Synthesis of fluorinated telomers
Part 7.[†] Telomerization of 1,1-difluoro-2-chloroethylene and 1,2-difluoro-1,2 dichloroethylene with methanol

Jérôme Guiot, Bruno Ameduri,* Bernard Boutevin and Alain Fruchier

Laboratory of Macromolecular Chemistry (CNRS UMR 5076), Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34296, Montpellier cedex 5, France.
E-mail: ameduri@cit.enscm.fr

Received (in Montpellier, France) 4th June 2002, Accepted 11th September 2002
First published as an Advance Article on the web 8th November 2002

Radical telomerizations of 1,1-difluoro-2-chloroethylene and 1,2-difluoro-1,2-dichloroethylene with methanol, leading to chlorofluoroalcohols, are presented. The optimization of the synthesis conditions led to 3-chloro-2,2-difluoropropanol and 2,3-dichloro-2,3-difluoropropanol in 80% and 89% conversion, respectively, much higher than those reported in the literature. The best conditions were achieved when 2,5-bis(*tert*-butylperoxy)-2,5–dimethylhexane (DHBP) was used as the initiator at 407 K with an initial ($[MeOH]_0/[alkene]_0$) molar ratio, R_0, of 40. The unsymmetrical alkene led to one isomer only, in contrast to the formation of two isomers from chlorotrifluoroethylene. Furthermore, this study has shown the influence of the fluorine and chlorine atoms of the olefin in directing the radical reaction. Hence, by its polar and steric effects, the chlorine atom in these alkenes does not favor the radical addition of $HOCH_2^{\bullet}$. In contrast, the inductive effects of the fluorine atom increase the reactivity of the hydroxymethyl radical. A decreasing reactivity series of different chlorofluoroolefins with respect to the radical addition of methanol is proposed with the optimal conditions for each telomerization: $F_2C{=}CCl_2 > F_2C{=}CFCl > ClCF{=}CFCl > F_2C{=}CHCl$ and an overall reactivity series of different fluoroalkenes with methanol is also suggested.

Fluorinated alcohols have already been shown to be of great interest for intermediate synthesis.[1–7] Various preparations of these hydroxyl derivatives are described in the literature. For instance, the Grignard reaction can lead to these products.[8,9] The chemical modification of several functions can also be used with acids,[10,11] alkane halides,[12] thiols,[13] and amines.[14] Another way to achieve the synthesis of such compounds is the polymerization of a fluorinated alkene in the presence of a chain transfer agent, (called *telogen*), to yield a series of low molecular weight products. Such a reaction is termed *telomerization*.[15–18] In this work, we have chosen to use this reaction.

Alcohols are known to participate in chain transfer reactions essentially by hydrogen abstraction from a cleavable C–H bond on the carbinol carbon, the electron-withdrawing hydroxyl group making this chain transfer possible. However, their chain transfer constants are usually considered as too low for these compounds to be regarded as efficient telogens, insofar as the "activation" in hydrogen abstraction is due to the hydroxyl function, which is in most cases is of low importance. For this reason, few investigations involving alcohols as telogens and fluorinated alkenes have been described, and apparently excessive by-product formation coupled with unfavorable product distributions have deterred any commercial development. In fact, one of the most important steps in the telomerization process is the homolytic cleavage of the C–H bond in the α-position of the alcohol in the course of the initiation steps. The dissociation energy of this bond (BDE) is different depending on the structure of the telogen, the lowest being for methanol (393 kJ.mol^{-1})[19] among the linear aliphatic alcohols. Thus, methanol could be a convenient and easily available telogen to be used for the synthesis of fluorinated telomers bearing a hydroxyl endgroup.

Radical reactions between fluoroolefins and methanol have also been reported in the literature. In the telomerization of vinylidene fluoride (VDF) with methanol, Oku *et al.*[20] proved that the di-*tert*-butylperoxide initiated telomerization of VDF with methanol was feasible. This was previously confirmed,[21] leading, however, to only fair yields, the remaining products arising from the concomitant formation of non-functional oligomers produced from the direct initiation of *tert*-butoxy and even methyl radicals onto VDF. This study also showed that the thermal, photochemical and redox initiations were unsuccessful. With trifluoroethylene (TrFE) and methanol, telomers of low molecular weights ($\overline{DP}_{n\mathrm{cum}} = 3 - 8$) were also successfully prepared (over 70% yield) by Chambers and Powell.[22] The telomerization of chlorotrifluoroethylene (CTFE) with methanol was first investigated by Liska and Simek[23] and, more recently by our group, using a large excess of methanol that led mainly to the monoadduct.[24] The radical addition of methanol onto bromotrifluoroethylene was also successfully investigated by Demiel.[25] In reaction with tetrafluoroethylene (TFE), methanol proves to be an efficient chain transfer agent under radical conditions, as shown in research pioneered by Joyce.[26] Later, Blickle *et al.*[27] and Sotokawa *et al.*[28] confirmed these results. The first two adducts, $HOCH_2CF_2CF_2H$ and $HOCH_2(C_2F_4)_2H$, were successfully isolated by Paleta and Dedek.[29] Furthermore, the kinetics of telomerization of TFE with methanol was investigated by Kostov *et al.*.[30] In the case of the reaction of hexafluoropropylene (HFP) with methanol, Haszeldine *et al.*[31] reported that under thermal, photochemical or peroxide-initiated conditions, the monoadduct was

---

[†] For part 6 see ref. 24.

