

In order to check whether the mechanism was radical, 2,2-diphenyl-1-picrylhydrazyl (DPPH) was used as radical scavenger (exp. 10). Table 1 shows that without any DPPH, the yield was 39% whereas it drastically decreased when this reaction was performed in the presence of the radical scavenger.

Hence, although we have no evidence that the mechanism could be ionic (IBr reacted violently with amines used as cation scavengers), it is likely that the addition of IBr to CTFE involves radicals, as that of ICl to CTFE [28] or to TrFE [32].

#### 2.3. Addition of Br(CTFE)I to allyl alcohol

In contrast to Rogozinski et al. [38] who could not react BrCCl<sub>2</sub>CHClBr with allyl alcohol, Burton and Kehoe [39], Ojima and Fuchikami [40], and Hu et al. [21] successfully added 1,2-dibromo-1-chlorotrifluoroethane to various  $\alpha$ -olefins in the presence of CuCl/ethanolamine, iron dodeca-carbonyl and metallic complexes.

In our experiments, radical addition was chosen to be initiated by AIBN at 80°C (i.e. half life of 1 h) since it led to the best yields of a similar reaction involving ClCF<sub>2</sub>CFClI (yield=81%) [18]. The reaction was monitored by gas chromatography showing a product having a retention time longer that those of the reactants. After 4 h and since the halogenated mixture was not totally consumed, an additional amount of initiator was introduced as in previous work [18]. After distillation, pure fractions were characterised by <sup>1</sup>H and <sup>19</sup>F NMR.

The <sup>1</sup>H NMR spectrum suggests the CH<sub>2</sub>–CHXCH<sub>2</sub>OH structure (X=I or Br) as previously observed for ClCF<sub>2</sub>CFClCH<sub>2</sub>CHICH<sub>2</sub>OH. The signal attributed to the methylene  $\gamma$  to the hydroxyl function is complex because this methylene is adjacent to two asymmetric carbons. This also indicates that halogenated alcohol (I,a) is present as two diastereoisomers, in equal amounts.

The presence of the methylene of the CH<sub>2</sub>OH end-group was proved by adding a drop of Cl<sub>3</sub>CNCO to the NMR tube: its signal was low field shifted from 3.85 to 4.70 ppm. However, <sup>1</sup>H NMR spectroscopy was not able to confirm the formation of (I,a), (II,a), (II,a') and (III,a) products. The <sup>19</sup>F NMR spectrum exhibits three signals, only: that centred at -61.90 ppm (the AB part of an ABX system, BrCF<sub>2</sub>) and two doublets of quartets assigned to the CFCl groups of both diastereoisomers. The <sup>2</sup>J<sub>FF</sub> coupling constant of the XCF<sub>2</sub> end-group was 154.7 Hz let us assume that this was for



Fig. 3. <sup>13</sup>C NMR spectrum of BrCF<sub>2</sub>CFCICH<sub>2</sub>CHICH<sub>2</sub>OH (expansion of the 106–128 ppm zone; BrCF<sub>2</sub> (○, \*) and CFCI (●, +)).

X=Br. It is rather close to that of the ClCF<sub>2</sub> end-group  $(^{2}J_{FF}=169.3 \text{ Hz})$  in ClCF<sub>2</sub>CFClCH<sub>2</sub>CHICH<sub>2</sub>OAc [17].

Finally, the <sup>13</sup>C NMR spectrum confirms the formation of (I,a) only. Indeed, the XCF<sub>2</sub> end-group signals (in the 105–140 ppm range) are in excellent agreement with the BrCF<sub>2</sub>CFCl structure as shown in Fig. 3. This is also in agreement with the values of the <sup>1</sup> $J_{CF}$  coupling constants in BrCF<sub>2</sub> and ICF<sub>2</sub> end-groups being 312 and 367 Hz, respectively [36].

In order to confirm that the reactivity of  $BrCF_2CFCII$  is higher than that of  $BrCF_2CFCIBr$  towards alkenes,  $BrCF_2CFCIBr$  was reacted with allyl alcohol in the presence of AIBN. A similar reaction was performed [39,40] using metal complexes but to our knowledge, AIBN was not previously used to initiate such a reaction. In similar conditions as above, the reaction occurred but in a poor yield (10% after distillation of  $BrCF_2CFCICH_2CHBrCH_2OH$ (III,a)). Such a product was co-injected with the total product mixture of the reaction described above for GC, and the corresponding signal of (III,a) having a retention time of 7.39 min appeared close to that of (I,a) (RT=8.36 min). The peak assigned to (III,a) was observed on the gas chromatogram of I,a but in a very low amount (ca. 5%).

