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Synthesis and polymerization of fluorinated monomers bearing a reactive lateral group

Part 2. [1] Synthesis of nonconjugated dienes

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Abstract

The synthesis of various ω-perfluorovinyl synthons, especially 1,1,2-trifluoro-1,4-pentadiene 1 ($F_2C{=}CFCH_2CH{=}CH_2$) is described. These products were prepared according to a three-step scheme via the photochemical addition of iodine monochloride to chlorotrifluoroethylene (CTFE) leading to ICF_2CFCl_2/$ICFClCF_2Cl$ isomers, the relative amount of which depending on the way of initiation. Their reaction with allyl acetate under radical conditions gave at least four isomers from the expected or rearranged compounds $ClCF_2CFClCH_2CHXCH_2Y$ or $Cl_2CFCF_2CH_2CHXCH_2Y$ (with X, Y = I or OAc groups), the dechlorination and/or 'deiodoacetatisation' of which produced **1** and various 4,4,5,5,5-perhalogenopentanes as by-products. An optimization of the synthesis of **1** is proposed. All the compounds were characterized by ^1H and ^{19}F NMR. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Chlorotrifluoroethylene; Allyl acetate; Radical addition; Dehalogenation; Thermal rearrangement; 1,1,2-Trifluoro-1,4-pentadiene; ^1H; ^{19}F nuclear magnetic resonance

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1. Introduction

Perfluorovinyl functional monomers have already shown great interest for use in copolymerization with fluorinated or nonfluorinated commercially available comonomers [2–6]. In order to investigate this copolymerization, our interest has first been focused on the synthesis of the fluorinated monomers. Before describing the preparation of hydroxy, epoxy and carboxy-containing monomers, we have considered it worth studying the synthesis of fluorinated dienes containing one perfluorovinyl end group.

Perfluoro-1,3-butadiene was first synthesized in 1952 [7] from the coupling reaction of 1-iodo-1,2-dichloro-1,2,2-trifluoroethane followed by a bis-dehalogenation. Such a monomer can be polymerized anionically in the presence of cesium fluoride [8], cesium *tert*-butanolate or cesium naphthalene [9] and it was copolymerized in a radical way with *n*-alkyl vinyl ether [10].

Various preparations of perfluorovinyl dienes or trienes were extensively reviewed by Fearn [11,12] and Chambers [13] or described in the literature. For instance, Ausimont isolated perfluorodienes in high yields by the deiodofluorination of the corresponding α,ω-diiodo [14] or α,ω-dibromo [15] perfluoroalkanes in the presence of organometallic compounds, whereas Miller [16] performed the coupling of perfluoroallyl iodide.

Longer perfluorodienes were obtained by dehalogenation of monoadducts or telomers of tetrafluoroethylene (TFE) [11,12], trifluoroethylene [17], chlorotrifluoroethylene (CTFE) [17–19] or 1-chloro-1,2-difluoroethylene [19], or cotelomers of TFE and hexafluoropropene [11,12] with 1-chloro-1,2-dibromo-1,2,2-trifluoroethane [18] and especially 1-iodo-1,2-dichloro-1,2,2-trifluoroethane (**2**) [11,12,17,19].

Halogenated butadienes with lower fluorine contents were obtained by the addition of trifluoroiodoethylene [20] or 1-iodo-2-fluoroethylene [21] to ethylene followed by dehydroiodination. Successful synthesis was also performed from the addition of 1-iodo-1,2-dichloro-1,2,2-trifluoroethane **2** to 1,1-difluoroethylene [22,23] or 1,1-difluoropropene [22] followed by dehydroiodination and dehalogenation in about 35% overall yield. Without using any heavy metal, Tarrant et al. [24] synthesized 1,1,2-trifluoro-1,3-butadiene by addi-