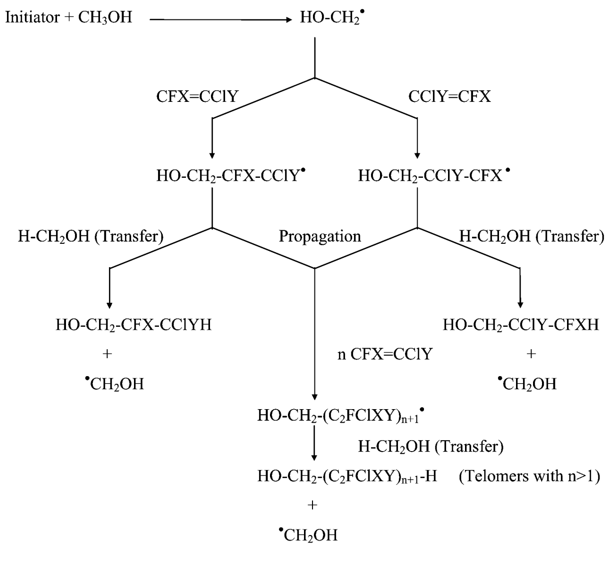
obtained in high yields *via* a radical chain mechanism. Finally, another, more exotic fluoroalkene, perfluoro-2-butene, was reacted with methanol under γ-ray initiation, leading to the monoadduct mainly.[32]

As a matter of fact, telomerization reactions of 1,2-difluoro-1,2-dichloroethylene (DCDFE) with methanol were carried out by several authors[33–37] in contrast to many other transfer agents: R_XO–F (where R_X represents a perhaloalkyl group containing 1 to 10 carbon atoms),[38] Cl_3C–F,[39] $CHCl_2$–F,[40] $ClCH_2$–F,[40] several alcohols [such as $HOCH_2CH_2$–H, $HOCH_2CH_2CH_2$–H, $(CH_3)_2C(OH)$–H[33,35] and fluorinated ones[41]], various ethers such as THF, dioxane and diethyl ether,[42] several acetates: CH_3COOCH_2–H, $CH_3COOCH(CH_3)$–H, $CH_3COOC(CH_3)_2$–H,[35] $(RO)_2P(O)$–H (where R stands for CH_3, C_2H_5 or n-C_3H_7).[43] In addition, a few telomerization reactions of 1,1-difluoro-2-chloroethylene (CDFE) have been carried out with various transfer agents: CCl_3–F,[44] CF_3–I[45] and CH_3–CH_2–OH.[46] In this way, the radical addition of methanol to 1,2-difluoro-1,2-dichloroethylene initiated by di-*tert*-butylperoxide,[35,37] γ-rays[34] or UV radiation,[36] yielded mainly the monoadduct . However, no work has been reported on the radical telomerization of CDFE with methanol.

The present work intends to complete the study concerning the telomerization of both fluoroalkenes with methanol and especially the synthesis of the monoadducts HO–CH_2–CFCl–CFCl–H and HO–CH_2–CF_2–CH_2–Cl.

Results and discussion

Radical addition of methanol onto chlorofluorinated alkenes is an appropriate and easy method to obtain halogenated alcohols.[23,24,33–37,46] Recently, we have reported that the peroxidic addition of methanol onto chlorotrifluoroethylene (CTFE)[24] was regioselective since $HOCH_2CF_2CFClH$ was the major product (95%). Optimal conditions were achieved when that reaction was initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethyl hexane (DHBP) at 407 K, and with a 40-fold excess of methanol over CTFE. In these conditions, the CTFE conversion was 92%. Hence, it was worth investigating similar radical additions onto other chlorofluoroalkenes (Scheme 1) such as 1,1-difluoro-2-chloroethylene (CDFE) and 1,2-difluoro-1,2-dichloroethylene (DCDFE), and to compare the results in terms of monoaddition, regioselectivity and yields to those describes in previous work.[24]



Scheme 1 Radical addition of methanol to chlorofluoro olefins. (Y, X = Cl, F or H).

Telomerization of 1,1-difluoro-2-chloroethylene with methanol

To the best of our knowledge, the only work describing the synthesis of $HOCH_2CF_2CH_2Cl$ was reported by Boguslavskaya *et al.*[47] in 1971. It consisted in reacting Cl^+ cation and F^- anion (produced *in situ* from ClF) with 2-fluoroprop-2-enol to give the chlorofluoroalcohol in 76.3% yield, as follows:

$$H_2C{=}CFCH_2OH \xrightarrow{Cl^+} [ClCH_2C^+FCH_2OH] \xrightarrow{F^-} HOCH_2CF_2CH_2Cl$$

The originality of our approach to produce the above chlorofluoroalcohol involves the peroxidic addition of a 40-fold excess of methanol to 1,1-difluoro-2-chloroethylene (CDFE) using 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP) and di-*tert*-butyl peroxide (DTBP) as the initiators. The initial $[\text{initiator}]_0/[\text{CDFE}]_0$ molar ratio was 2.5% and both reactions were monitored at temperatures for which the half-lives of the initiators were close to one hour (Table 1). The choice of these conditions was made from the optimal conditions found in the case of the telomerization of CTFE with methanol. The large excess of methanol enables one to favor the monoadduct:

$$\text{HO-CH}_3 + F_2C{=}CHCl \xrightarrow{\text{ROOR}} \text{HO-CH}_2\text{-}(C_2F_2HCl)\text{-H}$$

Interestingly, DHBP led to better yields, and in both cases, the reaction was regioselective, producing $HOCH_2CF_2CH_2Cl$ selectively.