The low reactivity of BrCF<sub>2</sub>CFClBr is based on the rather high bond dissociation energy of the C–Br bond in the CFClBr end-group. Even its radical addition on allyl acetate (shown to be more reactive than allyl alcohol in telomerisation reactions [41]) at 92°C initiated by dibenzoyl peroxide led to 15% yield, only, after 10 h with an additional amount of initiator every 3 h. Under the same conditions, the addition of ClCF<sub>2</sub>CFClI to such an  $\omega$ -acetoxy monomer was almost quantitative after 5 min [17].

#### 2.4. Reduction of iodohalogenated alcohol I, a

The attempt to perform the selective reduction of the iodine atom of BrCF<sub>2</sub>CFClCH<sub>2</sub>CHICH<sub>2</sub>OH (I, a) was carried out in the presence of an equimolar amount of tributylstannane at 5–20°C as done previously [18]. The reaction was monitored by gas chromatography, the retention time of I, a being 8.36 min. After 3 h, a first peak having a retention time of 6.19 min appeared while that of the alcohol I, a decreased. After 8 h, the signal assigned to the iodinated alcohol was absent whereas that at 6.19 min. increased, while another signal at 4.50 min. was observed. Both these products were distilled, the heavier one (RT=6.19 min) having the expected BrCF<sub>2</sub>CFClC<sub>3</sub>H<sub>6</sub>OH (I, b) structure as shown by the high field shift of the CHI group  $(\delta = 4.50 \text{ ppm})$  to 1.90 ppm in the <sup>1</sup>H NMR spectrum (assigned to the central methylene group of I, b). The  $^{19}$ F NMR characteristics show the presence of two groups of signals; that centred at -62 ppm being unchanged from that of the iodinated precursor, whereas only one doublet  $({}^{3}J_{FcFa}=30.7\text{Hz})$  of quartets  $({}^{3}J_{FcFb}={}^{3}J_{FcH}=10.3\text{ Hz})$ was present proving the loss of the second asymetric carbon, observed in I. a.

The <sup>1</sup>H NMR spectrum of the second product exhibits, beside the same signals observed for the above product, a triplet ( ${}^{2}J_{\text{HF}} = 54.8 \text{ Hz}$ ) of doublets ( ${}^{3}J_{\text{HF}} = 3.2 \text{ Hz}$ ) characteristic of a HCF<sub>2</sub> end-group. This shows that tributyl-stannane efficiently reduced the bromine atom to a proton, even at rather mild temperatures.

The <sup>19</sup>F NMR spectrum shows an interesting triplet  $({}^{3}J_{\text{FcH}} = 10.4 \text{ Hz})$  of doublets  $({}^{3}J_{\text{FcFa}} = 10.7 \text{ Hz})$  of doublets  $({}^{3}J_{\text{FcFb}} = 9.7 \text{ Hz})$  of doublets  $({}^{3}J_{\text{FcH}} = 3.3 \text{ Hz})$  centred at -125.3 ppm and an expected AB part at

 $-130.3\ \text{ppm}$  assigned to the CFCl and HCF\_2 groups, respectively.

The yields of BrCF<sub>2</sub>CFClC<sub>3</sub>H<sub>6</sub>OH ( $\underline{I}, \underline{b}$ ) and HCF<sub>2</sub>CFClC<sub>3</sub>H<sub>6</sub>OH ( $\underline{I}, \underline{b}'$ ) were 50 and 29%, respectively. A similar reaction performed with a two-fold excess of hydride led to the selective formation of ( $\underline{I}, \underline{b}'$ ) in 55% yield after distillation.

# 2.5. Dehalogenation of $BrCF_2CFClC_3H_6OH(I, b)$

The debromochlorination of I, b into 4,5,5-trifluoro-4-ene pentanol I, c was performed in the presence of activated zinc in anhydrous DMF. The reaction was carried out at 90°C and monitored by GC, the respective retention times for the trifluorovinyl and halogenated alcohol being 2.75 and 6.19 min. After 6 h, the conversion of I, b was 90% and after work up, the total product mixture was distilled giving 66% yield of I, c. This hydroxy monomer was characterised by NMR. The <sup>1</sup>H NMR spectrum exhibits 19 bands of an interesting doublet  $({}^{3}J_{HF}=22.5 \text{ Hz})$  of doublets  $({}^{4}J_{HF}=2.4 \text{ Hz})$  of doublets  $({}^{4}J_{HF}=3.9 \text{ Hz})$  of triplets interesting  $({}^{3}J_{\rm HH}$ =6.7 Hz) assigned to the methylene group adjacent to the trifluorovinyl end-group. In addition, it shows signals similar to those of the I, b precursor, as expected. The <sup>19</sup>F NMR spectrum clearly identifies the three signals assigned to the fluorine atoms, centred at -106.1, -125.2 and -174.6 ppm.

