

Novel fluorinated monomers bearing reactive side groups Part 1. Preparation and use of ClCF₂CFCII as the telogen

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Abstract

The addition of ICl to chlorotrifluoroethylene leading to a ClCF₂CFCII (**I**)/Cl₂CFCF₂I (**II**) mixture is described. Four different ways of initiation (thermal, photochemical, or the presence of redox catalysts or radical initiators) were used in order to get optimized yields and amounts of isomer **I**. Thermal initiation led to quantitative yields whereas the photochemically induced reaction usually produced the highest proportion of isomer **I**. Excellent yields of isomer **I** were obtained at 140 °C. The batch process was more interesting in both selectivity and yield. The activation energy of the reaction was 27 kJ mol⁻¹ and elucidation of the mechanism was proposed in terms of a radical process.

Keywords: Chlorotrifluoroethylene; Iodine monochloride; Telomerization; Initiation; Transfer agent; Activation energy

1. Introduction

Fluorinated telomers are very interesting intermediates for various materials involved in many applications: surfactants [1], membranes [2], derivatives for textile treatment [3,4], photocrosslinkables for the protection of metals, glass, or leather [5], microemulsions [6], fluorosilicones [7], thermostable Kelf oils [8], fluorinated polyesters [9] or polyurethanes [10] for coatings, and so on.

Such halogenated telomers can be prepared either from fluorinated commercially available monomers or from fluorinated telogens, or used together. Among the monomers, chlorotrifluoroethylene (CTFE) can be telomerized by many transfer agents. These telogens may possess various bonds, cleaved by the initiation step in the process of telomerization [11–13]: C–H [14], C–F [15], C–Cl [16], C–Br [17], S–H [18], S–S [19], P–H [20] or X–X, where X designates a halogen atom [21–27].

But, if chlorinated or brominated telogens are efficient for the telomerization of CTFE, perfluoroalkyl iodides have shown poor reactivity. Recent investigations show that whether photochemical, thermal or radical initiators are used, the yields of monoadduct are poor to negligible [28]. Only redox catalysts appear interesting and yet by-products are formed by the transfer of copper salts. However, the use of CF₃CFCII in the telomerization of such olefins has recently

shown a high efficiency, owing to the reactive CFCII end-group which is more reactive than a CF₂I terminal group [28]. Interestingly, ClCF₂CFCII produced from the addition of ICl on CTFE also appears to be a potential transfer agent for CTFE. Such a reaction was reported more than 40 years ago by Haszeldine [23] and earlier by Barr et al. [24] to give CF₂ClCFCII as the exclusive ICl adduct in almost quantitative yields. This reaction takes place readily under slight pressure in the absence of solvent. Several years later, Hauptschein [25,26] bubbled CTFE into ICl and produced in high yield a mixture of ClCF₂CFCII and Cl₂CFCF₂I, the ratio of which depended upon the reaction temperature; i.e. from room temperature to 50 °C the adduct consists of at least 20%–30% of the isomer Cl₂CFCF₂I (**II**) whereas at lower temperatures (below 0 °C) the reaction led mainly to ICl-CFCF₂Cl (**I**). Fearn [27] also investigated this reaction either at –10 °C for six weeks (with 72.6% yield based on iodine monochloride) or at room temperature for 65 h (82.5% yield with a high Cl₂CFCF₂I content).

However, it seems that the results reported in these works were not detailed or definitive enough, and even controversial, and it seemed worth repeating the studies. Actually, the authors did not try to use different methods of initiation (by preference, the thermal method was employed) and only ultraviolet absorption, refractive indexes and elemental analyses were considered as the characteristics of the monoadducts obtained. Furthermore, no NMR spectra of the products were reported.

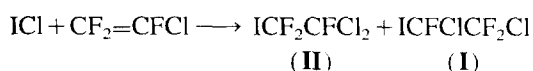
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Thus, the objective of this paper concerns a deeper investigation of the addition of ICl onto CTFE and involves a study of the different ways of initiation in order to determine the best compromise between yield and selectivity [to isomer I].