The ^{19}F NMR spectrum of the total product mixture exhibits a quintet ($^3J_{F(H\text{-}1)} = {}^3J_{F(H\text{-}3)} = 12.7$ Hz) centered at -113.7 ppm that confirms the formation of a unique isomer. The ^1H NMR confirms this attribution, because of the presence of two triplets ($^3J_{HF} = 12.7$ Hz and $^3J_{HF} = 12.4$ Hz) located at 3.77 and 3.89 ppm, respectively. This shows that the $HOCH_2^{\bullet}$ radical added exclusively onto the difluoromethylene side of CDFE. This observation can be explained by the nucleophilic character of $HOCH_2^{\bullet}$[48] and the electrophilic carbon atom bearing both fluorine atoms of CDFE.

Telomerization of 1,2-difluoro-1,2-dichloroethylene with methanol (DCDFE)

According to the literature,[33–37] the only method to produce $HOCH_2CFClCFClH$ concerns the radical addition of methanol onto DCDFE. Table 2 lists the different initiating systems (γ-rays, UV irradiation or di-*tert*-butylperoxide) leading to the expected chlorofluoroalcohols in low yield (10–16%). Interestingly, this reaction, when initiated by 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane under similar conditions as above, led to the expected alcohol in much better yields (65%).

$$\text{HO-CH}_3 + ClFC{=}CFCl \xrightarrow{\text{ROOR}} \text{HO-CH}_2\text{-CFCl-CFCl-H}$$

As in the case of the radical additions of methanol onto CTFE and CDFE, this peroxidic initiator shows a better efficiency producing the corresponding chlorofluoroalcohols in high yields.

The ^{19}F NMR spectrum of the distilled chlorofluoroalcohol (Fig. 1) exhibits five signals centered at -118.9, -130.9, -130.5, -148.7 and -153.2 ppm. Those at -130.9 and -130.5 ppm are assigned to the CFCl group adjacent to the methylene group while those centered at -148.7 and -153.2 ppm are attributed to the CFCl–H endgroup. As expected, the presence of two signals corresponding to the same fluorinated group indicates that chlorofluoroalcohol $HOCH_2CFClCFClH$ contains two diastereoisomers (as evidenced by the presence of two asymmetric carbon atoms). This statement is confirmed by both the ^1H NMR spectrum (Fig. 2) that shows, beside the signal centered at 4.12 ppm assigned to the $HOC\underline{H_2}$ group, two doublets of doublets centered at 6.41 and 6.48 ppm assigned to the CFClH endgroup, and the ^{13}C NMR spectrum,

Table 1 Experimental conditions[a] and CDFE conversion for the radical addition of methanol to 1,1-difluoro-2-chloroethylene

Expt	Initiator[b]	T/K	CDFE conversion (%)	
			HO–CH$_2$–CF$_2$–CH$_2$–Cl	HO–CH$_2$–CClH–CF$_2$–H
1	DTBP	419	48	0
2	DHBP	407	80	0

[a] R_0 ([MeOH]$_0$/[CDFE]$_0$) = 40, C_0 ([Initiator]$_0$/[CDFE]$_0$) = 0.025, reaction time = 7 h. [b] DTBP (di-*tert*-butyl peroxide) and DHBP (2,5-bis (*tert*-butylperoxy)-2,5 dimethylhexane).

whose signals are all doubled. In addition, in the ^{19}F NMR spectrum, the doublet ($^3J_{FH}$ = 9.6 Hz) of triplets ($^3J_{FH}$ = 12.8 Hz) centered at −118.9 ppm is attributed to the difluoromethylene group of HOCH$_2$CF$_2$CCl$_2$H. The presence of this isomer was confirmed: (*i*) by the ^{13}C NMR spectrum that exhibits a triplet ($^1J_{CF}$ = 251.4 Hz) centered at 118.9 ppm characteristic of the CF$_2$ group and (*ii*) by the ^{1}H NMR spectrum that shows a triplet ($^3J_{HF}$ = 8.9 Hz) centered at 5.99 ppm corresponding to the CF$_2$CCl$_2$H endgroup. The formation of this isomer arises from the radical addition of methanol onto F$_2$C=CCl$_2$ present as an impurity in 1,2-dichloro-1,2-difluoroethylene. Indeed, a ^{19}F NMR characterization of commercially available 1,2-difluoro-1,2-dichloroethylene reveals the presence of a signal centered at −89.0 ppm assigned to F$_2$C=CCl$_2$, besides the characteristic peaks of DCDFE.