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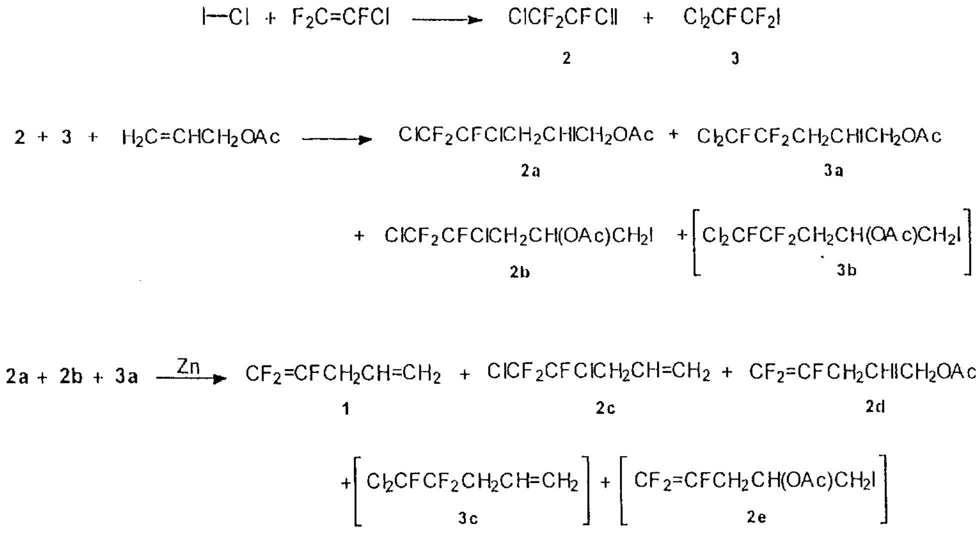


Scheme 1.

tion of dibromodifluoromethane to 1-fluoropropene followed by dehydrobromination.

Other longer conjugated dienes [25] were prepared by the addition of 1-chloro-1,2-dibromo-1,2,2-trifluoroethane (**A**) to either propylene, isobutylene or octene, followed by a similar two step-procedure as above.

The preparation of fluorinated nonconjugated dienes containing an ω-hydrogenated double bond was performed by several authors using various strategies starting from either brominated **A** or iodinated **2** reactants. The first synthesis was reported in 1954 by Tarrant and Gillman [25] who added **A** to allyl chloride yielding $BrCF_2CFClCH_2CHBrCH_2Cl$. Such a monoadduct, dehalogenated by activated zinc, produced 1,1,2-trifluoro-1,4-pentadiene **1** with an overall yield of 30% from allyl chloride [25].

A similar investigation was performed 6 years later by Durrell et al. [26] involving allyl acetate instead of allyl chloride with a slightly better overall yield.

The same fluorinated diene was produced by coupling allyl bromide with perfluorovinyl zinc bromide in the presence of CuBr in 80% yield [27]. In addition, Hu et al. [28] reacted **A** to one double bond of 1,5-hexadiene followed by a dehalogenation leading to a fluorinated 1,7-octadiene in ca. 60% overall yield. Interestingly, the process of dehalogenation was improved by adding $CuCl_2$ to zinc and was successful at room temperature in 30 min.

From fluoro iodinated reactants, three key reactions were found in the literature. Hung [29] achieved the synthesis of 1,1,2-trifluoro-1,5-hexadiene by telomerization of ethylene with iodotrifluoroethylene **B** followed by a dehydroiodination. Hung et al. [30] added **B** to one side of a nonconjugated diene and, after reduction of the central iodine atom, obtained a new ω-perfluorovinyl diene. Finally, 1,1,2-trifluoro-1,4-pentadiene and 1,1,2,3,3-pentafluoro-1,5-hexadiene were prepared by elimination reactions on $ClCF_2CFClCH_2CHICH_2OCOCH_3$ and $F_2C{=}CFCF_2CH_2CHICH_2OH$ in the presence of zinc [31]. Both products were synthesized by addition of $ClCF_2CFClI$ **2** or perfluoroallyl iodide to allyl acetate or allyl alcohol, respectively. However, Gorbunova et al. [31] did not mention the formation of various by-products as the starting perhalogenated reactant which should be composed of two isomers each, reactive with allyl acetate. Consequently, various halogenated iodoacetates and thus fluoroolefins should be produced. Such a synthesis requires a deeper investigation which constitutes the goal of this present paper.