2. Results and discussion

According to the literature discussed above, it is clear that two isomers were produced; but the authors considered only the monoaddition reaction of ICl onto CTFE without taking into account the possibility of telomerization or the reaction mechanism [23–27].

The reaction was performed with different ways of initiation and under various conditions:



Our results are summarized in Table 1.

Several initiations were investigated: as those described by Hauptschein [25,26] or from redox catalysts, radical initiators, thermally and photochemically, since Bissel showed that the addition of ICl to trifluoroethylene could also be light

catalyzed [29]. For each experiment, the yield was determined by gas chromatography using chlorobenzene as the internal standard and the proportions of isomers I and II were provided from ^{19}F NMR spectroscopy. For instance, the ^{19}F NMR spectrum (Fig. 1) of $\text{IC}_2\text{F}_3\text{Cl}_2$ exhibits an AB system ($J_1 = 14$ Hz and $J_2 = 164$ Hz), the X part as a triplet ($J = 14$ Hz) centred at -63.5 (a) and -72.5 ppm (b) being assigned to the CF_2Cl and CFCII groups, respectively. A doublet at -55.3 ppm ($J = 14$ Hz) and a triplet at -67.5 ppm ($J = 14$ Hz) are also observed. They correspond to the CF_2I and CFCI_2 groups of the $\text{ICF}_2\text{CFCl}_2$ isomer II, respectively.

On the other hand, since ICl is usually produced from I_2 and Cl_2 and according to a radical mechanism the presence of I_2 is probable, owing to the recombination of $\text{I}\cdot$ radicals. Thus, the addition of I_2 or Cl_2 onto CTFE may be expected. Hence, it was worth checking for the presence of XCF_2CFCIX , with $\text{X} = \text{I}$ or Cl , in the mixture. The ^{19}F NMR spectrum of 1,1,2-trichloro-1,2,2-trifluoro (i.e. where $\text{X} = \text{Cl}$) exhibits a triplet and a doublet centred at -72.4 and -68.1 ppm, assigned to CFCI_2 and CF_2Cl groups, respectively. ICF_2CFCII was prepared by photochemical addition of I_2 onto $\text{CF}_2=\text{CFCl}$ and its ^{19}F NMR spectrum shows a doublet and a triplet centred at -120.0 and -115.9 ppm, correspond-

Table 1
Addition of iodine monochloride to chlorotrifluoroethylene: various reactions, conditions and methods of initiation ^a

Exp. No.	R_0	Solvent	Initiator or catalyst	C_0	Reaction temp. (°C)	Reaction time (h)	Y_{GC} (%)	$Y_{\text{dist.}}$ (%)	I/II (%)
1	flow	CH_2Cl_2	thermal	–	–5; –8	4	25.6	17.1	99.1:0.9
2	flow	CH_2Cl_2	thermal	–	–8; –10	12	29.4	18.7	88.4:11.6
3	flow	CH_2Cl_2	thermal	–	–6; –8	12	36.3	29.8	87.4:12.6
4	flow	CH_2Cl_2	thermal	–	–8; –10	15	50.6	47.4	92.8:7.2
5	1.0	CH_3CN	CuCl	0.04	140	15	43.0	35.7	97.3:2.7
6	1.0	CH_3CN	CuCl_2	0.04	140	15	33.7	34.1	97.9:2.1
7	1.0	CH_3CN	$\text{Cu}^+/\text{Cu}^{2+}$	0.04	140	18	44.1	36.2	97.1:2.9
8	1.0	CH_3CN	FeCl_3/Ni	0.04	140	18	27.8	20.4	98.1:1.9
9	0.9	CH_2Cl_2	AIBN	0.02	80	4	–	49.3	92.1:7.9
10	0.8	CH_2Cl_2	DBP	0.02	90	4	–	41.3	89.0:11.0
11	0.9	CH_2Cl_2	P-16	0.02	60	4	–	41.1	90.0:10.0
12	1.0	CH_2Cl_2	$(^t\text{BuO})_2$	0.03	140	4	–	35.2	99.3:0.7
13	1.0	CH_2Cl_2	thermal	–	50	6 (3)	45 (30)	–	89.3:10.7
14	1.0	CH_2Cl_2	thermal	–	70	5 (3)	100 (60)	–	91.5:8.5
15	1.0	CH_2Cl_2	thermal	–	100	1.8	100	–	88.2:11.8
16	1.0	CH_3CN	thermal	–	140	21	28.0	23.6	99.1:0.9
17	0.5	CH_3CN	thermal	–	140	21	19.2	16.3	–
18	1.0	CH_2Cl_2	sun light	–	50	15	69.0	53.6	95.8:4.2
19	1.0	CH_2Cl_2	sun light $\Phi_2\text{CO}$	0.02	50	17	72.9	67.7	96.1:3.9
20	0.85	CH_2Cl_2	sun light $\Phi_2\text{CO}$	0.02	25	12	–	68.1	97.1:2.9
21	0.83	CH_2Cl_2	sun light HQ	0.02	25	12	–	29.2	97.0:3.0
22	1.2	CH_2Cl_2	sun light HQ	1.0	25	7	<2	–	–
23	1.02	CH_2Cl_2	DMF/sun	1.22	40	6	3.1	–	–
24	1.05	CH_2Cl_2	DPPH/sun	0.03	40	6	20.2	18.2	–