Interestingly, the regioselective HOCH$_2$CF$_2$CCl$_2$H by-product indicates that HOCH$_2^•$ radical is added to the difluoromethylene side of F$_2$C=CCl$_2$. Such an observation can be explained by both the electrophilic carbon atom (of this chlorofluoroalkene) bearing both fluorine atoms and the steric hindrance of the other carbon atom bearing both chlorine atoms. This confirms the study of Paleta *et al.*[49] that pointed out the unfavorable steric and polar effects. On the contrary, the reportedly[48] nucleophilic HOCH$_2^•$ radical is likely to add onto the electrophilic carbon atom bearing the highest number of fluorine atoms. This may be explained by the inductive character of fluorine that makes the carbon atoms electron-withdrawing.

Furthermore, it was possible to assess the conversion rate of these chlorofluoroolefins from the ^{19}F NMR spectra: while DCDFE led to a conversion rate of 45%, F$_2$C=CCl$_2$ reacted quantitatively. Thus, an overall ranking on the telomerization of these four chlorofluoroalkenes with methanol can be drawn from Table 3. The following decreasing reactivity series of these fluoroolefins is observed: F$_2$C=CCl$_2$ (100%) > F$_2$C=CFCl (92%) > F$_2$C=CHCl (80%) > ClCF=CFCl (45%).

However, according to Modena *et al.*[35] who reported the radical addition of THF and 2-propanol onto DCDFE, the DCDFE conversion rate increases with the initiator concentration. Hence, four telomerization reactions of DCDFE with methanol were carried out with different peroxide concentrations (Fig. 3). Interestingly, when C_0 = 10%, the DCDFE conversion rate reached 89% and the overall yield was *ca.* 65%, which is much higher than those noted in the literature (Table 2). When C_0 is greater than 10%, the conversion rate decreased. Our results show that the conversions of the fluoroalkenes are higher than 40% when C_0 ranges between 2.5% and 20%. This is encouraging in comparison to the investigations of Modena *et al.*[35] who have found that the conversion rate of CFCl=CFCl was lower than 30%, when it reacted with *i*-PrOH and tetrahydrofuran. Hence, it is interesting to propose another reactivity scale from the optimal conditions of this telomerization involving the different fluoroalkenes: F$_2$C=CCl$_2$(100%) > F$_2$C=CFCl(92%) > ClCF=CFCl(89%) > F$_2$C=CHCl (80%).

Table 2 Experimental conditions and overall yields for the radical addition of methanol to 1,2-difluoro-1,2-dichloroethylene (DCDFE)

Experimental conditions[a]	Overall yield (%)	Reference
Co^{60} irr, 700 h, 313 K, R_0 = 3	16	33
Di-*tert*-butylperoxide (C_0 = 0.5), 5 h, 423 K, R_0 = 9	10	35
UV, 313 K, R_0 = 5	11	36
2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane (C_0 = 0.1), 7 h, 407 K, R_0 = 40	65	This work

[a] R_0 = [MeOH]$_0$/[DCDFE]$_0$, C_0 = [Initiator]$_0$/[DCDFE]$_0$.

Conclusions

This investigation concerned the synthesis of several chlorofluoroalcohols, mainly 3-chloro-2,2-difluoropropanol and 2,3-dichloro-2,3-difluoropropanol, by telomerization reactions of 1,1-difluoro-2-chloroethylene (CDFE) and 1,2-difluoro-1,2-dichloroethylene (DCDFE) with methanol, respectively. The preparation of 3-chloro-2,2-difluoropropanol was original (with 80% conversion), resulting from a regioselective addition of HOCH$_2^•$ onto the CF$_2$ of CDFE. Radical telomerization of 1,2-difluoro-1,2-dichloroethylene with methanol was optimized, leading to the corresponding 2,3-dichloro-2,3-difluoropropanol in 65% yield, which was greatly improved compared to those obtained in previous studies from other radical-induced systems. This work also shows the unfavorable influence of the presence of a chlorine atom, through a steric effect, and in contrast, the favorable one of the presence of fluorine atoms by an inductive effect for the addition of HOCH$_2^•$ radical onto a chlorofluoroolefin. Such halogenated alcohols are potential intermediates for further original functional derivatives, currently under investigation.

Experimental

Materials

2,5-Bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP) and di-*tert*-butylperoxide (DTBP) were generously offered by Akzo France (60202 Compiègne). 1,2-Difluoro-1,2-dichloroethylene (DCDFE) and 1,1-difluoro-2-chloroethylene (CDFE) were supplied by Fluorochem (Derbyshire, U.K.). Surprisingly, DCDFE contains 10% of 1,1-difluoro-2,2-dichloroethylene. Methanol was of analytical purity grade and was provided by Sigma-Aldrich Chimie (38299 Saint Quentin-Fallavier, France). The reagent did not require any purification prior to use.