2. Results and discussion

1,1,2-Trifluoro-1,4-pentadiene **1** was prepared in three steps: from the addition of dichlorotrifluoroiodoethane **2** (obtained by reacting iodine monochloride with chlorotrifluoroethylene (CTFE) to allyl acetate, followed by a simultaneous dehalogenation and deiodoacetatisation, as shown in Scheme 1. Each step is described below. Compounds **2e**, **3b**, **3c**, although expected, have not been observed and their formulae are represented between parentheses.

2.1. Addition of iodine monochloride to chlorotrifluoroethylene

This reaction was extensively investigated previously [1], leading to a mixture of both **2** and **3** whatever the method of initiation. In this work and contrary to previous studies, a photochemical initiation from a mercury lamp was utilized, irradiating two big Carius tubes filled with about 100 g of CTFE. Yields were similar to those previously observed producing mainly isomer **2** (95%). Even after two treatments with a basic solution of sodium thiosulfate, a red purple liquid still containing iodine was distilled. Molecular iodine was presumably generated by coupling of I˙ radicals in the termination step. However, when the reaction was carried out under sunlight radiation, the isomer ratio was slightly modified but only one work-up was necessary to obtain a distilled colourless liquid which turned pink under UV light owing to traces of iodine. It seems that both the wavelength and the power of the radiation may influence such a reaction. The mercury lamp may supply more UV radiation than sunlight (whereas the sunlight-emission is stronger in visible) and its power is higher (several W/cm^2) compared to that of sunlight (70 mW/cm^2). But, no deeper investigation (especially on the flow of photons) of such initiation has been performed. ^{19}F parameters of compounds **2** and **3** have been quoted in the experimental part.

2.2. Addition of $ClCF_2CFCl\ I/Cl_2CFCF_2I$ to allyl acetate

Although the CFClI end group is known to be more reactive than CF_2I [11,12,32–34], both **2** and **3** are able to react with allyl acetate and the literature dealing with the addition of perfluoroalkyl iodides to allyl acetate is abundant. As previously discussed, dibenzoyl peroxide and bis(4-*tert*-butylcyclohexyl)-peroxydicarbonate were chosen to initiate the reaction [35,36]. In both reactions, these initiators were used at temperatures corresponding to the half life of the radical initiator close to 1 h, i.e., 92°C and 60°C for the peroxide and percarbonate, respectively.

The mixture of 2 and 3 isomers containing traces of iodine reacts immediately as soon as the initiator has been introduced. The instantaneous reaction is exothermic and reaches ca. 160–180°C, whichever the initiator employed, as previously observed [35,36], leading to a mixture of compounds, which contains the rearranged isomer **2b** (**3b** has not been observed) besides the normal **2a** and **3a**. Depending on the conditions, the amount of the rearranged isomer **2b** could reach 35–40%, as previously observed [35].

When thermal rearrangement occurs, $ClCF_2CFClI$ **2** is the only isomer which reacts with allyl acetate. This is easily seen from both ^{19}F NMR spectra of distilled unreacted $Cl(C_2F_3Cl)I$ and $Cl(C_2F_3Cl)CH_2CHXCH_2Y$ (where (X,Y) represents (I, OAc) or (OAc,I)). The spectrum of $Cl(C_2F_3Cl)I$ shows an apparent absence of $ClCF_2CFClI$ **2** and is mostly Cl_2CFCF_2I **3**.

The use of solvents such as tetrahydrofuran or toluene reduces the exothermicity of the reaction and thus, produces only the expected **2a** and **3a** isomers.