# 2.6. Dehydrochlorination of $HCF_2CFClC_3H_6OH(I, b')$

This reaction was performed in the presence of an equimolar amount of methanolic potassium hydroxide. As above, the reaction was monitored by GC (the retention times of I, b' and I, c were 4.50 and 2.75 min., respectively) and was shown to be rather slow, since after 14 h only 40% of I, b' was consumed. A two-fold excess of potassium hydroxide did not increase the yield of I, c but seemed to produce a further dehydrochlorination leading to II, d or II, d' with an internal double bond. This was shown in the  ${}^{1}H$ NMR spectrum by the presence of small signals at 6.2 ppm. However, the absence of signal at 8.1 ppm may indicate that II, d' was not produced since it should lead to an aldehyde by tautomeric equilibrium. The <sup>19</sup>F NMR spectrum allowed identification of the three fluorine atoms of I, c as shown above. This trifluorovinyl alcohol was not distilled but its yield was deduced from GC (12%). The low yield of this reaction presumably results from the high bond dissociation energy of the C-H bond of the HCF<sub>2</sub> end-group.

#### 3. Conclusion

The preparation of 4,5,5-trifluoro-4-ene pentanol was achieved from a four-step procedure. The first step involved the radical addition of iodine monobromide to CTFE, initiated thermally or photochemically. Although four pro-

ducts (including two I(CTFE)Br isomers) were produced whatever the way of initiation without any formation of diadduct, the photochemical induced reaction is the best since it minimised the amount of by-products X(CTFE)X (X=I and Br) and afforded the best overall yields. However, these yields were worse than those obtained from radical addition of iodine monochloride. Although no evidence for an ionic mechanism could be given, the radical character of this reaction was noted, similar to those of the addition of ICl to CTFE and to trifluoroethylene. When the mixture of products formed reacted with allyl alcohol, only BrCF<sub>2</sub>CFCII was efficient leading to BrCF<sub>2</sub>CFClCH<sub>2</sub>CHI-CH<sub>2</sub>OH in fair yields. The poor reactivity of BrCF<sub>2</sub>CFClBr (present in the mixture) towards allyl alcohol was shown by its direct addition to allyl alcohol in the same initiation conditions, but leading to 10% yield, only. Its reduction in the presence of tributyl stannane produced two derivatives: BrCF<sub>2</sub>CFClC<sub>3</sub>H<sub>6</sub>OH (I, b) and HCF<sub>2</sub>CFClC<sub>3</sub>H<sub>6</sub>OH (I, b'), the unexpected latter compound coming from the reduction of the bromine to hydrogen. Both these alcohols have been used as precursors of 4,5,5-trifluoro-4-ene pentanol (I, c): the former underwent a dechlorobromination in the presence of zinc in fair yield, in contrast to the latter which only reacted with difficulty in the presence of base.

The overall yield of <u>I</u>, <u>c</u> via photochemical initiation of the first step and dehalogenation step was 8.3% whereas that from the dehydrochlorination of <u>I</u>, <u>b'</u> was 1%. The poor overall yield of the first step accompanied by the formation of two by-products is thus a limiting step. Such yields are much lower than that (40%) obtained for the synthesis of the same trifluorovinyl pentanol via a similar route starting from the photochemical addition of iodine monochloride to CTFE and a dechlorination as the final step.

Hence, the following decreasing reactivity series can be proposed:

- 1. for the radical addition of X–Y onto CTFE: Br<sub>2</sub>>I-Cl>IBr
- for the radical addition of X(C<sub>2</sub>F<sub>3</sub>Cl)Y onto allyl alcohol: ClCF<sub>2</sub>CFClI>BrCF<sub>2</sub>CFClI>>BrCF<sub>2</sub>CFClBr.

# 4. Experimental

#### 4.1. General comments

Chlorotrifluoroethylene (CTFE) was kindly given by Solvay S.A. whereas all other reactants were supplied by Aldrich (except AIBN from Merck) and did not require purification prior to use.

Thermal reactions (exp. 5–8) and the reaction in the presence of a radical scavenger (2,2-diphenyl-1-picrylhy-drazyl, DPPH) were carried out in Carius tubes (thickness: 3 mm; outside diameter: 30 mm; length: 205 mm).

The photochemically initiated reactions were performed in big borosilicate Carius tubes (thickness: 3 mm; outside diameter: 50 mm; length: 310 mm) under irradiation of a mercury lamp Philips HPK 125 W located 15–20 cm from the vertical tube, the reaction mixture being stirred magnetically.