Apparatus and analyses

The reactions were carried out in a 1000 and 2000 ml Hastelloy (C276) Parr Systems autoclave equipped with inlet and outlet

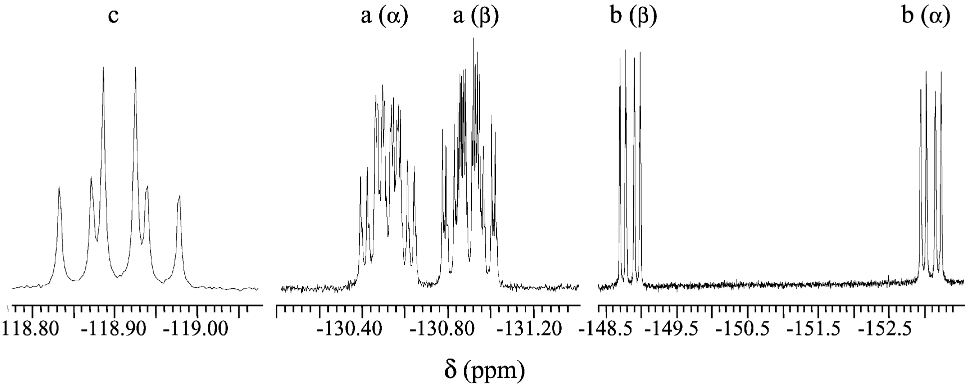


Fig. 1 ^{19}F NMR spectrum of $HO–CH_2–CF^{a(\alpha,\beta)}Cl–CF^{b(\alpha,\beta)}Cl–H$ and $HO–CH_2–CF^{c}_2–CCl_2–H$.

valves, a manometer with a security disk and fitted with a mechanical stirrer and a specific electric heating mantle. The stirring speed was fixed by an electronic driving device, which also controlled the temperature of the autoclave *via* a thermocouple and an integrated heating-power regulator.

The products were characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopy at room temperature. Spectra were recorded on Bruker AC 200 and 250 instruments, using deuterated chloroform as the solvent. The letters s, d, t, q and m stand for singlet, doublet, triplet, quintet and multiplet, respectively. Coupling constants and chemical shifts are given in hertz (Hz) and ppm, and TMS ($CFCl_3$) as the reference for ^{1}H (^{19}F) nuclei, respectively. In all cases, the yields were calculated by using hexafluorobenzene of analytical purity grade provided by Aldrich, as external standard in the ^{19}F NMR spectra. The experimental conditions to record ^{1}H (or ^{19}F) NMR spectra were the following: flip angle 90° (30°) ; acquisition time 4.5 s (9.0 s); pulse delay 2 s (5 s); number of scans 16 (64).

Model reaction: radical addition of methanol to 1,1-difluoro-2-chloroethylene

Into the same autoclave as above, were introduced 21.8 g (0.075 mol) of 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane and 975 g (30.4 mol) of methanol. Then, the autoclave was left closed for 20 min and purged with 20 bars of nitrogen pressure to check for any leaks and was degassed afterwards. Next, 96.6 g (0.726 mol) of 1,1-difluoro-2-chloroethylene was introduced by double weighing. The mixture was heated up to 407 K while stirring and the reaction was allowed to run for 7 h (Table 1). After reaction, the autoclave was cooled to room temperature and then put in an ice bath. Then the total product mixture (pale yellow liquid) was characterized by ^{19}F NMR spectroscopy to assess the nature and the yield of the formed products. The mixture was then concentrated and 3-chloro-2,2,-difluoropropanol was purified by distillation at 334–336 K under 20 mmHg.

3-Chloro-2,2-difluoropropanol.

$$HO—\underset{1}{CH_2}—\underset{2}{CF_2}—\underset{3}{CH_2}Cl$$

Colourless liquid, bp = 334–336 K/20 mmHg. ^{1}H NMR ($CDCl_3$) δ: 3.45 (br s, shifted with dilution, –OH, 1H); 3.77 (t, $^{3}J_{HF} = 12.7$ Hz, H-3, 2H); 3.89 (t, $^{3}J_{HF} = 12.4$ Hz, H-1, 2H). ^{19}F NMR ($CDCl_3$) δ: −113.7 (q, $^{3}J_{F(H\text{-}1)} = {}^{3}J_{F(H\text{-}3)} = 12.7$ Hz, CF_2). ^{13}C NMR ($CDCl_3$) δ: 41.34 (t, $^{2}J_{CF} = 32.7$ Hz, C-3); 61.39 (t, $^{2}J_{CF} = 30.8$ Hz, C-1); 120.10 (t, $^{1}J_{CF} = 244.5$ Hz, C-2).