If allyl alcohol is allowed to react with the mixture **2**/**3**, no thermal rearrangement is observed as will be described in a forthcoming paper. As in the case of allyl acetate, a mixture of **2a** and **3a** coming from the reactivity of both telogen isomers **2** and **3** is obtained. A similar behaviour was also noted when perfluoroalkyl iodides are added to the allyl alcohol in similar conditions [37].

It is noteworthy to mention that when no thermal rearrangement occurs, both isomers of the telogen are equally reactive since the amount of isomers **2a** and **3a** are similar to that of starting **2** and **3** isomers.

For the study of mixtures of **2a**, **3a**, **2b** and **3b**, ^{1}H and ^{19}F NMR spectra are complementary. Compounds **2a** and **3a** or **2b** and **3b** should show similar proton but different fluorine spectra while the pairs **2a**,**2b** or **3a**,**3b** should have similar fluorine but different proton spectra. These are formed of complex systems of five anisochronous spins as each compound bears at least one chiral carbon atom, two protons being also coupled with one or two fluorine atoms with large coupling constants. Moreover, two asymmetric carbons are present in **2a** and **2b**, allowing each of them to exist as two diastereoisomers. For all these reasons, the ^{1}H spectra of the different mixtures have been partially analysed only. For example, the rearranged isomer **2b** is detected in the mixture of **2a** and **3a** by the complex signal at 5.15 ppm due to the central CH bearing the acetoxy group.

Fluorine spectra are obviously simpler for two reasons: spin-systems are smaller and proton-noise-decoupled spectra can be obtained. Under these conditions, fluorine spectra of **2a** or **2b** show ABX spin-systems, the AB part being typical of a small ratio $\Delta\upsilon/J$ with four large inner transitions associated to four very small outer bands which are sometimes difficult to detect. The two diastereoisomers of these compounds give separated signals and the X parts have been tentatively assigned to the AB moieties on the basis of the RMS error of the iterative calculations, found to be slightly better in one case. Results of the analyses are reported in Section 4.

2.3. Synthesis of fluorinated nonconjugated diene

The addition of the iodoacetate mixture to a slurry of zinc in methanol or ethylene glycol could allow the formation of five products **1**, **2c**, **2d**, **2e** and **3c** (see Scheme 1). Gorbunova et al. [31] only observed the formation of diene **1**, and we were interested to show which compounds are really produced.

An optimization of the reaction was attempted by varying the [zinc]/[iodoacetate] initial molar ratio, the reaction time, the use of methanol or ethylene glycol and the presence or absence of an argon flow throughout the reaction. The reaction has been monitored by gas chromatography (GC) and ^{1}H and ^{19}F NMR. The fluorinated diene **1** has the shortest retention time (0.4 min), whereas the signals assigned to **2c** and **2d** appear at 1.3 and 2.1 min, respectively.

It is noticed that a five-fold excess of zinc over iodoacetate is required to get a large amount of diene **1**. It seems that deiodoacetatisation occurs first, followed by dechlorination.

Higher temperature and longer time increase the iodoacetate conversion and thus, the use of ethylene glycol as the solvent is better. The argon flow does not have a great influence on the yield of the reaction. In addition, whatever the amount of rearranged iodoacetate the reaction occurs, as previously observed, when such an intermediate contains a perfluorinated chain [38].

Whatever solvent was used, diene **1** was distilled as soon as formed. However, this procedure leads also to the formation of compounds **2c** and **2d**, while **2e** and **3c** have not been observed.

Fluorodiene **1** was characterized by ^{1}H and ^{19}F NMR without ambiguity.

The presence of the hydrogenated double bond is shown by different signals centered at 5.23 and 5.81 ppm assigned to the $=CH_2$ and =CH groups, respectively. The first multiplet can be composed of two complex signals corresponding to both protons: that in cis position about the proton of =CH– group with a chemical shift centred at 5.23, whereas that corresponding to the other proton is centred at 5.19 ppm. The =CH group is a doublet ($^{3}J_{H_4H_{5c}}=17.1$ Hz) of doublets ($^{3}J_{H_4H_{5t}}=10.1$ Hz) of triplets ($^{3}J_{H_3H_4}=6.3$ Hz). The methylene group of the allyl structure shows a different shape of signal according to the nature of the adjacent fluorinated group. It is a complex doublet ($^{3}J_{HF}=22.5$ Hz) of signals centered at about 3.03 ppm, low field shifted from that of $R_FCH_2CH{=}CH_2$ (where R_F represents a perfluorinated group) [38].