^a Y_{GC} = yield from gas chromatography; $Y_{\text{dist.}}$ = yield after distillation; DBP = dibenzoyl peroxide; P-16 = Perkadox-16; $\Phi_2\text{CO}$ = benzophenone; HQ = hydroquinone.

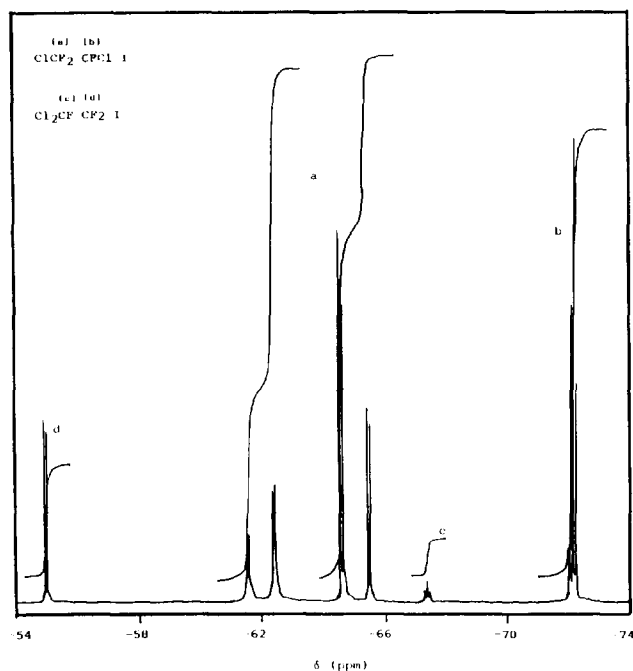


Fig. 1. ^{19}F NMR spectrum of $\text{IC}_2\text{F}_3\text{Cl}_2$.

ing to CF_2I and CFCII groups, respectively. However, such chemical shifts were not present in the ^{19}F NMR spectrum of the $\text{IC}_2\text{F}_3\text{Cl}_2$ mixture, indicating that neither ICF_2CFCII nor $\text{ClCF}_2\text{CFCI}_2$ were produced.

The reaction performed at low temperatures (as in Hauptschein's work [25]) gave the maximum isolated yield of 42%, the **I/II** isomer ratio being 92.8:7.2 (calculated from NMR spectroscopy) which is lower than that observed by Hauptschein using UV analysis. These results obtained according to Hauptschein's procedure are rather different, since for similar conditions the yield varies from 17% to 42%. An eventual possible explanation may be the flow of CTFE bubbling into the solution of ICl . For that reason, further reactions were studied using batch procedures and with different methods of initiation (Table 1).