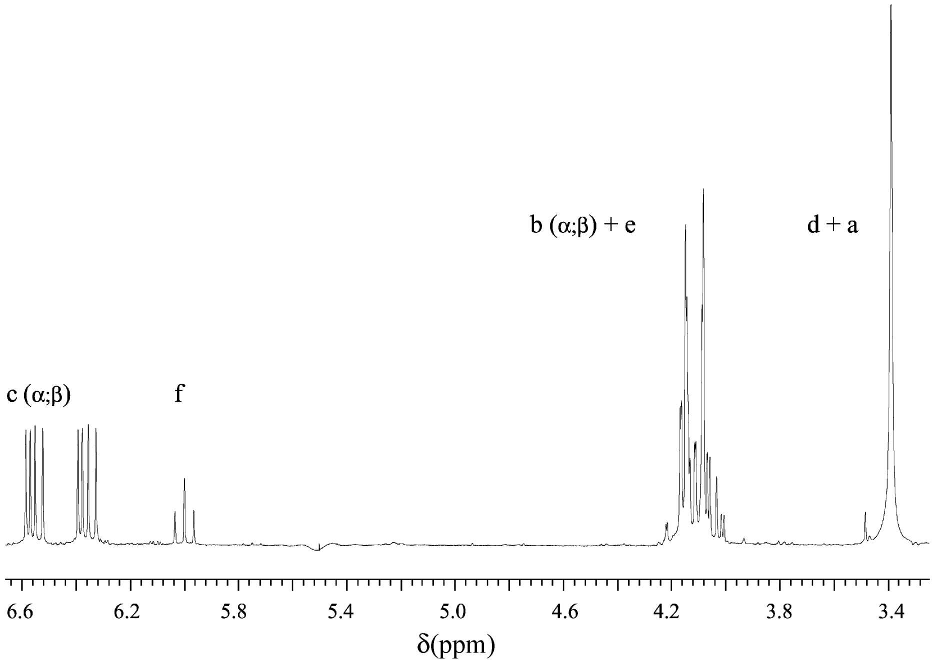


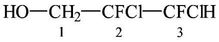
Fig. 2 ^{1}H NMR spectrum of $H^{a}O–CH^{b}_2–CFCl–CFCl–H^{c}$ and $H^{d}O–CH^{e}_2–CF_2–CCl_2–H^{f}$.

Table 3 Results of the telomerization[a] of various fluorochloroalkenes with methanol

F-Alkene	C_0 (%)	Alkene conversion (%)	Monoadducts	Regioselectivity (%)
CF_2=CFCl	2.5	92	HO–CH_2–CF_2CFCl–H	95
			HO–CH_2–CFClCF_2–H	5
CF_2=CCl_2	2.5	100	HO–CH_2–$CF_2$$CCl_2$–H	100
			HO–CH_2–$CCl_2$$CF_2$–H	0
CF_2=CHCl	2.5	80	HO–CH_2–CF_2CHCl–H	100
			HO–CH_2–CHClCF_2–H	0
CFCl=CFCl	2.5	45	HO–CH_2–CFClCFCl–H	100
CF_2=CCl_2	10.0	100	HO–CH_2–$CF_2$$CCl_2$–H	100
			HO–CH_2–$CCl_2$$CF_2$–H	0
CFCl=CFCl	10.0	89	HO–CH_2–CFClCFCl–H	100

[a] Experimental conditions: initiator DHBP [2,5-bis(*tert*-butylperoxy)-2,5 dimethylhexane] 2.5%, $T = 407$ K, $t = 7$ h, $[MeOH]_0/[F\text{-}Alkene]_0 = 40$.

2,3-Dichloro-2,3-difluoropropanol.



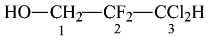
$$HO-\underset{1}{CH_2}-\underset{2}{CFCl}-\underset{3}{CFClH}$$

Two diastereoisomers, α and β, colourless liquid, bp = 336–339 K/20 mmHg.

Diastereoisomer α. ^{19}F NMR ($CDCl_3$, Fig. 1) δ: −130.5 (ddt, $^3J_{F(F\text{-}3)} = 19.5$ Hz, $^3J_{F(H\text{-}1)} = 15.5$ Hz, $^3J_{F(H\text{-}3)} = 7.0$ Hz, F-2); −153.2 (ddm, $^2J_{F(H\text{-}3)} = 49.2$ Hz, $^3J_{F(F\text{-}2)} = 19.5$ Hz, F-3). ^1H NMR ($CDCl_3$, Fig. 2) δ: 3.40 (br s, shifted with dilution, –OH, 1H); 4.12 (m, H-1, 2H); 6.41 (dd, $^2J_{H(F\text{-}3)} = 49.2$ Hz, $^3J_{H(F\text{-}2)} = 7.2$ Hz, H-3, 1H). ^{13}C NMR ($CDCl_3$) δ: 65.12 (d, $^2J_{C(F\text{-}2)} = 24.4$ Hz, C-1) or 65.20 (dd, $^2J_{C(F\text{-}2)} = 24.4$ Hz, $^3J_{CaF2} = 2.4$ Hz, C-1); 97.86 (dd, $^1J_{C(F\text{-}3)} = 248.7$ Hz, $^2J_{C(F\text{-}2)} = 34.3$ Hz, C-3) or 98.29 (dd, $^1J_{C(F\text{-}3)} = 251.7$ Hz, $^2J_{C(F\text{-}2)} = 31.02$ Hz, C-3); 110.00 (dd, $^1J_{C(F\text{-}2)} = 250.9$ Hz, $^2J_{C(F\text{-}3)} = 25.9$ Hz, C-2) or 110.70 (dd, $^1J_{C(F\text{-}2)} = 251.9$ Hz, $^2J_{C(F\text{-}3)} = 22.4$ Hz, C-2).