The perfluorovinyl group can easily be characterized by ^{19}F NMR, each of the fluorine atoms giving unique signals centred at − 106.28, − 125.09 and − 174.35 ppm. The first one (F_{1t}) is a doublet ($^{2}J_{F_{1t}F_{1c}}=87.5$ Hz) of doublets ($^{3}J_{F_{1t}F_2}=32.7$ Hz) of doublets ($^{4}J_{F_{1t}H_3}=2.7$ Hz). The second one (F_{1c}) comes from the coupling of F_{1c} with F_2 (d, $^{3}J_{F_{1c}F_2}=114.3$ Hz), then coupled with F_{1t} (d, $^{2}J_{F_{1t}F_{1c}}=87.5$ Hz) and finally, with the methylene group ($^{4}J_{F_{1c}H_3}=4.1$ Hz). The last fluorine atom (F_2) couples with F_{1c} (d, $^{3}J_{F_2F_{1c}}=114.3$ Hz) then with F_{1t} (d, $^{3}J_{F_2F_{1t}}=32.7$ Hz) and also with the adjacent methylene group as a triplet ($^{3}J_{F_2H_3}=22.0$ Hz).

NMR spectroscopy also allows to determine the ratios of compounds **1**, **2c** and **2d** produced. For instance, the gross of experiment no. 1 (Table 1) was characterized by ^{19}F NMR. It was noted the expected signal centred at − 106.28; − 125.09 and − 174.35 corresponding to the fluorine atoms of the perfluorovinyl end-group of **1** and also a doublet ($^{3}J_{F_4H_{3b}}=28.1$ Hz) of doublets ($^{3}J_{F_4H_{3a}}=8.8$ Hz) of doublets ($^{3}J_{F_4F_{5a}}=9.5$ Hz) centred at − 120.45 ppm and an AB system ($^{2}J_{F_{5a}F_{5b}}=169.0$ Hz; $^{3}J_{F_4F_{5b}}=9.3$ Hz and $^{3}J_{F_4F_{5a}}=9.5$ Hz) centred at −67.1 ppm assigned to CFCl and $ClCF_2$ groups of **2c**, respectively. The ratio of integration of CFCl and CF= groups of **2c** and **1** has led to respective amounts of both products.

By ^{1}H NMR of the same gross, a similar approach was used to deduce the amount of product **2d** from the integration of the singlet centred at 2.05 ppm assigned to acetoxy end-group of it, compared with that of the ethylenic protons of **1** and **2c**.

Table 1
Experimental conditions and yields of the products **1**, **2c** and **2d** by action of zinc on iodoacetates in ethylene glycol

Exp. no.	[Zinc]/ [iodoacetate]	T (°C)	t (h)	Argon flow	Overall yield	1 (%)	2c (%)	2d (%)
1	5.0	58*	5	no	23	76	18	6
2	5.0	130	2	yes	45	97	3	0
3	2.5	130	3	no	74	72	26	2
4	5.0	90	5	no	35	100	0	0
5	5.0	130	12	no	82	98	2	0

*This experiment has only been performed in methanol.

3. Conclusion

The photochemical addition of iodine monochloride to chlorotrifluoroethylene leads to two isomers $ClCF_2CFClI$ **2** and Cl_2CFCF_2I **3** with a larger amount of **2**.