The autoclave used in this work was made of Hastelloy (HC 276) having a volume of 200 ml, equipped with a valve, a manometer, a rupture disk, and a magnet bar for stirring.

Gas chromatography/mass spectrometry analyses were performed with a Hewlett-Packard apparatus composed of a chromatograph type 5972 coupled to a mass detector type 2567 with quadrupole scanning at 90 eV. The BPX5 column was 25 m long and 0.19 mm in inner diameter. The oven temperature was raised from 100°C to 230°C at a heating rate of 5°C min<sup>-1</sup>. Helium was the eluent at 0.12 ml min<sup>-1</sup> and the injection temperature was 220°C.

After reaction, the products were worked-up with an alkaline sodium bisulphite solution and analysed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with an SE-30 column,  $3 \text{ m} \times 1/8$  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°C and 255°C, respectively. The temperature programme started from 50°C and reached 250°C at a heating rate of 15°C min<sup>-1</sup>. 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 characterised by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy at room temperature (ca. 23°C). <sup>19</sup>F NMR and <sup>1</sup>H NMR spectra were recorded on Bruker AC-200, -250 or WM-360 instruments, using deuterated chloroform and tetramethyl silane or CFCl<sub>3</sub> as solvent and internal references, respectively. The letters s, d, t, qi and m designate singlet, doublet, triplet, quintet and multiplet, respectively.

#### 4.2. Radical addition of iodine monobromide to CTFE

The weights of reactants are given in Table 1. Hereafter is presented the experimental procedure for experiment 9.

A Carius tube equipped with a magnet bar and containing 120.02 g (0.58 mol) of iodine monobromide, 2.5 g (13.7 mmol) of benzophenone and 300.0 g of methylene chloride was frozen and degassed before 69.75 g (0.60 mol) of CTFE was condensed at  $-80^{\circ}$ C. After sealing, the tube was exposed to a UV lamp at room temperature for 14 h.

It was necessary to dilute IBr with methylene chloride and to pour the solution into the Carius tube rather than melting the reactant before introduction in the tube. Although the overall yield was similar (37%), the latter procedure led to a partial decomposition of IBr into iodine and bromine and consequently gave an increase of byproducts (BrCF<sub>2</sub>CFClBr, 40% and ICF<sub>2</sub>CFClI, 15%) with a decrease of I(C<sub>2</sub>F<sub>3</sub>Cl)Br (45%) (Table 1).

The gross was characterised by  ${}^{19}$ F NMR in CDCl<sub>3</sub> (Fig. 2), the spectrum of which indicates the presence of 4 products, 2 being isomers.

#### 4.2.1. 1,2-Dibromotrifluorochloroethane (III)

BrCF<sub>2</sub>CFClBr δ: -59.90 (AB part of ABX system  $\delta_{Fa}$ =-59.13 ppm,  $\delta_{Fb}$ =-60.85 ppm, <sup>2</sup> $J_{FaFb}$ =166.8 Hz, <sup>3</sup> $J_{FaFc}$ =13.5 Hz, <sup>3</sup> $J_{FbFc}$ =14.1 Hz, BrCF<sub>2</sub>); -69.25 (X part, t, <sup>3</sup> $J_{FF}$ =13.9 Hz, CFClBr).

MS *m*/*z*: 79/20 and 81/19 (Br)<sup>++</sup>; 116/18 (C<sub>2</sub>F<sub>3</sub>Cl); 145/ 25, 147/32, 149/9 (CFClBr)<sup>++</sup>; 176/6, 178/7 (C<sub>2</sub>BrF<sub>2</sub>Cl); 195/75, 197/100, 199/19 (BrCF<sub>2</sub>CFCl)<sup>++</sup>; 239/2, 241/3, 243/2 (M–Cl)<sup>++</sup>; 274/2, 276/3, 278/3 M<sup>++</sup>

#### 4.2.2. 1,2-Diiodotrifluorochloroethane (IV)

ICF<sub>2</sub>CFCII  $\delta$ : AB part of ABX system  $\delta_{Fa}$ =-43.45 ppm,  $\delta_{Fb}$ =-52.27 ppm, <sup>2</sup> $J_{FaFb}$ =188.5 Hz, <sup>3</sup> $J_{FaFc}$ =16.1 Hz, <sup>3</sup> $J_{FbFc}$ =18.9 Hz, ICF<sub>2</sub>; -65.85 (X part, dd, <sup>3</sup> $J_{FcFa}$ =16.0 Hz, 16.0 Hz, <sup>3</sup> $J_{FcFb}$ =19.1 Hz, CFCII).