Diastereoisomer β. ^{19}F NMR ($CDCl_3$, Fig. 1) δ: −130.9 (dddd, $^3J_{F(H'\text{-}1)} = 19.6$ Hz, $^3J_{F(F\text{-}2)} = 19.6$ Hz, $^3J_{F(H''\text{-}1)} = 13.5$ Hz, $^3J_{F(H\text{-}3)} = 4.1$ Hz, F-2); −148.7 (dd, $^1J_{F(H\text{-}3)} = 48.2$ Hz, $^3J_{F(F\text{-}2)} = 19.6$ Hz, F-3). ^1H NMR ($CDCl_3$, Fig. 2) δ: 3.40 (br s, shifted with dilution, OH, 1H); 4.12 (m, H-1, 2H); 6.48 (dd, $^1J_{H(F\text{-}3)} = 48.2$ Hz, $^3J_{H(F\text{-}2)} = 4.0$ Hz, H-3, 1H). ^{13}C NMR ($CDCl_3$) δ: 65.20 (dd, $^2J_{C(F\text{-}2)} = 24.4$ Hz, $^3J_{C(F\text{-}3)} = 2.4$ Hz, C-1) or 65.12 (d, $^2J_{C(F\text{-}2)} = 24.4$ Hz, C-1); 98.29 (dd, $^1J_{C(F\text{-}3)} = 251.7$ Hz, $^2J_{C(F\text{-}2)} = 31.02$ Hz, C-3) or 97.86 (dd, $^1J_{C(F\text{-}3)} = 248.7$ Hz, $^2J_{C(F\text{-}2)} = 34.3$ Hz, C-3); 110.70 (dd, $^1J_{C(F\text{-}2)} = 251.9$ Hz, $^2J_{C(F\text{-}3)} = 22.4$ Hz, C-2) or 110.00 (dd, $^1J_{C(F\text{-}2)} = 250.9$ Hz, $^2J_{C(F\text{-}3)} = 25.9$ Hz, C-2).

3,3-Dichloro-2,2-difluoropropanol.



$$HO-\underset{1}{CH_2}-\underset{2}{CF_2}-\underset{3}{CCl_2H}$$

Colourless liquid, bp = 336–339 K/20 mmHg. ^{19}F NMR ($CDCl_3$, Fig. 1) δ: −118.9 (dt, $^3J_{F(H\text{-}1)} = 12.8$ Hz, $^3J_{F(H\text{-}3)} = 9.6$ Hz, CF_2). ^1H NMR ($CDCl_3$, Fig. 2) δ: 3.45 (br s, shifted with dilution, OH, 1H); 4.10 (m, CH_2, 2H); 5.99 (t, $^3J_{HF} = 8.9$ Hz, CH, 1H). ^{13}C NMR ($CDCl_3$) δ: 61.35 (t, $^2J_{(C\text{-}1)F} = 29.7$ Hz, C-1); 67.64 (t, $^2J_{(C\text{-}3)F} = 32.7$ Hz, C-3); 118.89 (t, $^1J_{(C\text{-}2)F} = 251.4$ Hz, C-2).

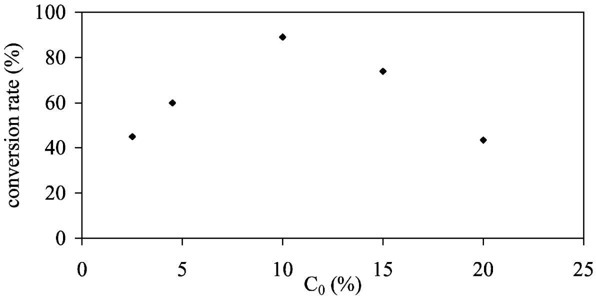


Fig. 3 Conversion rate of CFCl=CFCl *versus* the initial $[initiator]_0/[CFCl{=}CFCl]_0$ molar ratio, C_0. Experimental conditions: initiator DHBP [2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane], $T = 407$ K, $t = 7$ h, $[MeOH]_0/[olefin]_0 = 40$.

Acknowledgement

The authors thank the Solvay S.A. Company (Brussels, Belgium) for the gifts of CDFE and DCDFE and for financial support.

References

1 J. R. Lacher, J. D. Park and F. E. Rogers, *J. Org. Chem.*, 1961, **26**, 2089.
2 P. Bouvier and H. Gault *Fr. Pat.* 1,445,618, 1965 (assigned to CNRS).
3 P. Moreau, N. Redwane and A. Commeyras, *Bull. Soc. Chim. Fr.*, 1984, **II**, 1117.
4 C. Wakselman, T. Nguyen and H. Molines, *Fr. Pat.* 2,654,723, 1989 (assigned to CNRS).
5 B. Ameduri, B. Boutevin, G. K. Kostov and P. Petrova, *J. Fluorine Chem.*, 1998, **92**, 69.
6 B. Ameduri, B. Boutevin, G. K. Kostov and P. Petrova, *J. Fluorine Chem.*, 1999, **93**, 117.
7 B. Ameduri, R. Bongiovanni, V. Lombardi, A. Pollicino, A. Priola and A. Recca, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 4227.
8 P. Moreau, R. Albadri, N. Redwane and A. Commeyras, *J. Fluorine Chem.*, 1980, **15**, 103.
9 J. D. Park, E. R. Larsen, H. V. Holler and J. R. Lacher, *J. Org. Chem.*, 1958, **23**, 1166.
10 I. Kageyama, A. Katsushima, T. Sakato and K. Suemiro, *Kogyo Kagaku Zasshi*, 1962, **65**, 1207.
11 P. Bouvet and J. P. Lalu, *Fr. Pat.* 2,034,142, 1970 (assigned to Ugine Khullman).
12 T. Hayashi and M. Matsuo, *Jap. Pat.* 37,520, 1970 (assigned to Asahi Glass).
13 A. Cambon, *Fr. Pat.* 8,408,376, 1984 (assigned to Atochem).
14 L. Foulletier and J. P. Lalu, *Fr. Pat.* 1,288,865, 1970 (assigned to Ugine Khullman).
15 C. M. Starks, *Free Radical Telomerization*, Academic Press, New York and London, 1974.
16 B. Boutevin and Y. Pietrasanta, in *Comprehensive Polymer Science*, ed. J. C. Bevington, G. Allen, R. Eastmond and S. Russo, Pergamon, Oxford, 1989, vol. 3, p. 185.
17 G. Gordon and Y. Loftus, *Telomerization*, in *Encyclopedia of Polymer Science and Technology*, ed. R. E. Kirk and D. F. Othmer, Wiley, New York, 1989, vol. 16, p. 533.
18 B. Ameduri and B. Boutevin, *Top. Curr. Chem.*, 1997, **192**, 165.
19 J. Fossey, D. Lefort, and J. Sorba, *Free Radicals in Organic Chemistry*, J. Wiley, New York, 1995.
20 J. Oku, R. J. H. Chan, H. K. Hall and O. R. Hughes, *Polym. Bull.*, 1986, **16**, 481.
21 M. Duc, B. Ameduri, B. Boutevin, M. Kharroubi and J. M. Sage, *Macromol. Chem., Phys.*, 1998, **199**, 1271.
22 R. D. Chambers and R. L. Powell, *Br. Pat.* 2292151A, 1996 (assigned to ICI).