The power and/or the wave length of the lamp seems to have a direct effect on the yield and on the formation of isomers. $Cl(C_2F_3Cl)I$ is an efficient transfer agent for the telomerization of allyl acetate leading to the monoadduct in high yield. However, the presence of free iodine or solvent seems to slightly lower its reactivity and to direct the amount of thermally rearranged compound produced when an exotherm occurs. The exothermicity of the reaction favours the reactivity of isomer **2**, thus leading to two iodoacetate isomers. If no increase of temperature is noted, both isomers **2** and **3** are equally reactive. The thermally rearranged isomer produced from telogen **3** has not been formed.

The action of zinc on the above mixture shows dechlorination, deiodoacetatisation or both, leading to nonconjugated diene **1** and to at least two products. It is observed that the deiodoacetatisation is quicker than the dechlorination. Whatever the amount of rearranged product, the iodoacetate was able to undergo dechlorination and deiodoacetatisation in order to produce this diene.

This diene **1** is an interesting intermediate for the synthesis of original functional ω-perfluorovinyl monomers which are under investigation.

4. Experimental

4.1. General comments

Chlorotrifluoroethylene (CTFE) was kindly supplied by Elf Atochem. Iodine monochloride, allyl acetate and zinc were provided by Aldrich and did not require purification prior to use.

After reaction, the products were worked-up and analyzed by gas chromatography (GC) using a Delsi apparatus (model 330) equipped with a SE 30 column, 3 m × 1/8 in (i.d.). The nitrogen pressure at the entrance to the column was maintained at 0.6 bar and the detector and injector temperatures were 260°C and 255°C, respectively. The temperature programme started from 50°C and reached 250°C at a heating rate of 15°C/min. The GC apparatus was connected to a Hewlett Packard integrator (model 3390).

The products were characterized by ^{1}H and ^{19}F NMR spectroscopy at 20°C. Spectra were recorded on Bruker AC-200, AC-250 or WM-360 instruments, using deuterated chloroform as solvent. All chemical shifts are given in ppm/

TMS for ^{1}H and in ppm/$CFCl_3$ for ^{19}F NMR, the coupling constants being in Hz.

4.2. Synthesis of 2 and 3

This reaction was performed in Carius tube (thickness: 3 mm, outside diameter: 40 mm; length: 310 mm) either as previously under sunlight [1] or under irradiation of mercury lamp Philips HPK 125 W, using an equimolar mixture of iodine monochloride and CTFE (T=35–40°C, t=12 h).

Treatment with a saturated sodium hydroxide solution of sodium thiosulfate eliminates almost all iodine produced from the reaction initiated by sunlight, but for that irradiated with the mercury lamp, even a second thiosulfate work up does not totally remove iodine. Obtained total yields were 68.5 and 54.3% for the above reactions, respectively. B.p. 99–101°C, lit., 98–101°C [1], 45°C/100 mm Hg [23]. 1-Iodo-1,2-dichloro-1,2,2-trifluoroethane **2**, ^{19}F NMR ($CDCl_3$): ABX system: $\delta(F_{2a})$ -62.31, $\delta(F_{2b})$ -65.25, $\delta(F_1)$ -72.87, $J(F_{2a}–F_{2b})$ 163.9, $J(F_{2a}–F_1)$ 14.4, $J(F_{2b}–F_1)$ 15.6; 1-iodo-2,2-dichloro-1,1,2-trifluoroethane **3**, ^{19}F NMR ($CDCl_3$): A_2X system: $\delta(F_1)$ -55.60, $\delta(F_2)$ -67.65, $J(F_1–F_2)$ 14.4.