MS *m*/*z*: 66/10, 68/3 (CFCl)<sup>++</sup>; 116/60, 118/28 (C<sub>2</sub>F<sub>3</sub>Cl); 127/53 (I)<sup>++</sup>; 177/5 (CF<sub>2</sub>I)<sup>++</sup>; 193/12 (CFClI)<sup>++</sup>; 243/82, 245/32 (ICFClCF<sub>2</sub>)<sup>++</sup>; 254/100 (I<sub>2</sub>)

#### 4.2.3. Chloroiodo-2-bromotrifluoroethane (I)

Its mass spectrum also exhibits fragments coming from isomer II.

MS m/z: 50/12 (CF<sub>2</sub>)<sup>++</sup>; 66/21, 68/9 (CFCl)<sup>++</sup>; 79/8, 80/ 18 (Br)<sup>++</sup>; 116/80, 118/20 (C<sub>2</sub>F<sub>3</sub>Cl)<sup>++</sup>; 127/100 (I)<sup>++</sup>; 145/ 20, 147/23, 149/7 (CFClBr)<sup>++</sup>; 193/11, 195/85, 197/99, 199/ 22 (BrCF<sub>2</sub>CFCl)<sup>++</sup>; 206/12, 208/20 (IBr); 243/13, 245/5 (CF<sub>2</sub>CFClI)<sup>++</sup>; 287/4, 289/4 (BrCF<sub>2</sub>CFI)<sup>++</sup>

#### 4.2.4. Chlorobromo-2-iodotrifluoroethane (II)

ICF<sub>2</sub>CFClBr  $\delta$ : AB part of an ABX system:  $\delta_{Fa}$ =-50.95 ppm,  $\delta_{Fb}$ =-54.15 ppm,  ${}^{2}J_{FaFb}$ =188.1 Hz,  ${}^{3}J_{FaFc}$ =15.7 Hz;  ${}^{3}J_{FbFc}$ =18.8 Hz; -66.20(X part, t,  ${}^{3}J_{FF}$ =16.1 Hz).

The mixture was difficult to purify because of close boiling points between BrCF<sub>2</sub>CFClBr (Bp=91°C [36]) and IC<sub>2</sub>F<sub>3</sub>ClBr (Bp=82°C/195 mm Hg [23] or 120.1°C/768 mm Hg [29]), but ICF<sub>2</sub>CFClI decomposed at these temperatures [28,33].

The distillation of the gross (from exp. 9) led to 73.2 g (0.226 mol) of a red liquid (yield=39%) Bp=110°C.

# 4.3. Radical addition of (I)+(II)+(III)+(IV) to allyl alcohol

In a three-necked round-bottom flask equipped with a condenser and a device with a nitrogen flow, were introduced 73.2 g (0.23 mol) of  $Br(C_2F_3Cl)I$  and 15.1 g (0.26 mol) of allyl alcohol. The mixture was heated under stirring up to 80°C and 1.3 g (7.9 mmol) of AIBN were added. The reaction mixture was stirred at this temperature for 4 h after which 1.3 g of AIBN was added and the medium was left stirring for 4 h more. After distillation of unreacted starting materials, 56.7 g (0.149 mol) of a brown viscuous liquid was redistilled.

Bp 95–99°C/0.02 mm Hg. Yield=64.7%.

#### 4.3.1. 2-Iodo-4-chloro-5-bromo-4,5,5-trifluoropentanol

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ :2.45 (broad s, shifted with dilution and with Cl<sub>3</sub>CNCO, CH<sub>2</sub>O<u>H</u>, 1H); 2.95 m, CFClCH<sub>2</sub>, 2H); 3.85 (m, shifted to 4.70 with Cl<sub>3</sub>CNCO, C<u>H</u><sub>2</sub>OH, 2H); 4.50 m, CHI, 1H).

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ:-61.90 (AB part of an ABX system,  $\delta_{A}$ =-61.5, <sup>2</sup>*J*<sub>FaFb</sub>=154.8Hz, <sup>3</sup>*J*<sub>FaFx</sub>=11.5 Hz;  $\delta_{B}$ =-62.3, <sup>2</sup>*J*<sub>FbFa</sub>=154.7 Hz, <sup>3</sup>*J*<sub>FbFx</sub>=18.5 Hz, BrCF<sub>2</sub>, 2F); -116.2(dq, <sup>3</sup>*J*<sub>FxH</sub>=35.5 Hz, <sup>3</sup>*J*<sub>FxFa</sub>=11.0 Hz, BrCF<sub>2</sub>C<u>F</u>, 1F of one diastereoisomer); -118.74(dq, <sup>3</sup>*J*<sub>FxH</sub>=25.5 Hz, <sup>3</sup>*J*<sub>FxFb</sub>= 16.8 Hz, 1F of the other diastereoisomer).