The conditions of the reaction were fixed by two initial molar ratios: R_0 represents the ratio of $[\text{ICl}]_0$ to $[\text{CTFE}]_0$, whereas C_0 is defined by the $[\text{initiator or catalyst}]_0$ to $[\text{CTFE}]_0$ ratio. Usually, R_0 equals 1 since our objective concerns the obtaining of the monoadduct and C_0 is about $1-4 \times 10^{-2}$ as used in previous work [11,12,30,31].

2.1. Redox catalysis

In order to favour obtaining the monoadduct, redox catalysts were first chosen. Three metallic salts were used at 140 °C. The cupric salt (Cu^{2+}) gave in 34% yield a mixture of isomers **I/II** in a 81:19 ratio. No major difference in yield and selectivity between Cu^+ , Cu^{2+} and $\text{Cu}^+/\text{Cu}^{2+}$ was noted. The use of such a mixture of copper salts confirms previous work performed on the bis-telomerization of allyl acetate with α,ω -bis(trichloromethylated) telogens leading to a very good monoselectivity [31]. A low yield was

obtained when the reaction was catalyzed with ferric chloride, but isomer **I** was also produced with an excellent selectivity. Hauptschein [25] performed several reactions in an iron vessel at 40–50 °C and found a quite unexpected high proportion of isomer **II**. However, in our case, it seems that the temperature has an influence on the selectivity when redox catalysts are employed.

2.2. Radical initiators

For initiation produced by radical initiators, different peroxides, azo compounds or peresters were used separately at a temperature chosen at which their half-lives were close to 1 h: bis(4-t-butylcyclohexyl)peroxydicarbonate (Perkadox-16) (P-16) at 60 °C; azo-bis(isobutyronitrile) (AIBN) at 80 °C; dibenzoyl peroxide (Bz_2O_2) at 90 °C; and di(t-butyl)peroxide, (^tBuO)₂, at 140 °C.

Table 1 shows clearly that the best yield from the reaction with a radical initiator was obtained when AIBN was used, but that in the presence of peroxide the yield was lower. This difference may be related to the radicals produced during decomposition of the initiators and, as in previous work [32], the following decreasing series of reactivity may be proposed: $\text{AIBN} > \text{Bz}_2\text{O}_2 \sim \text{P-16} > (^t\text{BuO})_2$.

Interestingly, whatever the initiator used, no poly(CTFE) was produced and this can be related to the behaviour of ICl acting as an efficient transfer agent by contrast to R_fI [28]. But, the presence of di- and tri-adducts are noted on the GC chromatogram, in contrast to the redox catalysts that only produced the monoadduct. Moreover, the use of AIBN, Bz_2O_2 or P-16 does not influence the amount of both isomers which is close to 90:10. However, when (^tBuO)₂ was employed, isomer **I** was obtained selectively. Probably the low reactivity of (^tBuO)₂ suggests a better selectivity for this reaction together with the temperature effect.

Thus it was interesting to study this reaction in a thermal manner without any initiator.

2.3. Thermal initiation

Three kinetic studies were conducted at 40 °C, 70 °C and 100 °C in sealed tubes using chlorobenzene as internal standard. These experiments were monitored by gas chromatography taking into account the areas of the peaks of $\text{IC}_2\text{F}_3\text{Cl}_2$ and $\text{C}_6\text{H}_5\text{Cl}$. The yields of the product $\text{IC}_2\text{F}_3\text{Cl}_2$ in these reactions increased linearly with time, the higher the temperature the greater the yield (Fig. 2). For instance, it took only 1.8 h at 100 °C to obtain a quantitative yield.

The rate of the reaction R was determined from the slopes of the straight lines (yield of $\text{C}_2\text{F}_3\text{ICl}_2$ versus time). A plot of $\log R$ versus $1/T$ (T represents the temperature) decreased linearly (Fig. 3) and the slope provides the activation energy E_a ($E_a = 27 \text{ kJ mol}^{-1}$). Tedder and Walton [33–38] performed many studies on the determination of the activation energies of thermal or photochemical monoadditions of CCl_4 [33] and of linear [34,35] or branched [36–38] perfluoro-

Table 2

Activation energies (E_a) in kJ mol^{-1} for the addition of $\text{Cl}_3\text{C}\cdot$ and various $\text{R}_1\cdot$ radicals on both sides of different fluorinated olefins (according to Tedder and Walton)