4.3. Addition of 2 and 3 to allyl acetate

4.3.1. Starting from the telogen produced under sunlight irradiation

Dibenzoyl peroxide or bis(*tert*-butylcyclohexyl)peroxydicarbonate as initiators (0.002 mol) were added very carefully to the mixture of 55.8 g (0.2 mol) of **2** and **3** and 20 g (0.2 mol) of allyl acetate at 90°C or 60°C in a three-necked round bottom flask equipped with a condenser and a thermometer. After about 5 min, an exotherm occurred up to 160–180°C and the mixture turns colourless, then immediately dark red. The telogen conversion was quantitative. 61.5 g of orange liquid was distilled. (yield 81%) b.p.=107–110°C/0.5 mm Hg. (lit. 113°C/2 mm Hg [31]). The two diastereoisomers of 2-iodo-4,5-dichloro-4,5,5-trifluoropentyl acetate **2a** are obtained as an equimolecular amount and were not separated. The ^{1}H NMR spectrum of the mixture is too complex to allow an unambiguous analysis. ^{19}F NMR ($CDCl_3$): ABX system when protons are irradiated; diastereoisomer I: $\delta(F_{5a})$ -67.96, $\delta(F_{5b})$ -68.13, $\delta(F_4)$ -118.95, $J(F_{5a}–F_{5b})$ 169.3, $J(F_{5a}–F_4)$ 9.5, $J(F_{5b}–F_4)$ 9.8, $J(F_4–H_{3a})$ 9.6, $J(F_4–H_{3b})$ 34.5; diastereoisomer II: $\delta(F_{5a})$ -67.75, $\delta(F_{5b})$ -68.13, $\delta(F_4)$ -121.54, $J(F_{5a}–F_{5b})$ 169.5, $J(F_{5a}–F_4)$ 8.8, $J(F_{5b}–F_4)$ 9.4. Some J(H–F) can be determined when ^{1}H are not irradiated. The signal of F_4 at -121.54 ppm is not first-order. ^{13}C NMR ($CDCl_3$): most of the peaks are doubled and are not assigned to each diastereoisomer: $\delta(CH_3)$ 20.5(s), δ(C=O) 169.72(s) and 169.82(s), $\delta(C_1)$ 67.57(d, $^4J_{CF}=3.6$) and 68.70(s), $\delta(C_2)$ 14.27(s) and 16.21(s), $\delta(C_3)$ 42.48(d, $^2J_{CF}=19.8$) and 43.26(d, $^2J_{CF}=20.1$), $\delta(C_4)$ 109.91(dt, $^1J_{CF}=261.0$, $^2J_{CF}=19.1$) and 110.49(dt, $^1J_{CF}=258.8$, $^2J_{CF}=19.1$), $\delta(C_5)$ 124.93(td, $^1J_{CF}=299.3$, $^2J_{CF}=32.9$) and 125.32(td, $^1J_{CF}=299.3$, $^2J_{CF}=32.7$).

When this product underwent a thermal rearrangement, 1-iodomethyl-3,4-dichloro-3,4,4-trifluorobutyl acetate **2b** is obtained up to a yield of 30%. ^{1}H NMR ($CDCl_3$): only H_1 at 5.15 ppm can be assigned in the mixture: ^{19}F NMR ($CDCl_3$): the satellite transitions corresponding to the AB parts of the two diastereoisomers have not been identified. The two AB systems are centered at about -67.9 ppm. Only the X parts are clear. Diastereoisomer I: $\delta(F_3)$ -119.1, $J(F_{5a}–F_4)$ 9.6, $J(F_{5b}–F_4)$ 9.6, $J(F_4–H_{3a})$ 9.6, $J(F_4–H_{3b})$ 29.3; Diastereoisomer II: $\delta(F_3)$ -121.7, $J(F_{5a}–F_4)$ 9.0, $J(F_{5b}–F_4)$ 9.0, $J(F_4–H_{3a})$ 9.0, $J(F_4–H_{3b})$ 30.7.

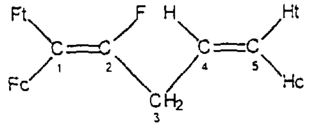
4.3.2. Starting from the telogen produced after irradiation by the mercury lamp