23 F. Liska and S. Simek, *Collect. Czech. Chem. Commun.*, 1970, **35**, 1752.

24 J. Guiot, J. Alric, B. Ameduri, A. Rousseau and B. Boutevin, *New J. Chem.*, 2001, **25**, 1185.

25 A. Demiel, *J. Org. Chem.*, 1960, **25**, 993.

26 R. M. Joyce, Jr., *US Pat.* 2559628, 1951 (assigned to DuPont).

27 P. Blickle, R. Heumueller, K. Hintzler, W. Schwertfeger and K. Von Werner, *Ger. Pat.* 3915759, 1989 (assigned to Hoescht).

28 T. Satokawa, T. Fujii, A. Omori and Y. Fujita, *Jap. Pat.* 54154707 780421, 1993 (assigned to Daikin Ind. Ltd.).

29 O. Paleta and V. Dedek, *J. Fluorine Chem.*, 1989, **42**, 345.

30 G. Kostov, G. Kotov and E. Balbokov, *React. Kinet. Catal. Lett.*, 1998, **63**, 107.

31 R. N. Haszeldine, R. Rowland, R. P. Sheppard and A. E. Tipping, *J. Fluorine Chem.*, 1985, **28**, 291.

32 M. A. Kurykin, L. S. German, L. I. Kartasheva and A. K. Pikaev, *J. Fluorine Chem.*, 1996, **77**, 193.

33 M. Hiroshige, *J. Org. Chem.*, 1962, **27**, 2325.

34 K. Kondo and T. Yanagimara, *Jap. Pat.* 55,000,305, 1980 (assigned to Toyo Soda Mfg Co. Ltd.).

35 S. Modena, A. Fontana and G. Moggi, *J. Fluorine Chem.*, 1985, **30**, 109.

36 K. Kondo and T. Yanagimara, *Jap. Pat.* 62053,941, 1987 (assigned to Toyo Soda Mfg Co. Ltd.).

37 G. Moggi, *Eur. Pat.* 163533, 1989 (assigned to Montefluos).

38 A. Marraccini, A. Pasquale and M. Vincenti, *Eur. Pat.* 348980, 1990 (assigned to Ausiomont).

39 O. Paleta and A. Pošta, *Collect. Czech. Chem. Commun.*, 1967, **32**, 1427.

40 O. Paleta, *Coll. Czechoslov. Chem. Commun.*, 1971, **36**, 2062.

41 Q. Huang and D. D. Desmarteau, *J. Fluorine Chem.*, 2001, **112**, 363.

42 H. Muramastu, K. Inukai and T. Ueda, *J. Org. Chem.*, 1964, **29**, 2220.

43 H. Muramastu, K. Inukai and T. Ueda, *J. Org. Chem.*, 1964, **29**, 2224.

44 O. Paleta, J. Kvicala, J. Gunter and V. Dedek, *Bull. Soc. Chim. Fr.*, 1986, 920.

45 R. Gregory, R. N. Haszeldine and A. E. Tipping, *J. Chem. Soc.*, 1968, **30**, 20.

46 R. D. Chambers, A. H. S. Gilani, A. F. Gilbert, J. Hutchinson and R. L. Powell, *J. Fluorine Chem.*, 2000, **106**, 53.

47 L. S. Boguslavskaya, V. S. Yarovykh and K. V. Bulovyatova, *Zh. Org. Khim.*, 1971, **7**, 1338.

48 R. D. Chambers, P. Diter, S. N. Dunn, C. Farren, G. Sandfrord, A. S. Bastanov and A. K. Howard, *J. Chem. Soc., Perkin Trans. 1*, 2000, 1639.

49 O. Paleta, V. Cirkva, Z. Budkova and S. Böhm, *J. Fluorine Chem.*, 1997, **86**, 155.