	$\overset{\downarrow}{\text{C}}\text{FH}=\overset{\downarrow}{\text{C}}\text{H}_2$ $\text{CFH}=\overset{\downarrow}{\text{C}}\text{H}_2$	$\overset{\downarrow}{\text{C}}\text{H}_2=\overset{\downarrow}{\text{C}}\text{F}_2$ $\text{CH}_2=\overset{\downarrow}{\text{C}}\text{F}_2$	$\overset{\downarrow}{\text{C}}\text{HF}=\overset{\downarrow}{\text{C}}\text{F}_2$ $\text{CHF}=\overset{\downarrow}{\text{C}}\text{F}_2$	$\overset{\downarrow}{\text{C}}\text{F}_2=\overset{\downarrow}{\text{C}}\text{F}_2$	$\overset{\downarrow}{\text{C}}\text{F}_2=\overset{\downarrow}{\text{C}}\text{F}(\text{CF}_3)$ $\text{CF}_2=\overset{\downarrow}{\text{C}}\text{F}(\text{CF}_3)$	Ref.
$\text{Cl}_3\text{C}\cdot$	8.4 5.6 $\Delta E = 2.8^a$	–	12.2 16.4 $\Delta E = 4.2$	12.2	38.8	[33]
$\text{F}_3\text{C}\cdot$	8.0 2.1 $\Delta E = 5.9$	5.0 13.4 $\Delta E = 8.4$	8.0 11.3 $\Delta E = 3.3$	7.1	–	[34,35]
$\text{CF}_3\text{CF}_2\cdot$	10.5 2.5 $\Delta E = 8.0$	5.5 15.5 $\Delta E = 10.0$	9.2 13.9 $\Delta E = 4.7$	6.3	–	[34]
$\text{C}_2\text{F}_5\text{CF}_2\cdot$	13.4 3.4 $\Delta E = 10.0$	7.1 22.7 $\Delta E = 15.6$	13.0 17.2 $\Delta E = 4.2$	8.9	–	[34]
$(\text{CF}_3)_2\dot{\text{C}}\text{F}$	14.7 3.4 $\Delta E = 11.3$	5.0 25.2 $\Delta E = 20.2$	11.3 17.2 $\Delta E = 5.9$	14.3	–	[36,37]
$(\text{CF}_3)_3\text{C}\cdot$	18.1 4.2 $\Delta E = 13.9$	4.6	12.6 23.1 $\Delta E = 10.5$	17.2	–	[38]

^a $\Delta E = (E - E_c) - (E' - E_c)$, $E_c = E_a$ of ethylene.

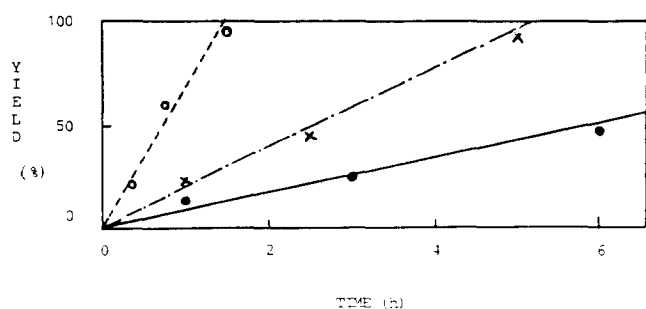


Fig. 2. Yield from thermal addition of ICl to chlorotrifluoroethylene versus time (— for 40°C , - - - for 70°C ; ···· for 100°C).