As stated above, a mixture composed of **2** and **3** (7.7 g/0.27 mol), allyl acetate (27.29 g/0.273 mol) and dibenzoyl peroxide (0.9 g/3.7 mmol) was stirred in a three-necked round bottom flask with or without 20–30 mol of solvent at 93°C. The reaction was monitored by GC until high telogen conversion is reached. A slight exotherm (up to 110°C) was observed without change of colour of the medium. After evaporation of the solvent and of the unreacted starting materials, the gross was distilled. b.p., 58–62°C/0.05 mm Hg. Two isomers **2a** and **3a** were obtained (94% and 6%, respectively) which were not separated. 2-Iodo-4,5-dichloro-4,5,5-trifluoropentyl acetate **2a** is described above. 2-Iodo-5,5-dichloro-4,4,5-trifluoropentyl acetate **3a**: ^{19}F NMR ($CDCl_3$): ABX system under proton irradiation: $\delta(F_{4a})$ -109.60, $\delta(F_{4b})$ -110.89, $\delta(F_5)$ -73.70, $J(F_{4a}–F_{4b})$ 245.9, $J(F_{4a}–F_5)$ 8.8, $J(F_{4b}–F_5)$ 8.8.

4.4. Synthesis of perfluorovinyl monomers

A mixture containing 0.35 mol (23.1 g) of activated zinc and 92 g of ethylene glycol was stirred in a three-necked round bottom flask equipped with a distillation device, an argon inlet and a dropping funnel. A 0.07 mol (27.0 g) of the mixture of halogenated iodoacetates **2a**, **2b** and **3a** was dropwise added to the solution at 120°C. The nonconjugated diene **1** was distilled as soon as formed.

1



1,1,2-Trifluoro-1,4-pentadiene **1**, b.p., 38°C lit. 38°C [25,27], 37–39°C [31] colourless liquid. ^{1}H NMR ($CDCl_3$): $\delta(H_3)$ 3.029, $\delta(H_4)$ 5.805, $\delta(H_{5c})$ 5.231, $\delta(H_{5t})$ 5.192, $J(H_3–H_4)$ 6.3, $J(H_3–H_{5c})$ 1.5, $J(H_3–H_{5t})$ 1.5, $J(H_4–H_{5c})$ 17.1, $J(H_4–H_{5t})$ 10.1, $J(H_{5c}–H_{5t})$ 1.5, $J(H_{5c}–F_2)$ 0.8, $J(H_{5t}–F_2)$ 0.4. ^{19}F NMR ($CDCl_3$): $\delta(F_{1c})$ -125.09, $\delta(F_{1t})$ -106.28, $\delta(F_2)$ -174.35, $J(F_{1c}–F_{1t})$ 87.5, $J(F_{1c}–F_2)$

114.3, $J(F_{1t}–F_2)$ 32.7, $J(F_{1c}–H_3)$ 4.1, $J(F_{1t}–H_3)$ 2.7, $J(F_2–H_3)$ 22.0.

4.5-Dichloro-4,5,5-trifluoropentene **2c**, b.p. = 23–26°C/24 mm Hg colourless liquid. ^{1}H NMR: ($CDCl_3$) $\delta(H_{1c})$ 5.329, $\delta(H_{1t})$ 5.365, $\delta(H_2)$ 5.893, $\delta(H_{3a})$ 3.095, $\delta(H_{3b})$ 2.915, $J(H_{1c}–H_2)$ 16.8, $J(H_{1t}–H_2)$ 10.3, $J(H_2–H_{3a})$ 6.1, $J(H_2–H_{3b})$ 7.3, $J(H_{3a}–H_{3b})$ 15.0. ^{19}F NMR ($CDCl_3$): $\delta(F_4)$ −120.45, $\delta(F_{5a})$ −67.24, $\delta(F_{5b})$ −67.00, $J(H_{3a}–F_4)$ 8.8, $J(H_{3b}–F_4)$ 28.1, $J(F_4–F_{5a})$ 9.5, $J(F_4–F_{5b})$ 9.3, $J(F_{5a}–F_{5b})$ 169.0. 1,1,2-Trifluoro-4-iodo-5-acetoxy pentene (CF_2=$CFCH_2CHICH_2OAc$) **2d** could not be isolated pure. Its chemical shifts in NMR overlap with those of the perfluorovinyl group of **1** and of CH_2CHICH_2OAc of **2d**.

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