<sup>13</sup>C NMR (CDCl<sub>3</sub>) both diastereoisomers have been characterised but their concentrations being identical, the assignments of the signals are arbitrary.

Isomer <u>A</u>  $\delta$ : 119.29 (ddd, <sup>1</sup> $J_{CFa}$ =313.0 Hz, <sup>1</sup> $J_{CFb}$ =313.0Hz, <sup>2</sup> $J_{CFx}$ =34.9 Hz, BrCF<sub>2</sub>); 111.10 (ddd, <sup>1</sup> $J_{CFx}$ =258.6, <sup>2</sup> $J_{CFa}$ =<sup>2</sup> $J_{CFb}$ =29.6 Hz, CFCl); 68.19 (s, CH<sub>2</sub>OH); 42.38 (d, <sup>2</sup> $J_{CFx}$ =19.9 Hz, <u>CH<sub>2</sub>CFCl</u>); 26.04 (s, CHI).

Isomer <u>B</u>  $\delta$ : 118.79 (ddd,  ${}^{1}J_{CFa}={}^{1}J_{CFb}=313.0$  Hz,  ${}^{2}J_{CFx}=35.0$  Hz, BrCF<sub>2</sub>); 110.49 (ddd,  ${}^{1}J_{CFx}=260.6$  Hz,  ${}^{2}J_{CFa}={}^{2}J_{CFb}=29.3$  Hz, CFCl); 66.91 (d,  ${}^{4}J_{CF}=4.0$  Hz, CH<sub>2</sub>OH); 42.09 (d,  ${}^{2}J_{CFx}=19.8$  Hz, CFClCH<sub>2</sub>); 22.97 (s, CHI).

# 4.4. Radical addition of 1,2-dibromo-2chlorotrifluoroethane to allyl alcohol

## 4.4.1. Synthesis of 1,2-dibromo-2-chlorotrifluoroethane

The addition of bromine to CTFE was performed in a Carius tube containing a magnet bar and 35.0 g (0.22 mol) of bromine. After cooling and degassing under vacuum, 33.0 g (0.28 mol) of CTFE was carefully transferred into the vessel at about  $-80^{\circ}$ C. At higher temperatures ( $-35-60^{\circ}$ C), CTFE reacted with bromine as noted by a white smoke. The tube was then sealed and allowed to progressively warm up to  $-20^{\circ}$ C. The heat evolution was reduced by immersing the vessel in an acetone/liquid nitrogen bath, while the orange mixture progressively turned colourless on reacting. Then, the mixture was warmed up to room temperature and stirred for an additional hour. Finally, the tube was frozen into liquid nitrogen, opened and the total product mixture was distilled to give 29.8 g (0.15 mol) of a colourless liquid (yield=69%), Bp=91°C (lit. val. [23]: 92-92.5°C; [35] 92.5°C).

# 4.4.2. Preparation of 4-chloro-2,5-dibromo-4,5,5trifluoropentanol

In a three-necked round-bottomed flask swept by an argon flow and equipped with a condenser and a thermometer were introduced 31.0 g (0.109 mol) of BrCF<sub>2</sub>CFClBr and 6.60 g (0.109 mol) of allyl alcohol.

The mixture was heated up to  $80^{\circ}$ C and 0.25 g (1.5 mmol) of AIBN was added every 15 min for 1 h. Then the reaction was left stirring for 6 additional hours. After distillation under reduced pressure, was obtained 3.8 g (0.011 mol, 10.4% yield) of a colourless liquid which crystallised in the cold room. Bp=74–77°C/0.15 mm Hg ( $T_{\rm m} = 18^{\circ}$ C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 2.90 (m, CFClCH<sub>2</sub>, 2H); 3.15 (broad s, low field shifted to 7–9 ppm with Cl<sub>3</sub>CNCO, OH, 1H); 3.82 (m, shifted to 4.63 ppm in the presence of Cl<sub>3</sub>CNCO, C<u>H<sub>2</sub></u>OH, 2H); 4.53 (m, CHBr, 1H).

<sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  : -62.08 (AB part of an ABX system,  $\delta_{A}$ =-61.64, <sup>2</sup> $J_{FaFb}$ =155.6 Hz, <sup>3</sup> $J_{FaFc}$ =11.3 Hz;  $\delta_{B}$ =-62.47, <sup>2</sup> $J_{FaFb}$ =155.6 Hz, <sup>3</sup> $J_{FbFc}$ =13.2 Hz); -117.08 (X part of the first diastereoisomer, dq, <sup>3</sup> $J_{FcFa}$ =11.1Hz, <sup>3</sup> $J_{FcH}$ =32.6Hz); -118.53 (X part of the second diastereoisomer, dq, <sup>3</sup> $J_{FcFb}$ =13.2 Hz, <sup>3</sup> $J_{FcH}$ =26.9 Hz).