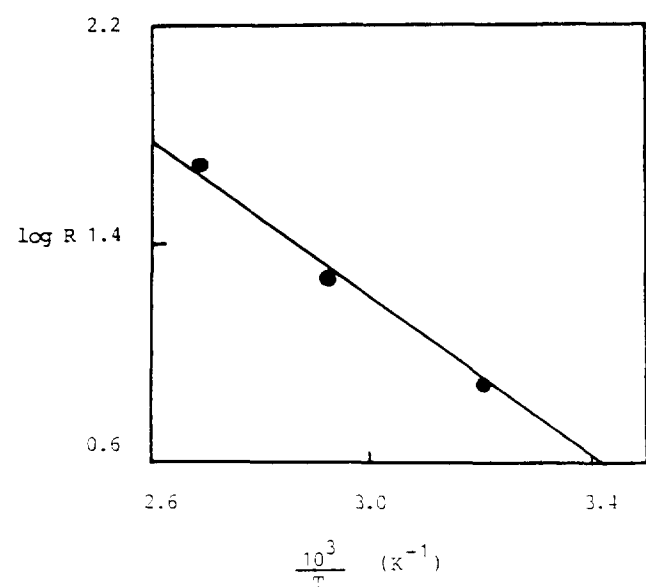


Fig. 3. Plot of $\log R$ versus $1/T$ (R determined from the slope of the straight lines of Fig. 2).

roalkyl iodides onto vinyl fluoride (VF), vinylidene fluoride (VDF), trifluoroethylene (VF_3), tetrafluoroethylene and hexafluoropropene (HFP) (Table 2). It was observed that

Table 3

Influence of the temperature on the proportions of isomers (gross means the product mixture for the reaction)

Run No.	R_0	Reaction temp. ($^\circ\text{C}$)	Reaction time (h)	I/II (%)
1	1	70	1.0	92:8
2	1	70	2.2	92:8
3	1	70	5.0	91:9
4	1	100	1.5	88:12
5	Gross of run 1	170	15.0	90:10
6	Gross of run 2	170	15.1	91:9
7	Gross of run 3	170	15.0	90:10
8	Gross of run 4	170	15.1	86:14

except for the addition of $\text{R}\cdot$ onto the CH_2 side of VF or VDF, most activation energies are in the $10\text{--}39 \text{ kJ mol}^{-1}$ range and most of them are higher than 15 kJ mol^{-1} . This may be correlated with the heat required for most reactions. Previous work has shown that the telomerization of VDF with $\text{C}_4\text{F}_9\text{I}$ starts at 150°C [39].

The change of the I/II isomer ratio was investigated versus time and temperatures (Table 3). It was not possible to increase the amount of isomer I with time since, for example, no change of ratio occurred between 1 and 6 h when the reaction was performed at 40°C .

Various samples of $\text{C}_2\text{F}_3\text{Cl}_2\text{I}$ (mainly from product mixtures but also worked-up with sodium bisulfite and distilled compound with or without work-up) were first characterized by ^{19}F NMR spectroscopy and then heated at 170°C for about 15 h. It was noted that no major difference in the isomer ratio was observed from the initial to the heated samples. However, it seems there was a slight increase of isomer II for high temperatures.

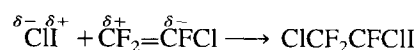
2.4. Photochemical initiation

Finally, photochemical initiation was studied using sunlight with or without a sensitizer (e.g. benzophenone). In

these conditions, the amount of isomer **II** was reduced to 10% and even to 5% when the reaction was performed at 20 or 45 °C, respectively. At 40 °C, such a reaction required only 1.5 h to achieve complete conversion of ICl. Several ways of stirring were studied: with a magnetic stirrer, the tube being in a vertical position; or, mechanically at 100 rpm, the tube describing a circle. Whatever the method of stirring, both yield and ratio of isomers were not changed.

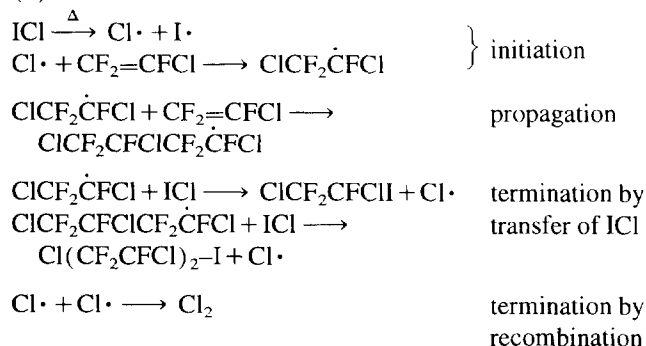
2.5. Mechanism

To our knowledge, the mechanism of this reaction has never been described. It can either be ionic:

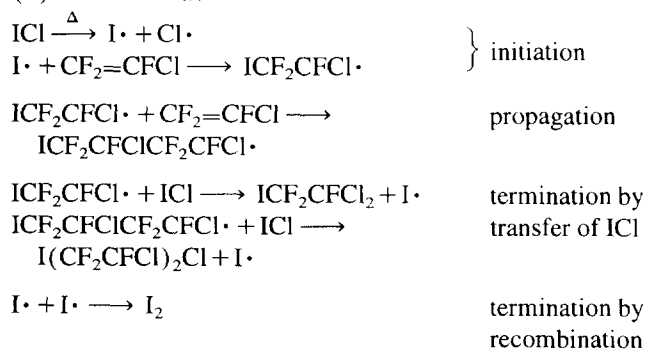


or radical:

(a) From Cl• attack



(b) From I• attack



Thus, it can be deduced that if I• reacts onto CTFE, isomer **II** is produced, whereas addition of Cl• leads to isomer **I**. From the experimental work (Table 1), isomer **I** is favoured, probably because of the higher reactivity of Cl• than that of I•. This behaviour is similar to that of most telomerizations of olefins with perfluoroalkyl iodides (R_FI) for which R_F• reacts preferentially, allowing the formation of I₂ by recombination of I•, whereas R_F-R_F is not observed.

In order to check which kind of mechanism was produced, radical or ion scavengers were added into the reaction.

2.5.1. Use of radical scavengers

Two types of radical scavenger were used, i.e. hydroquinone and 2,2-diphenyl-1-picrylhydrazyl (DPPH), and four experiments were conducted using similar conditions (Table

Table 4

Experimental conditions employed Temp. = 30 °C, time = 6 h, sun light; R₀ and c₀ designate the initial [ICl]₀/[CTFE]₀ and [scavenger]₀/[CTFE]₀ molar ratio) and yield of the addition of ICl onto CTFE in the absence or presence of scavengers: HQ (hydroquinone), DPPH (2,2-diphenyl-1-picrylhydrazyl) and DMF (dimethyl formamide)

Run No.	Scavenger	R ₀	c ₀	Yield of IC ₂ F ₃ Cl (%)
1	none	1.05	0	70
2	HQ	1.02	0.02	29
3	HQ	1.06	1.00	0
4	DPPH	1.05	0.03	18
5	DMF	1.02	1.22	3

4) under sunlight. Table 4 shows that without any scavenger the yield was 70% whereas it drastically decreases when this reaction was performed in the presence of radical scavengers. For instance, the yield decreased from 29% to 0% when the initial [hydroquinone]/[CTFE] molar ratio (R₀) increased from 0.02 to 1.00, respectively. Similarly, the use of DPPH led to a poor yield (18%).

From these results it can be claimed that the addition of ICl onto CTFE occurs through a radical mechanism. This is also shown from the reaction between ICl and dibenzoyl peroxide at 90 °C, which gave chlorobenzene in poor yield from the recombination of a phenyl radical (produced by the decomposition of the initiator) with Cl• created from ICl in the initiation step.

2.5.2. Use of ion scavengers

It is well known that amines and amides are interesting cation scavengers owing to the basic nature of the nitrogen atom, and two were initially selected for study. However, triethylamine reacted violently with ICl producing an orange smoke and was not tried further whereas DMF (which dissolves ICl) could be employed (Table 4). This amide slows down the addition of ICl onto CTFE.

According to these conclusions, the mechanism of the reaction is not easy to understand. It seems both radical and ionic mechanisms may be involved at the same time, with better evidence however for radical behaviour.

3. Experimental details

3.1. General comments

Chlorotrifluoroethylene and 1,1,2-trichloro-1,2,2-trifluoro were kindly supplied by Elf Atochem. Iodine and iodine monochloride were provided by Aldrich and did not require any purification prior to use.

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

tained 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⁻¹. The GC apparatus was connected to a Hewlett Packard integrator (model 3390) which automatically calculated the area of each peak on the chromatogram.