## 4.5. Reduction of I, a by tributylstannane

An ampoule saturated with argon and equipped with a septum, contained 51.0 g (0.13 mol) of <u>I</u>, a. It was cooled in an ice bath and then 38.9 g (0.13 mol) of tributylstannane were added dropwise via a syringe. After complete addition, the solution was left stirring 30 mn and then the ice bath was withdrawn. The mixture was left reacting at room temperature for 10 additional hours to ensure complete conversion of <u>I</u>, a. After distillation, 6.65 g (0.038 mol) of a colourless liquid was obtained (yield=29%). Bp=83–86°C/25 mm Hg.

# 4.5.1. 4-Chloro-4,5,5-trifluoropentanol (I,b')

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.90(qi, <sup>3</sup> $J_{HH}$ =6.2 Hz, <u>C</u>H<sub>2</sub>CH<sub>2</sub>OH, 2H); 2.23(m, CFClC<u>H<sub>2</sub></u>, 2H); 2.75 (broad singlet, shifted with dilution or in the presence of Cl<sub>3</sub>CNCO); 3.68 (t, shifted to 4.50 ppm in the presence of Cl<sub>3</sub>CNCO, <sup>3</sup> $J_{HH}$ =6.6 Hz, <u>CH<sub>2</sub>OH</u>, 2H); 5.81 (td, <sup>2</sup> $J_{HF}$ =54.8 Hz, <sup>3</sup> $J_{HF}$ =3.2 Hz, HCF<sub>2</sub>, 1H).

<sup>19</sup>*F* NMR (CDCl<sub>3</sub>) δ: -125.33(tddd, X part of an ABX system,  ${}^{3}J_{FcH}$ =10.4 Hz,  ${}^{3}J_{FcFa}$ =10.7 Hz,  ${}^{3}J_{FcFb}$ =9.7 Hz,  ${}^{3}J_{FcH}$ =3.3 Hz, CF<sub>c</sub>Cl, 1F); -130.30 (AB part,  $\delta_{Fa}$ =-129.35,  ${}^{2}J_{FaFb}$ =284.4 Hz,  ${}^{3}J_{FaFc}$ =10.6 Hz,  ${}^{2}J_{FaH}$ =55.0 Hz,  $\delta_{Fb}$ =-131.28,  ${}^{2}J_{FbFa}$ =283.7 Hz,  ${}^{3}J_{FbFc}$ =9.9 Hz,  ${}^{2}J_{FbH}$ =55.0 Hz) 16.5 g (0.064 mol) of a second pure fraction was distilled (colourless liquid) Bp, 90–92°C/21 mm Hg (yield=49.6%).

# 4.5.2. 4-Chloro-4,5,5-trifluoro-5-bromopentanol (I,b)

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.93(qi, <sup>3</sup> $J_{HH}$ =6.3 Hz, C<u>H</u><sub>2</sub>CH<sub>2</sub>OH, 2H); 2.29 (m, CFClCH<sub>2</sub>, 2H); 3.10 (broad singlet, shifted with dilution or with Cl<sub>3</sub>CNCO, OH, 1H); 3.64 (t, <sup>3</sup> $J_{HH}$ =6.4 Hz, low field shifted to 4.6 ppm in the presence of Cl<sub>3</sub>CNCO, C<u>H</u><sub>2</sub>OH, 2H).

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ: (AB part of an ABX system  $\delta_{FA}$ =-61.65, <sup>2</sup> $J_{FaFb}$ =155.2 Hz, <sup>3</sup> $J_{FaFx}$ =30.5 Hz,  $\delta_{FB}$ =-62.85, <sup>2</sup> $J_{FaFb}$ =155.2 Hz, <sup>3</sup> $J_{FbFx}$ =10.3 Hz); -118.32 (X part, dq, <sup>3</sup> $J_{FxFa}$ =30.7 Hz, <sup>3</sup> $J_{FxFb}$ =<sup>3</sup> $J_{FcH}$ =10.3 Hz, F<sub>x</sub>).

A similar reaction using 56.7 g (0.15 mol) of <u>I</u>, <u>a</u> and 87.3 g (0.30 mol) of SnBu<sub>3</sub>H led to an almost complete conversion of <u>I</u>, <u>b</u> after 14 h and <u>I</u>, <u>b'</u> (14.6 g, 0.083 mol) was produced only (yield=55%).

# 4.6. Dehalogenation of I, b

In a three-necked round-bottomed flask swept by an argon flow and equipped with a condenser was introduced via a septum 30 ml of dry DMF. Under vigorous stirring, 6.7 g (0.103 mol) of zinc activated by 1 ml of acetic acid and 1 ml of acetic anhydride were placed in the flask and then the slurry was heated up to 90°C. 8.7 g (0.034 mol) of I, b was then added dropwise and the temperature was maintained at 90°C, 6 h after complete addition. At this stage, the reaction, monitored by GC, showed that about 90% of I, b had reacted. After cooling, the excess of zinc was filtered off, the total product mixture was heated with HCl 10% and the fluorinated part extracted with diethyl ether. 4,5,5-trifluoro-4-ene pentanol (I, c) was rectified after distillation of the solvent. 3.15 g (0.022 mol) of a colourless liquid was obtained. Bp=48-50°C/21 mm Hg (lit. val. [42]: 95°C/ 155 mmHg). Yield=66%.

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ : 1.80 (qi, <sup>3</sup> $J_{HH}$ =6.8 Hz, C<u>H</u><sub>2</sub>CH<sub>2</sub>OH, 2H); 2.38 (dddt, <sup>3</sup> $J_{HF}$ =22.5 Hz, <sup>4</sup> $J_{HF}$ =2.4 Hz, <sup>4</sup> $J_{HF}$ =4.0 Hz, <sup>3</sup> $J_{HH}$ =6.8 Hz, CFCH<sub>2</sub>, 2H); 3.15 (broad singlet, shifted with dilution or with Cl<sub>3</sub>CNCO, OH, 1H); 3.66 (t, shifted to 4.40 ppm with Cl<sub>3</sub>CNCO, <sup>3</sup> $J_{HH}$ =6.3 Hz, CH<sub>2</sub>OH).

<sup>19</sup>F NMR (CDCl<sub>3</sub>) δ: -106.1 (ddt, <sup>2</sup> $J_{FFgem}$ =88.4 Hz, <sup>3</sup> $J_{FF}$ =32.0 Hz, <sup>4</sup> $J_{FH}$ =2.5 Hz); -125.2(ddt, <sup>2</sup> $J_{FF}$ =88.4 Hz, <sup>3</sup> $J_{FF}$ =113.6 Hz, <sup>4</sup> $J_{FH}$ =3.9); -174.6(ddt, <sup>3</sup> $J_{FF}$ =32.0 Hz, <sup>3</sup> $J_{FF}$ =113.6 Hz, <sup>3</sup> $J_{FH}$ =22.5 Hz).

<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ : 21.9(dd,  $^{2}J_{\rm CF}$ =22.4 Hz,  $^{3}J_{\rm CF}=2.3$  Hz,  $^{3}J_{CF}=2.2$  Hz, 28.2  $CFCH_2$ ; (d, CH<sub>2</sub>CH<sub>2</sub>OH); CH<sub>2</sub>OH); 61.2 128.5 (ddd. (s,  $^{2}J_{\rm CF}$ =53.7 Hz,  $^{2}J_{\rm CF}$ =15.8 Hz, CF);  ${}^{1}J_{\rm CF}=233.8$  Hz,  $^{1}J_{\rm CF}$ =285.9 Hz, 153.2 (ddd,  ${}^{1}J_{\rm CF}$ =272.5 Hz,  $^{2}J_{CF}$ =47.0 Hz, F<sub>2</sub>C).

#### 4.7. Dehydrochlorination of I, b'

In a two-necked round-bottomed flask equipped with a condenser was refluxed a mixture composed of 10.3 g (0.06 mol) of <u>I, b'</u> and 3.27 g (0.06 mol) of potassium hydroxide dissolved in 30 ml of methanol. The reaction was monitored by GC which showed the slight decrease of the peak attributed to <u>I, b'</u> (RT=4.50 min.) and the presence of a signal with a RT of 2.75 min. Another experiment requiring a two-fold excess of KOH showed the presence of another signal at 2.83 min assigned to a fluorinated compound containing an internal double bond (probably <u>II, d</u>). The <sup>19</sup>F NMR spectrum shows similar signals at -106.1, -125.2 and -174.6 ppm as above with multiplets centred at -110.2 and -185.4 ppm.

<sup>1</sup>H NMR (CDCl<sub>3</sub>): mixture of signals assigned to  $\underline{I, b'}$  to I, c and complex multiplet at 6.2.

#### Acknowledgements

The authors would like to express their gratitude to the Ministére Français de l'Enseignement Supérieur et de la Recherche for an associate professor position at ENSC Montpellier (to GK) and for a grant administrated by the Centre International des Etudiants et Stagiaires (to PP). Financial support and gift of chlorotrifluoroethylene from Solvay were also greatly appreciated. The authors also thank Prof. A. Fruchier (Head for NMR of ENSCM) for helpful discussions.

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