The products were characterized by ¹H and ¹⁹F NMR spectroscopy at room temperature. The ¹⁹F and ¹H NMR spectra were recorded on a Bruker AC-200, -250 or WM-360 instruments, using deuterated chloroform and CFC1₃ as solvent and internal reference, respectively. The letters d and t designate doublet and triplet, respectively.

3.2. Synthesis of *I*(C₂F₃Cl)Cl

This reaction was performed either from Hauptschein's procedure [25] or in Carius tubes.

(a) *At atmospheric pressure* (Experiment No. 4 in Table 1)

To a three-necked round-bottom flask, equipped with a condenser and flushed with nitrogen for 15 min, was introduced iodine monochloride (184.6 g, 1.13 mol) dissolved in 365.5 g of CH₂Cl₂. The nitrogen flow was then stopped and chlorotrifluoroethylene was bubbling through this solution at 5 °C to 10 °C for 15 h. After cooling to room temperature, the resulting dark red liquid was added dropwise into a stirred aqueous sodium bisulfite solution. The organic lower phase was washed with water and dried over magnesium sulfate. After filtration, the trifluorodichloroiodoethane mixture was distilled and gave 149.5 g of violet liquid, b.p. 98–101 °C; 45 °C/100 mmHg [25]. The yield was 47.4%. ¹⁹F NMR (CDCl₃) δ: -54.9 (d, *J* = 14 Hz, CFC1₂); -63.5 (AB system, *J*_{gem} = 14 Hz; *J*_{gem} = 15.8 Hz, *J*_{vic} = 164 Hz, CF₂Cl); -67.5 (t, *J* = 13.9 Hz, ICF₂); -72.0 (t, *J* = 14 Hz, CFCII) (leading to a relative amount of *I/II* of 92.8:7.2) ppm.

(b) *In a Carius tube*

Chlorotrifluoroethylene (11.0 g, 0.09 mol) was condensed into a Carius tube containing ICl (15.3 g, 0.09 mol) and 15 g of methylene dichloride, the whole being cooled in an acetone/liquid nitrogen bath. The tube was sealed and heated while shaking at the required temperature and for the time required (Experiments No. 13–17 in Table 1), in a thermostated oven.

In case of photoinitiation (Experiments No. 18–24), a bar magnet was used to stir the liquid in the tube exposed to sunlight.

In both these cases, the work-up was similar to that described above. However, when catalysts (copper or iron salts) were used (Experiments No. 5–8), it was first necessary to wash the product mixture with an acid solution (10% HCl), then with sodium carbonate and water, in order to remove the catalyst.

3.3. Synthesis of *ICF₂CFCII*

A sealed Carius tube containing I₂ (12 g, 0.047 mol) and CTFE (6.0 g, 0.052 mol) in 10 ml of methylene chloride was

exposed to sunlight while stirring by means of a bar magnet for 6 h at 28–30 °C. After reaction, 1,1,2-trifluoro-2-chloro-1,2-diiodoethane was distilled at room temperature because of its decomposition at 38–40 °C. There was obtained 7.3 g of a violet liquid, b.p. 18–20 °C/25 mmHg (yield = 42%). ¹⁹F NMR (CDCl₃) δ: -120.0 (d, *J* = 15 Hz, 2F, CF₂I); -115.9 (t, *J* = 15 Hz, 1F, CFCII) ppm.

4. Conclusions

Among four different initiation methods required for the addition of ICl onto CTFE, the thermal way offered good yields of C₂F₃Cl₂I whereas the selective formation of ClCF₂CFCII (*I*) could be achieved from the photochemically induced telomerization. Such a reaction was easy to perform and did not require much energy (*E*_a = 27 kJ mol⁻¹). However, the amount of isomer *I* could not be improved by thermal rearrangement of isomer *II*, whatever the purity of the crude product, whether distilled, or worked-up.

Owing to its quite reactive CFCII end-group, isomer *I* appears to be a very promising telogen for telomerizations of commercially available fluorinated monomers or other non-halogenated olefins, which are under investigation.

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